CORRELATION OF CRYSTALLOGRAPHIC SYMMETRY AND EMISSION IN SOLID STATE COPPER(I) HALIDE PHOSPHINE COMPLEXES

By

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Dedication

It is my honor to dedicate this thesis to my parents, who never doubted
my ability to achieve the goals that I set for myself.
Your love, patience and sacrifice made this work possible.
Through you, I learned extremely valuable lessons that will remain
always in my mind and in my heart.

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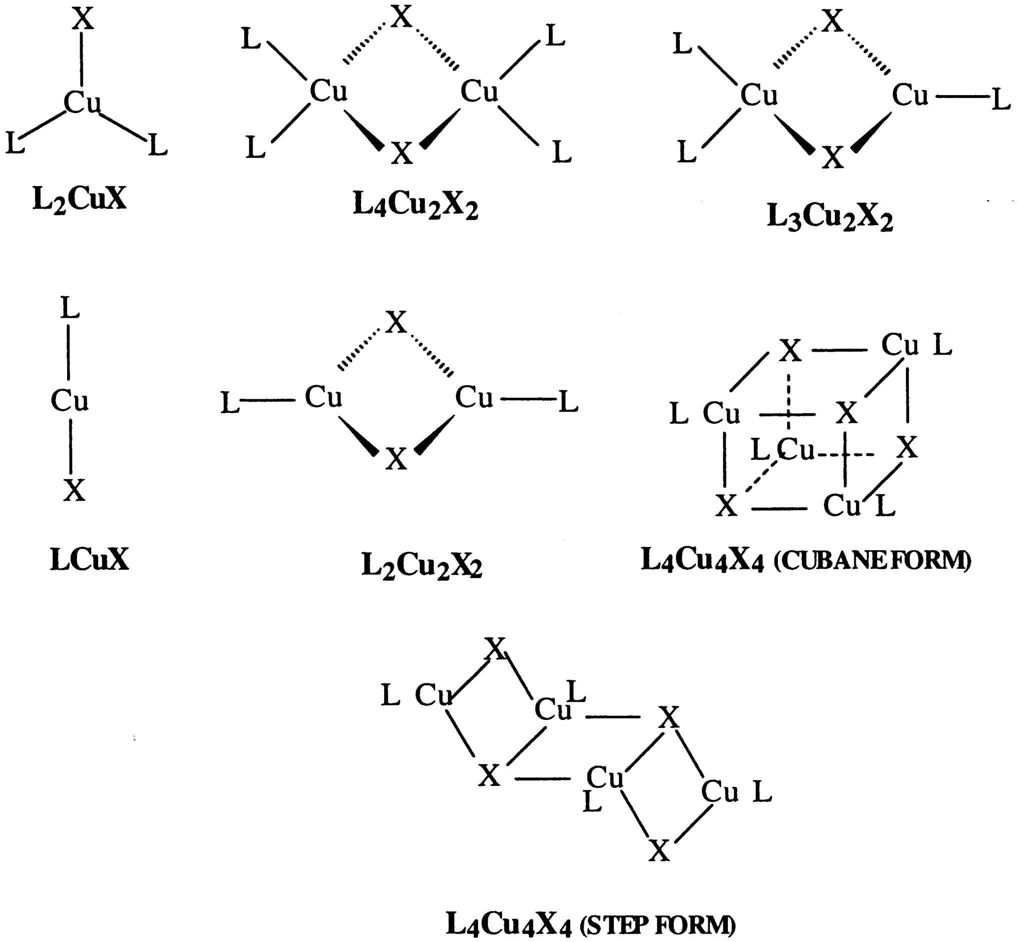
CHAPTER I

INTRODUCTION AND BACKGROUND

Copper(I) forms complexes of a wide variety of structural forms and stoichiometry with halides ($Cu_xX_y^{x-y}$, X=I, Br and Cl). These complexes are normally anionic (x<y) and highly stable. Counter ions of various types are possible. A further group of complexes are neutral, ($Cu_xX_yL_z$, x = y, L = ligand) involve electron pair donor organic ligands (N, P, S) and are of lesser stability. In these complexes Cu(I) may display two, three or four fold coordination. Some common motifs for copper(I) complexes are given in Figure 1.

The stability of copper halides increases in the following order: F < Cl < Br < I. This trend can be explained by the hard and soft acid base theory, which states that greatest stability is observed for hard acid-hard base and soft acid-soft base pairs. Iodide is the softest base in the halide series and copper is a soft acid. If one also considers that phosphine ligands (which are the ligands that will be used throughout this study) are soft, complexes of the form Cu_xX_y(phosphorus-based ligand)$_z$ should also be extremely stable.

The coordination chemistry of Cu(I) is both interesting and important due to its extensive structural and stoichiometric variation. Furthermore, Cu(I) chemistry has catalytic applications and, moreover, is involved in certain biochemical reactions. The presence of copper in copper-containing proteins establishes the need for modeling of its coordination sites[1].



L = Phosphine ligand
X = I, Br, Cl

Figure 1. Common Motifs of Copper(I) Halide Phosphine Complexes

The interest in the emission properties of these compounds arises from reports in 1938 by J. T. Randall[2] of their different colors of visible solid state emission when excited in the ultraviolet. It was not until the 70's that these complexes were investigated again by H. D. Hardt et al.[3] In this work, the ligands were simple hetero-aromatic and non-aromatic rings such as pyridine, quinoline and pyrroline. Whereas the earlier work concentrated on the color of the observed emission for the different complexes without structural investigation, the latter studies involved structural characterization. It was also reported that the color of emission and the emission maxima were temperature-dependant, a phenomenon termed "fluorescent thermochromism".

This temperature-dependency was investigated by Weber and Hardt.[4] A comparison was made of the powder diffraction patterns of the formate, actetate, propionate and butyrate salts of copper(I). The similarity of these powder patterns for the carboxylate structures suggested that the thermochromicity must be due to a subtle difference in packing. They have concluded that tight packing leads thermochromic emission and the loose packing leads to non-thermochromic emission.

When the fluorescent properties of hexamethylenetetraamine (HMTA) complexes of Cu(I) were studied by Hardt and Gechnizdjani[5], it was found that the complexes exhibited different fluorescent behavior and color, depending on the method of preparation and solvent used. When the solvent used was methanol or ethanol, the complexes showed fluorescent thermochromism, with the yellow room temperature emission changing from to red and violet, respectively at 77 K. When the structure is made more condensed by the inclusion of additional HMTA or by the presence of a second nitrogen base in the solid state, thermochromism was not observed. Thus, these studies suggested that a solid state Cu(I) complex in which the Cu atom has at least 1.33 nitrogen ligands available (i.e., a tight structure) will not show thermochromism due to limited mobility in the lattice.

Schramm et al.[6] proposed that the thermochromicity is related to the crystallographic symmetry. In their work, the Cu_4I_4(piperdine)$_4$ complex did not exhibit thermochromism. The X-ray structure of this complex revealed that it has a fourfold inversion axis (S_4) within the cubic cluster. A comparison was made between the thermochromism observed for tetrameric clusters, Cu_4I_4(morpholine)$_4$ (twofold axis) and Cu_4I_4(pyridine)$_4$ (no symmetry element). Schramm et al. suggested that a tetrameric complex ($Cu_4I_4L_4$, L = a nitrogen base) between copper iodide and a nitrogen base should not exhibit a thermochromism if the point symmetry of its cluster molecule is at least of fourfold order, i.e. if the Cu-N bond lengths are all equal by symmetry.

A similar conclusion was reached by Hardt and Pierre[7] for cubic clusters ($Cu_4I_4L_4$). When the emission properties of a group of copper iodide complexes were investigated, a red shift was observed on cooling. The shift was 15 nm for Cu_4I_4(piperdine)$_4$, 35 nm for Cu_4I_4(morpholine)$_4$ and 50 nm for Cu_4I_4(pyridine)$_4$. The Cu...Cu distances for all the three solid state complexes were very similar. However, the symmetry elements within these clusters were: a fourfold axis for Cu_4I_4(piperdine)$_4$, a twofold axis for Cu_4I_4(morpholine)$_4$ and a onefold axis for Cu_4I_4(pyridine)$_4$. Thus, they suggested that the extent of the red shift with temperature depends more on the symmetry of the cluster than the Cu...Cu distance. So, the higher the symmetry element, the lesser the red shift on cooling.

In an effort to investigate the effect of the existence of S_4 symmetry on thermochromicity, Rath et al.[8] studied Cu_4I_4(para-toluidine)$_2$(acetonitrile)$_2$ {p-tolu} and Cu_2I_2(para-chloroaniline)$_2$(acetonitrile)$_2$ {p-caa} complexes. The existence of a S_4 internal symmetry element in the Cu_4I_4 cluster for both of the complexes is excluded, since the cluster exists with mixed ligands. Both complexes emitted yellow non-thermochromically and displayed no shift in emission maxima. However, the wavelength of the emission maxima for p-tolu complex was 586 nm and for p-caa complex was 630 nm. P-tolu complex had no internal symmetry whereas p-caa complex had two-fold symmetry. The p-tolu complex should emit thermochromically according to the previous suggestions stating that the absence of crystallographically related Cu-I bonds leads to thermochromism. Since the p-caa complex exhibited emission pattern that is similar to that of p-tolu, the existence or the absence of a symmetry element in the cubic structure of $Cu_4I_4L_4$ is not a determining factor in the thermochromicity of the systems. Due to the observation that the average Cu...Cu distance in these two complexes are 2.699(3) and 2.682(7)Å, respectively, the two emission maxima are most likely due to metal centered interactions.

The effect of symmetry element on the emission properties of a compound was further studied by Tompkins et al.[9] Three compounds, with the same cubic motif were synthesized. However, the symmetry elements were different in these compounds, thus, the thesis stating that symmetry can not be generally correlated with thermochromicity can be examined. Cu_4I_4(isopropylnicotinate)$_4$ had a S_4 symmetry element at the center of the tetrameter, Cu_4I_4(phenylnicotinate)$_4$ had a twofold axis relating one-half of the cube to the other and Cu_4I_4(benzylnicotinamide)$_4$ had no symmetry element. While the first and the third complexes exhibited thermochromicity, the second one did not.

Bao et al.[10] suggested that the crystallographic symmetry may influence the emission maxima rather than affecting the thermochromicity. The emission of copper(I) complexes due to non-ligand based mechanisms (i.e. aliphatic amine complexes) was investigated. It was noticed that in these systems, without ligand centered excited state, emission could only originate from metal centered electron transitions. Four rhombohedral systems with the $Cu_2I_2L_4$ structure were investigated: Cu_2I_2(1-methylpiperazine)$_4$ (I), Cu_2I_2(4-methylpiperidine)$_4$ (II), Cu_2I_2(3,3-dimethylpiperidine)$_4$ (III) and Cu_2I_2(3-azaspiro[5.5]undecane)$_4$ (IV). Complexes (III) and (IV) both crystallize with a crystallographic center of symmetry and emit at 650 nm when excited at 330 nm. Structures (I) and (II) have no symmetry element and emit at 495–500 nm under identical conditions. *AB initio* calculations suggest that the emission is derived from a copper based LUMO to halide based HOMO transition in complexes (I) and (II) which is forbidden by selection rules for complexes (III) and (IV) respectively. These complexes must then display emission by transitions between copper dominated orbitals that are higher in energy then the LUMO. Bao et al. also synthesized some cubic clusters namely: Cu_4I_4(acetonitrile)$_2$(morpholine)$_2$ (V) and Cu_4I_4(morpholine)$_4$ (VI). The former has no symmetry element and emits at 575 nm. The latter, having a twofold rotation axis, emits at 640-680 nm. So, in (VI), the HOMO level was raised by the twofold axis, reducing the energy difference between the HOMO and LUMO levels. Therefore, emission maxima would appear at a longer wavelength.

The conclusions obtained from the above study can be given as follows: i) the study proved that the excitation and emission transition may be forced to involve different orbitals when crystallographic symmetry made the HOMO to LUMO transition forbidden. ii) The HOMO level is halide dominated and the LUMO level was copper dominated and thus excitation involved electron donation from the halide to copper. The imposition of forbiddance upon the orbital system caused excitation from the HOMO to a higher but copper dominated orbital followed by radiative decay to a lower, but also copper dominated orbitals. Thus, while the excitation wavelength is seen to depend upon the identity of the halide atom, emission in centrosymmetric cases may take place between copper dominated orbitals and thus be independent of the identity of the halide. Also, the emission is of lower energy and thus occurs at a higher maxima.

Durand et al.[11] synthesized some copper halide complexes with phosphine ligands with a variety of structural motifs. An effort to correlate the emission properties with the presence of symmetry elements was attempted but no conclusive results were reached partially because of the lack of application of a suitable computational method (such as *Ab Initio* calculations) to probe the nature of transitions leading to emission.

The complexes previously studied with nitrogen donor ligands displayed instability under atmospheric conditions. Thus, in the interest of working with complexes of greater stability and thus greater commercial applicability, interest turned to phosphorous electron donor ligands. The known copper halide phosphine complexes are given in Table 1.

Table 1. Known Copper Halide Phosphine Complexes

Compound	Motif Type	Unit Cell Dimensions / Å	Unit Cell Angles /deg	Space Group	Ref.
$Cu_4Br_4(PPh_3)_4.2CHCl_3$	$Cu_4X_4L_4$	a=28.461(9) b=15.983(4) c=18.044(5)	α=90.0 β=112.59(1) γ=90.0	*C2/c*	15
$Cu_4I_4(PEt_3)_4$	$Cu_4X_4L_4$	a=13.024(1) b=13.024(1) c=13.024(1)	α=90.0 β=90.0 γ=90.0	$I\bar{4}3m$	16
$Cu_4Cl_4(PPh_3)_4$	$Cu_4X_4L_4$	a=17.468(2) b=20.519(3) c=18.215(2)	α=90.0 β=90.0 γ=90.0	*Pbcn*	17
$Cu_4I_4(PPh_3)_4$	$Cu_4X_4L_4$	a=25.8447(61) b=16.1371(38) c=18.2638(46)	α=90.0 β=110.75(2) γ=90.0	*C2/c*	18
$Cu_4Cl_4(PEt_3)_4$	$Cu_4X_4L_4$	a=12.592(18) b=12.592(18) c=12.592(18)	α=90.0 β=90.0 γ=90.0	$I\bar{4}3m$	19
$Cu_4Br_4(PEt_3)_4$	$Cu_4X_4L_4$	a=12.7495(14) b=12.7495(14) c=12.7495(14)	α=90.0 β=90.0 γ=90.0	$I\bar{4}3m$	19
$Cu_4I_4(PPh_2Me)_4$	$Cu_4X_4L_4$	a=25.704(6) b=11.971(2) c=19.631(4)	α=90.0 β=110.70(1) γ=90.0	*C2/c*	20

$Cu_4Br_4(P\text{-}t\text{-}Bu_3)_4$ Bu= butyl	$Cu_4X_4L_4$	a=14.008(3) b=14.008(3) c=19.416(3)	α=90.0 β=90.0 γ=90.0	$P\bar{3}$	21
$Cu_4Br_4(PPh_3)_4$	$Cu_4X_4L_4$	a=17.662(5) b=20.748(7) c=18.351(6)	α=90.0 β=90.0 γ=90.0	*Pbcn*	22
$Cu_4Br_4(PPh_3)_4$	$Cu_4X_4L_4$	a=25.687(10) b=16.084(7) c=17.815(9)	α=90.0 β=110.92(3) γ=90.0	*C2/c*	23
$Cu_4I_4(PPh_3)_4$	$Cu_4X_4L_4$	a=19.47(1) b=26.94(1) c=13.528(5)	α=90.0 β=98.98(4) γ=90.0	$P2_1/n$	24
$Cu_4I_4(DMPP)]_4$ DMPP= 1-phenyl-3,4-dimethylphosphine	$Cu_4X_4L_4$	a=21.058(4) b=12.059(2) c=23.425(7)	α=90.0 β=111.50(2) γ=90.0	*C2/c*	25
$Cu_4Br_4(dppm)_2$ dppm= bis(diphenylphosphine)methane	$Cu_4X_4L_4$	a=17.808(3) b=16.943(2) c=16.369(4)	α=90.0 β=90.0 γ=90.0	*Pbca*	26
$Cu_4I_4(Hdpf)_4$ Hdpf= 1′-(diphenylphosphino)ferrocene-carboxylic acid	$Cu_4X_4L_4$	a=16.061(2) b=24.435(5) c=24.719(5)	α=90.0 β=101.08(1) γ=90.0	$P2_1/c$	27
$Cu_2I_2(PPh_2Me)_4.SO_2$	$Cu_2X_2L_4$	a=20.02(2) b=12.062(6) c=14.898(7)	α=116.30(3) β=68.44(3) γ=124.89(2)	$P\bar{1}$	28

$Cu_2I_2(P(CCPh)_3)_4$	$Cu_2X_2L_4$	a=12.985(34) b=15.642(41) c=21.375(58)	α=106.11(9) β=86.54(11) γ=93.48(9)	$P\bar{1}$	29
$Cu_2I_2(PPh_3)_3$	$Cu_2X_2L_3$	a=11.763(4) b=20.682(4) c=10.527(3)	α=90.0 β=105.66(2) γ=90.0	$P2$	28
$Cu_2Cl_2(PPh_3)_3$	$Cu_2X_2L_3$	a=19.27(2) b=9.81(1) c=27.02(3)	α=90.0 β=112.5(8) γ=90.0	$P2_1/c$	30
$Cu_2Br_2(PPh_3)_3.1.5C_6H_6$	$Cu_2X_2L_3$	a=14.122(3) b=19.573(4) c=25.985(7)	α=90.0 β=128.99(1) γ=90.0	$P2_1/c$	31
$Cu_2Br_2(PPh_3)_3$	$Cu_2X_2L_3$	a= 19.390(8) b=9.912(5) c=26.979(9)	α=90.0 β=112.33(3) γ=90.0	$P2_1/c$	23
$Cu_2I_2\{P(m\text{-tolyl})_3\}_3$	$Cu_2X_2L_3$	a=17.729(1) b=13.682(2) c=24.635(3)	α=117.769(4) β=104.966(4) γ=107.536(3)	$P1$	32
Cu_2I_2DPM DPM= bis(diphenylphosphino)methane	$Cu_2X_2L_2$	a=17.128(9) b=18.306(9) c=16.508(8)	α=90.0 β=90.0 γ=90.0	$Pbca$	33
Cu_2Br_2DPM DPM= bis(diphenylphosphino)methane	$Cu_2X_2L_2$	a=23.707(10) b=17.805(9) c=16.991(8)	α=90.0 β=136.10(5) γ=90.0	$P2_1/C$	33

$Cu_2Cl_2(P(C_6H_{11})_3)_2$	$Cu_2X_2L_2$	a=8.4977(12) b=9.2667(11) c=13.2797(18)	α=100.82(1) β=89.73(1) γ=113.66(1)	$P\bar{1}$	34
$Cu_2I_2(SNC_5H_5)_2(PC_{21}H_{21})_2$	$Cu_2X_2L_2$	a=9.988(6) b=10.825(5) c=13.535(8)	α=77.268(2) β=94.409(2) γ=68.102(2)	$P\bar{1}$	35
$Cu_2Cl_2(PPh_2Mes)_2$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2$	a=9.961(3) b=18.687(6) c=11.009(7)	α=90.0 β=114.63(4) γ=90.0	$P2_1/n$	36
$Cu_2Br_2(PPh_2Mes)_2$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2$	a=9.939(2) b=18.832(6) c=11.238(6)	α=90.0 β=115.36(3) γ=90.0	$P2_1/n$	36
$Cu_2I_2(PPh_2Mes)_2.0.75C_6H_6$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2L'$	a=36.877(8) b=36.877(8) c=9.047(5)	α=90.0 β=90.0 γ=90.0	$R3$	36
$Cu_2Cl_2(PPh_2Mes_2)_2.2MeCN$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2$	a=15.783(7) b=9.570(4) c=8.914(4)	α=72.43(3) β=76.37(3) γ=74.03(3)	$P\bar{1}$	36
$Cu_2Br_2(PPh_2Mes_2)_2.\ 3C_6H_6$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2$	a=9.694(6) b=30.15(2) c=20.66(2)	α=90.0 β=98.00(7) γ=90.0	$C2/c$	36
$Cu_2I_2(PPh_2Mes_2)_2.\ 2MeCN$ Mes= 2,4,6-trimethylphenyl	$Cu_2X_2L_2$	a=11.694(8) b=14.77(1) c=29.76(3)	α=90.0 β=90.0 γ=90.0	$P2_1nb$	36

$Cu_2Cl_2(tmtp)_2(bzimtH)_2$ Tmtp= tri-m-tolylphosphine bzimtH= benz-1,3-imidazoline-2-thione	$Cu_2X_2L_2$	a=12.636(8) b=15.325(6) c=13.696(8)	α=90.0 β=102.76(3) γ=90.0	$P2_1/a$	37
$Cu_2Br_2(tmtp)_2(tzdtH)_2$ Tmtp= tri-m-tolylphosphine tzdtH = 1,3-thiazolidine-2-thione	$Cu_2X_2L_2$	a=15.085(1) b=9.820(3) c=17.263(1)	α=90.0 β=99.77(3) γ=90.0	$P2_1/n$	37
$Cu_2Cl_2(P(C_6H_4Me\text{-}o)_3)_2$	$Cu_2X_2L_2$	a=9.162(1) b=10.470(2) c=20.459(3)	α=90.0 β=99.24(1) γ=90.0	$P2_1/n$	26
$Cu_2Br_2(P(C_6H_4Me\text{-}o)_3)_2$	$Cu_2X_2L_2$	a=9.199(2) b=10.203(2) c=11.257(3)	α=101.5(1) β=100.68(1) γ=99.19(1)	$P\bar{1}$	26
$Cu_2Cl_2(NPM)_2$ NPM= diphenylaminodiphenylphosphinomethane	$Cu_2X_2L_2$	a=9.975(1) b=19.917(3) c=11.153(2)	α=90.0 β=93.413(9) γ=90.0	$P2_1/c$	38
$Cu_2I_2(NPM)_2$ NPM= diphenylaminodiphenylphosphinomethane	$Cu_2X_2L_2$	a=9.936(1) b=20.476(4) c=11.368(1)	α=90.0 β=97.480(8) γ=90.0	$P2_1/c$	38
$Cu_2I_2(C_5H_5NS)_2(P\text{-}p\text{-}PhMe)_2$	$Cu_2X_2L_2L'_2$	a=9.796(8) b=10.351(9) c=14.754(9)	α=83.81(5) β=73.62(6) γ=63.12(6)	$P\bar{1}$	39
$Cu_2Br_2(C_5H_5N)_2PPh_3$	$Cu_2X_2L_2$	a=26.188(7) b=14.222(3) c=11.259(4)	α=90.0 β=94.51(2) γ=90.0	$C2/c$	40

CuCl(PPh$_3$)$_3$	CuXL$_3$	a=19.2775(14) b=19.2775(14) c=10.4720(9)	α=90.0 β=90.0 γ=90.0	*P*3	41
CuCl(PPh$_2$Me)$_3$	CuXL$_3$	a=20.229(14) b=17.180(10) c=10.309(5)	α=90.0 β=90.0 γ=90.0	*Pn*2$_1$*a*	41
CuBr(Ph$_3$)$_3$	CuXL$_3$	a=19.225(8) b=19.225(8) c=10.610(3)	α=90.0 β=90.0 γ=90.0	*P*3	42
CuI(P$_3$)$_3$	CuXL$_3$	a=19.025(6) b=19.025(6) c=10.915(6)	α=90.0 β=90.0 γ=90.0	*P*3	42
CuCl(P$_3$)$_3$.2Me$_2$CO	CuXL$_3$	a=20.24(4) b=13.06(2) c=10.88(2)	α=92.3(1) β=105.4(1) γ=106.5(1)	$P\bar{1}$	42
CuBr(P$_3$)$_3$.2Me$_2$CO	CuXL$_3$	a=14.565(3) b=14.412(4) c=13.262(4)	α=87.82(2) β=83.82(2) γ=71.80(2)	$P\bar{1}$	42
CuI(TMPP) TMPP= tris(2,4,6 trimethoxyphenyl)-Phosphine	CuXL$_3$	a= 15.292(7) b=15.292(7) c=12.748(5)	α=90.0 β=90.0 γ=90.0	*P*4$_3$	43
CuI(NPM)$_2$ NPM=diphenylaminodiphenylphosphinomethane	CuXL$_2$	a=12.417(5) b=16.609(6) c=21.321(8)	α=90.0 β=99.80(1) γ=90.0	*C*2/*c*	38

$CuCl(PPh_3)_2.0.5C_6H_6$	$CuXL_2$	a=12.848(5) b=10.136(5) c=13.468(5)	α=104.51(4) β=102.20(3) γ=74.80(4)	$P\bar{1}$	44
$CuI(PPh_3)_2$	$CuXL_2$	a=24.90(1) b=9.094(2) c=15.493(6)	α=90.0 β=116.74(4) γ=90.0	*C2/c*	44
$CuCl(PPh_2$-*o*-tol$)_2$	$CuXL_2$	a=22.413(15) b=16.034(4) c=19.092(2)	α=90.0 β=107.04(4) γ=90.0	*C2/c*	45
$CuBr(PPh_2$-*o*-tol$)_2$	$CuXL_2$	a=22.348(7) b=16.033(8) c=19.526(5)	α=90.0 β=108.73(2) γ=90.0	*C2/c*	45
$CuI(PPh_2$-*o*-tol$)_2$	$CuXL_2$	a=18.665(5) b=10.006(2) c=19.764(5)	α=90.0 β=115.29(2) γ=90.0	*C2/c*	45
$[PPh_3Me][CuI_2(PPh_3)_2]$	$[PR_3R][CuX_2L_2]$	a=12.138(5) b=14.776(6) c=28.197(14)	α=90.0 β=103.76(4) γ=90.0	$P2_1/c$	46
$[PPh_3Me][Cu_2I_3(PPh_3)_2]$	$[PR_3R][Cu_2X_3L_2]$	a=17.744(10) b=17.744(10) c=17.744(10)	α=90.0 β=90.0 γ=90.0	$P2_13$	46
$[NEt_4][CuCl_2PPh_3]$ Et= ethyl	$[NR_4][CuX_2L]$	a=17.891(8) b=9.365(4) c=15.881(7)	α=90 β=96.07(3) γ=90	$P2_1/c$	47

$[NPr_4][CuBr_2PPh_3]$ Pr= propyl	$[NR_4][CuX_2L]$	a=38.94(2) b=9.188(4) c=19.203(11)	α=90.0 β=110.62(4) γ=90.0	*C2/c*	47
$[NBu_4][CuBr_2PPh_3]$ Bu= butyl	$[NR_4][CuX_2L]$	a=19.483(11) b=17.231(12) c=10.744(8)	α=90.0 β=90.0 γ=90.0	$P2_1ab$	47
$[NPr_4][CuI_2PPh_3]$ Pr= propyl	$[NR_4][CuX_2L]$	a=40.29(3) b=9.426(10) c=18.93(2)	α=90.0 β=111.76(6) γ=90.0	*C2/c*	47
$[NEt_4]_2[Cu_2I_4(PPh_3)_2]$ Et= ethyl	$[NR_4][Cu_2X_4L_2]$	a=10.499(4) b=13.609(5) c=21.480((2)	α=90.0 β=115.09(6) γ=90.0	$P2_1/c$	47

Some mechanisms have been suggested to explain the emission behavior of metal-organic solids. Excitation of a copper(I) halide Lewis base complex may arise from one of the following five mechanisms[12-14]:

1) Metal to Ligand Charge Transfer (MLCT).
2) Ligand-Ligand Interaction (LLI).
3) Metal-Metal Interaction (MMI).
4) Single Metal Excitation (SME).
5) Donor Acceptor Pair (DAP).

In MLCT, an electron from the $3d^{10}$ orbital of copper(I) is excited to a π^*orbital of the aromatic ligand giving $3d^9\pi^*$ as the excited state configuration. This transition may occur in many copper(I) halide complexes with nitrogen donor ligands in which the nitrogen atom is part of an unsaturated system.

In LLI, the ligand emission arises from electronic excited states derived from the ligand system. Such interaction is described as $\pi-\pi^*$ transition between pi systems. This transition is observed when the pi systems of unsaturated ligands are packed in parallel fashion and close to each other (3.2 Å) so that the $\pi-\pi^*$ interaction is possible.

In MMI, the transition is represented as $3d^{10}3d^{10} \rightarrow 3d^9 3d^{10} 4s^1$ excitation. Such d-d emission occurs from an excited state essentially localized on one of two close metal ions. This type of interaction was suggested for solid copper(I) halide complexes, when the distance between two copper atoms is less than 2.6Å.

When the distance between two copper atoms is greater than 2.8 Å, excitation may arise from SME (Single Metal Excitation). So, when the interaction between two metals is unlikely because of their wide separation, excitation might be represented as $3d^{10} \rightarrow 3d^9 4s^1$.

When the ligand donates an electron to the metal atom, the excitation mechanism is termed as DAP (Donor acceptor pair). For example, an electron may be promoted from the iodine to the copper. It is the opposite of MLCT.

Most of phosphine complexes in the solid state emit in the visible when excited in the ultraviolet. The emission spectrum shows peaks of 30 nm in width highly Stokes shifted from the broad envelope of the excitation spectrum. The stability of many copper(I) complexes combined with the variety of emission maxima observed make them candidates for use as sensitizers for conducting materials. The main objective of this thesis is to understand the relationship between structure and emission maximum as inferred by solid state symmetry.

While the solid state site symmetry of a single emitting atom has been recognized as a factor in the emission color of that atom, the extension of this influence to the solid state symmetry of a cluster has not been previously realized. As mentioned before, previous work in this research group have shown that some symmetry elements (centers of symmetry, three fold rotation axes, 4 bar rotation axes but not mirrors or two fold axes) when imposed crystallographically upon a solid state cluster, change the wavelength of emission observed from that solid.

The principle has been established from observation of families of complexes which differ only in internal symmetry element but which emit at different maximum of wavelength. Indeed allotropes of the same compound that differ only in crystallographic symmetry have been identified and shown to emit at different wavelengths.

To understand this phenomena, the use of ab initio calculations based on the crystallographic information of the solid will help in showing whether the effective symmetry elements impose forbiddance upon the obvious HOMO-LUMO transition and therefore emission occurs between orbitals separated by lesser energy. Comparison of calculations made on centrosymmetric clusters with those on noncentric clusters makes this point clear.

The nonemission of certain solid state clusters is now understood in terms of the quenching effect of counter ions of the form phenyl-B (B= As, or N) which serve as quenchers, apparently absorbing light emitted by the copper center and reemitting in a radiationless manner. Inclusion of copper(II) or of oxygen coordinated to copper(I) also quenches emission.

Our understanding needs to be extended by using different ligands such as those containing phosphorous. Sixteen new complexes with phosphine ligands were synthesized and their exact structures obtained by X-ray crystallography.

A literature review reveals a lack of recognition of a correlation between solid state emission and crystallographic symmetry in copper halide phosphine systems. The present work addresses this area and uses *ab initio* method to probe the nature of the transitions leading to emission.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

Much of the present knowledge of molecular structure has been derived from studies of X-ray diffraction of crystals. The method involves directing an X-ray beam at a crystalline sample followed by recording the intensities of the diffracted beam. Then the structure of the crystal can be worked out from the position and intensities of the diffraction spots. The core electrons in the molecules diffract the X-rays and the electron density distribution in the solid can be determined.

A crystal is, by definition, a solid that has a regularly repeating internal structure (arrangement of atoms). This internal periodicity was surmised in the seventeenth century from the regularities of the shapes of crystals, and was proved in 1912 when it was shown that a crystal could act as a three-dimensional diffraction grating for X-rays, since X-rays have wavelengths comparable to the distances between atoms in crystals.

The basic "building-block" in a crystal is called the unit cell. The crystal lattice is a regular three-dimensional array of points upon which the contents of the unit cell ("the motif") may be considered to lie, arranged in infinite repetition to build up the crystal structure. The concept of the lattice is important when diffraction by a crystal is considered. There are seven crystal systems possible (Table 2). The essential symmetry elements are included in this table.[48]

Table 2 The Seven Crystal Systems and the Related Essential Symmetry

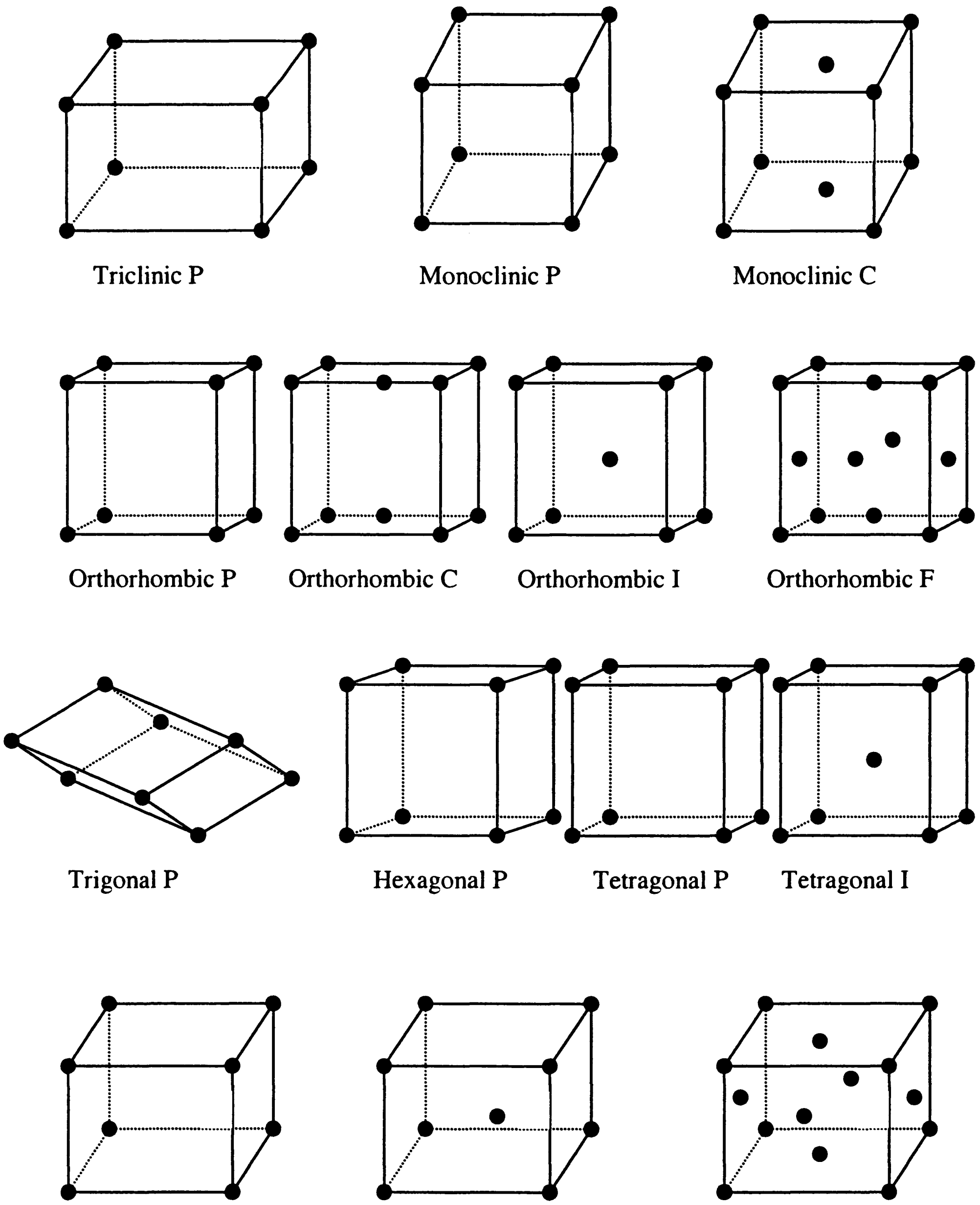
System	Unit Cell	Essential Symmetry	Space Lattices
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$ $a \neq b \neq c$	$1, \bar{1}$	P
Monoclinic	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ $a \neq b \neq c$	$2, m, 2/m$	P, C
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$ $a \neq b \neq c$	$222, mm2, mmm$	P, F, I, A(B or C)
Trigonal	$\alpha = \beta = \gamma \neq 90^\circ$ $a = b = c$	$3, \bar{3}, 32, 3m, \bar{3}m$	P
Hexagonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$ $a = b = c$	$6, \bar{6}, 6/m, 622, 6mm,$ $\bar{6}m\bar{2}, 6/mmm$	P
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$ $a = b \neq c$	$4, \bar{4}, 4/m, 422, 4mm,$ $\bar{4}2m, 4/mmm$	P, I
Cubic	$\alpha = \beta = \gamma = 90^\circ$ $a = b = c$	$23, m3, 432$ $\bar{4}3m, m3m$	P, F, I

If the cell contains lattice points only at the corners it is primitive (P), whereas a cell containing additional lattice points is centered. There are several types of centered lattice. The face centered lattice (F) contains additional lattice points in the center of each face. A side-centered lattice contains extra lattice points on only one pair of opposite faces. A body-centered lattice (I) has an extra lattice point at the body center. The combination of crystal system and lattice type gives the Bravais lattices.

When these four types of lattice are combined with the seven crystal systems, fourteen Bravais lattices (Figure 2) are obtained. The arrangement of structures on these lattices must be consistent with one of the 230 different combinations of symmetry elements (the 230 space groups) that are possible for arranging objects in a regularly repeating manner in three dimensions.

The easiest way to understand the optical problem of X-ray diffraction is to consider the X-ray waves as being reflected by planes in the crystal. When a beam of monochromatic X-rays strikes a crystal, the waves scattered by the atoms on each plane combine to from a reflected wave. If the path difference for waves reflected by successive planes is a whole number of wavelengths, the wave trains will combine to produce a strong reflected beam. In more formal geometric terms, if the spacing between the reflecting planes is d and the glancing angle of the incident X-ray beam is θ, the path difference for waves reflected by successive planes is $2d \sin \theta$. Hence the condition for diffraction is $n\lambda = 2d \sin \theta$, where n is an integer and λ is the wavelength.

When X-rays are diffracted by a crystal, the intensity of scattering at any allowed angle is the result of the combination of the waves scattered from different atoms to give various degrees of constructive and destructive interference. A structure determination



Triclinic P

Monoclinic P

Monoclinic C

Orthorhombic P

Orthorhombic C

Orthorhombic I

Orthorhombic F

Trigonal P

Hexagonal P

Tetragonal P

Tetragonal I

Cubic P

Cubic I

Cubic F

Figure 2 The 14 Three-Dimensional Bravais Lattices involves a matching of the observed intensity pattern to that calculated from a postulated model, and it is thus imperative to understand how this intensity pattern can be calculated for any desired model.

Since effects such as 1) background, 2) Lorentz, 3) polarization 4) crystal decomposition and 5) absorption alter the final results, the raw intensity data (I_{meas}) must be corrected.[49,50] The way these effects are handled is given below:

1) Background Factor: The following formula is used to correct for background:

$$I_{int} = (I_{meas} - L_{bg} - R_{bg}) \quad \text{x} \quad \text{scan speed} \tag{1}$$

$$\sigma I_{int} = (I_{meas} + L_{bg} - R_{bg})^{1/2} \quad \text{x} \quad \text{scan speed} \tag{2}$$

where I_{int} is the integrated intensity, I_{meas} is the measured intensity, L_{bg} is the left background (measured before peak scanned), R_{bg} is the right background (measured after peak scanned) and σI_{int} is the standard deviation of I_{int}. When $I_{int} \geq 2\sigma\ (I_{int})$ the reflection is considered to be present, i.e. observed. The term $2\sigma\ (I_{int})$ is the standard deviation of I_{int}.

2) Lorentz Correction (L): This factor takes into account the time that it takes for a given reflection to pass through the surface of the sphere of reflection. The value depends on the scattering angle and on the geometry of the measurement of the reflection. When the crystal is rotated at a constant speed, reflections with low 2θ spend more time in optimum diffraction geometry than those reflections with high 2θ. This factor is defined as to take care of this effect.

$$L = (\sin 2\theta)^{-1} \tag{3}$$

3) Polarization factor (P): It takes into account the fact that the reflection efficiency of components of the X-ray beam varies with the scattering angle. The

unpolarized X-ray beam consists of a perpendicular component (I_{perp}) and a parallel one (c). These components are diffracted with different efficiencies, which depend on the diffraction angle θ. At lower 2θ values, I_{perp} is diffracted with higher efficiency according to:

$$I_{perp} = K\, I_o \cos^2 2\theta \qquad (4)$$

$$I_{para} = K\, I_o \qquad (5)$$

where K is a reflection factor for the crystal planes and I_o is the intensity of the incident X-ray beam. The scattered intensity of the incident X-ray beam can be expressed as an average of the two components:

$$I = (\, I_{para} + I_{perp}\,) / 2 = K\, I_o / (1 + \cos^2 2\theta\,) / 2 \qquad (6)$$

where the term $(1 + \cos^2 2\theta\,) / 2$ is the polarization factor, P. Since P is a function of 2θ only, it is independent of the geometry of data collection.

4) Absorption factor (A): When an X-ray beam passes through a crystal, its intensity is reduced by scattering and by absorption. The extent of reduction by absorption depends on the pathlength of the beam through the crystal, the wavelength of the incident X-ray beam and the nature of atoms in the crystal. This factor is defined as:

$$A = (1 / V\,) \int e^{-\mu L}\, dv \qquad (7)$$

Where V is the volume of the crystal, μ is the linear absorption coefficient, and L the pathlength through the crystal of the beam diffracted by the volume dv.[51]

5) Decomposition Factor (D): As the data collection proceeds, there will be a decrease in intensity due to the decomposition of the crystal by the incident X-ray beam. Since the decomposition is assumed to be linearly proportional with time, this correction factor is given by:

$$D = I_{orig} / I_{avg} \tag{8}$$

where I_{orig} is the initial intensity of a standard reflection and I_{avg} is the average new intensity of the standard reflection in between any two observations. These "standard" reflections are remeasured after every 97 data points and the decrease in their intensities is used as a measure of how to correct the data measured for decomposition.

A general expression for the corrected integrated intensity (I_{corr}) for all the above mentioned factors is given by:

$$I_{corr} = I_{int} \times D \; / \, L\,P\,A \tag{9}$$

where I_{int} is the initial intensity.

Extinction is another systematic source for weakening the incident beam as it passes through the crystal. Part of this beam in a single perfect block may be multiply reflected so that it returns to its original direction but is out of phase with the main beam, thus reducing the intensity of the latter. Thus, the observed structural factors will be systematically smaller than the calculated structural factors.

The structure factor F_{hkl} represents the diffracted intensity in units of electron density, and its determination is the final aim of all experimental methods. This quantity expresses both the amplitude and the phase of the reflection *hkl*. It plays a central role in the solution and refinement of crystal structures because it represents the quantity related to the intensity of the reflection which depends on the structure giving rise to that reflection and is independent of the method and conditions of observation of the reflection. The set of structure factors for all the reflections *hkl,* diffracting below $2\theta=60^{\circ}$, are the primary quantities necessary for the derivation of the three-dimensional distribution of electron density, which is the image of the crystal structure, calculated by

Fourier methods. This image is the crystallographic analogue of the image formed in a microscope by recombination of the rays scattered by the object. In a microscope this recombination is done physically by the lenses of the microscope but in crystallography the corresponding recombination of diffracted beams must be done by mathematical calculation.

X-rays are scattered by electrons and the extent of the scattering depends on the atomic number of the atom and the angle of scattering, 2θ, and is represented by an atomic scattering factor F_j. By identifying the Miller indices (*hkl*) of the crystal plane giving rise to each diffracted beam, the direction of the beam is specified. From the measured intensity of the beam its amplitude may readily be deduced. For a group of atoms, the amplitude (relative to the scattering by a single electron) and the phase of the X-rays scattered, by one unit cell are represented by the structure factor $F_{hkl} = A_{hkl} + iB_{hkl}$ for each reflection.[48] For a known structure with atoms *j* at positions x_j, y_j, z_j this may be calculated from

$$A_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) \qquad (10)$$

$$B_{hkl} = \sum_j f_j \sin 2\,\pi(hx_j + ky_j + iz_j) \qquad (11)$$

where the summation is over all atoms in the unit cell. The phase angle α is $\tan^{-1}$ (B/A) and the structure factor amplitude $|F_{hkl}|$ is $(A^2 + B^2)^{1/2}$.

The electron density at a point *x,y,z* in a unit cell of volume V, is

$$p\,(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l |F_{hkl}| \cos\,[2\pi\,(hx + ky + lz) - \alpha_{hkl}] \qquad (12)$$

Therefore, if we knew $|F_{hkl}|$ and α (for each h,k,l) we could compute p for all values of x, y, and z and plot the values obtained to give a three-dimensional electron density map. Then, assuming atomic nuclei to be at the centers of areas of electron densities, we would know the entire structure. However, we can obtain only the structure factor amplitudes $|F_{hkl}|$ and not the phase angles, α, directly from experimental measurements. This is what is known in crystallography as "the phase problem".[48,52] We must usually derive values of α, either from values of A and B computed from suitable "trial" structures or by the use of purely analytical methods. Approximations to electron density maps can be calculated with experimentally observed values of $|F_{hkl}|$ and calculated values of α. If the trial structure is not too grossly in error, the map will be a reasonable representation of the correct electron density map, and the structure can be improved by refinement to give a better fit of observed and calculated $|F_{hkl}|$ values.

Since the phases cannot be compared with any observable quantities, the validity of the proposed structure must be tested by comparison of the calculated values of the amplitudes of the structure factor Fc with the observed amplitudes $|F_{hkl}|$.[49] This is done by calculating a discrepancy (or reliability) index defined by

$$R = \frac{\Sigma\big|\,|\mathrm{Fo}| - |\mathrm{Fc}|\,\big|}{\Sigma|\mathrm{Fo}|} \tag{14}$$

where the summation is usually taken over all the reflections giving significant intensities. R is one of the most frequently used measures for the correctness of a structure determination. It is a measure of the precision of the fit of the model used to the experimental data obtained.

Because of random errors in the observed structure factor amplitudes $|F_O|$, and approximations made in the model on which the calculated structure factors are based, it is never possible to obtain a set of $|Fc|$ which exactly reproduce the $|F_O|$, so structure refinement never reduces R to zero. For good quality diffractometer data, values of R in the region of 0.05 are quite common for fully refined structures. For initial approximate structures arising from the structure solution process R should not normally be greater than about 0.3 to be capable of satisfactory refinement.

The solution of a crystal structure therefore consists of applying some technique for obtaining the approximate phases of at least some of the X-ray reflections, and the process of structure refinement is one in which the knowledge of phases is extended to all reflections and is made as accurate as possible for all reflections.

There are two main methods for solving crystal structures. The first is known as the Direct method and the second is called the Patterson method. The former is used when there are no heavy atoms in the cell, i.e. all the atoms in the molecule have similar scattering power. Direct methods use the facts that the electron density in a structure can not take any value but must always be positive, and that the structure consists of discrete spherically symmetric atoms, to calculate mathematical probabilities for the phase values and thus to calculate an electron density map of the unit cell.[48] Theoreticians have worked on the mathematics of these methods and have developed many computer programs that employ them such as SHELXL.

The Patterson method relies on the presence of at least one heavy atom in the unit cell. This method was named after its pioneer A. L. Patterson, who pointed out that a Fourier synthesis using the structural factor $|F_{hkl}|$ values as coefficients produces a three dimensional electron density map (Equation 13), but that a similar Fourier synthesis using $| F_{hkl} |^2$ as the coefficients has peaks corresponding to all the interatomic vectors[52]:

$$P\,(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F_{hkl}|^2 \cos\,[2\pi\,(hu + kv + lw)] \qquad (13)$$

Thus, in this method a synthesis is performed on the data set, from which a three-dimensional map of the unit cell is calculated from the values of $P\,(uvw)$, not directly of the electron density in the unit cell but such that the values of $P\,(uvw)$ correspond to the vectors between all pairs of atoms in the cell.

To judge on the correctness of a structure, all the following criteria should be applied:[48,49]

1. The agreement of individual structure factor amplitudes with those calculated for refined model should be consistent with the estimated precision of the experimental measurements of the observations.
2. A difference map, phased with final parameters for the refined structure, should reveal no fluctuations in electron density greater than those expected on the basis of the estimated precision of the electron density.
3. Any anomalies in molecular geometry or packing should be scrutinized with great care and regarded with some skepticism.
4. The structure should be reasonable chemically with bond angles and distances consistent with those seen in the literature for similar atoms.

Figure 3 shows a flow chart for solving a crystal structure from data measured on a diffractometer.[53]

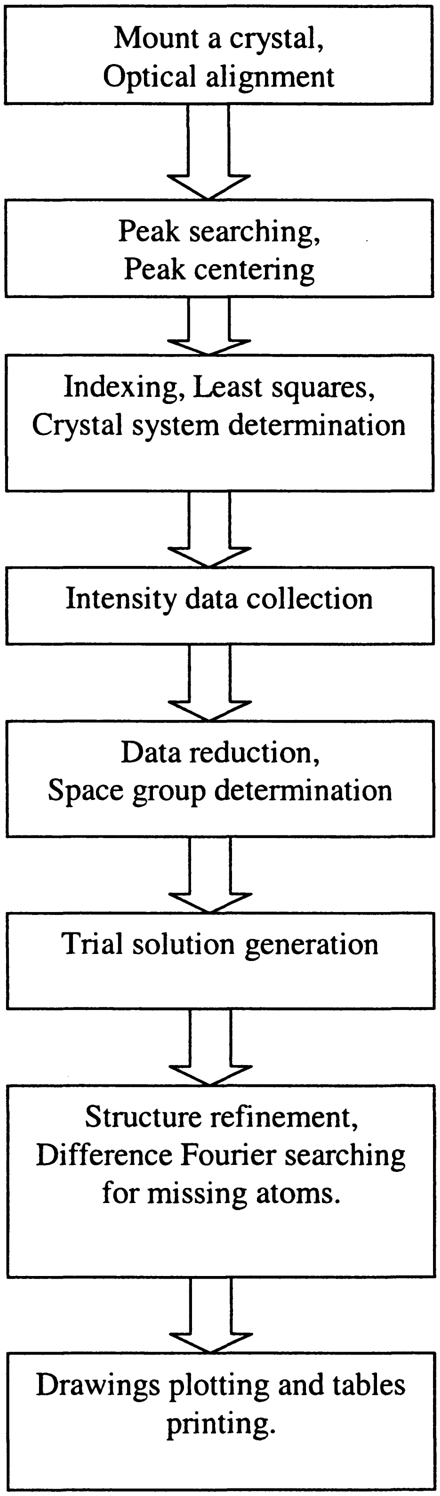


Figure 3 Flow Chart For Solving a Crystal Structure.

CHAPTER III

LUMINESCENCE

Luminescence is the light emitted by a substance in a high energy state as a result of some excitation process. The emission thus may take place at low temperatures, and is often called "cold light."

Under normal conditions, all of the electrons in a sample of matter will assume the distribution or state of lowest energy open to them. However, if energy in some form is supplied to the matter, an electron can be excited, that is, raised to a state of higher energy. Luminescence will then be produced if the electron emits light as it returns to the lower energy state. The color of the light, as determined by the frequency of the light waves, is related to the difference in energy of the two states; the Planck-Einstein equation ($E = h\nu$) states that the frequency ν is equal to the difference in energy E divided by Planck's constant h.

There are many types of luminescence, according to the manner in which the emitter was excited, such as: photoluminescence (excitation by electromagnetic radiation), chemiluminescence (excitation by chemical reaction), bioluminescence (excitation by biological process), sonoluminescence (excitation by ultrasonic waves) and radioluminescence (excitation by high-energy particles).[54,55] In this work, we are mainly concerned by the first type (photoluminescence).

A useful quantity known as the molecular multiplicity, M, is defined as $M = 2S + 1$, where S is the spin quantum number of the molecule, and is the sum of the net spin of the electrons in the molecule. If S equals to zero, the multiplicity will be one and it is referred to as a singlet state. The ground singlet state is designated as S_0, and the first and second excited singlet states are denoted S_1 and S_2. If the molecule exists in the excited state and the overall molecule have two unpaired electrons, the total S will be one ($S = +\frac{1}{2} +\frac{1}{2} = 1$) and thus M will equal to three; the multiplicity is referred to as a triplet state (T). The first triplet is denoted as T_1.

The best way to describe the excitation and deexcitation processes is by using a Jablonski energy-level diagram (Figure. 4). Here, the molecule is depicted as possessing three major contributions to its overall energy: electronic, vibrational and rotational (not shown in the figure). The time of electronic absorption of the electromagnetic radiation is about 10^{-15} sec. During this period, if the molecule absorbs a photon, it is excited to a higher singlet state (e.g., S_2). Now, there are several possibilities for the molecule to eliminate this excess energy. In condensed-phase systems, the molecule can rapidly dissipate its excess vibrational energy as heat with solvent molecules. Such a process is called vibrational relaxation (VR). Another possibility here is that the molecule can pass from a low vibrational level of S_2 to an equally energetic vibrational level of the first exited singlet, S_1. Such process is termed as internal conversions (IC). Both VR and IC processes are very rapid (~10^{-2} sec). Another non-radiative process is called intersystem crossing (ISC), which happens when the transition occur between states of different multiplicity (e.g., $S \rightarrow T$).

Photoluminescence can be characterized by its lifetime after removal of the excitation. When energy is absorbed by a substance, some of its electrons are

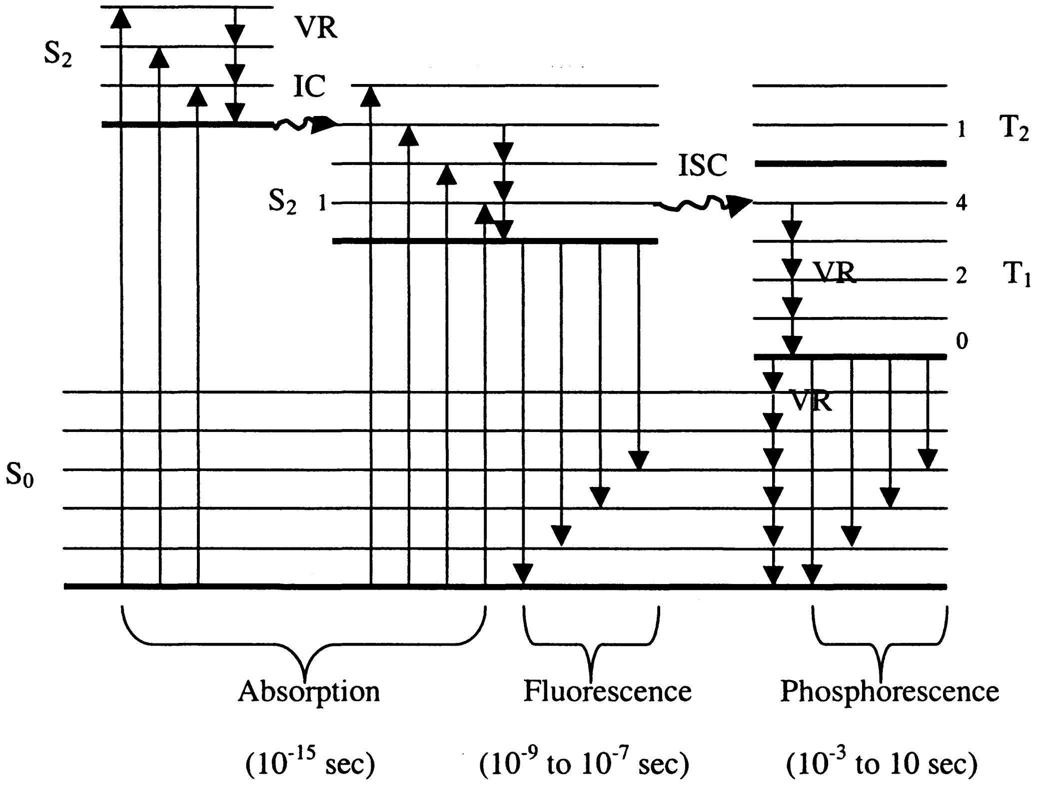


Figure. 4 Jablonski Energy-Level Diagram Depicting Absorption and Emission.

temporarily excited to a higher energy state than their normal state. As the electrons return to their normal energy state, they lose energy, which is emitted by the substance in the form of radiation at a characteristic wavelength. Fluorescence and phosphorescence, which are forms of luminescence, are distinguished by how long the emitted radiation lasts. Fluorescence ceases in about one hundred millionth of a second (10^{-8} second) after the exciting source is removed, whereas phosphorescence continues for seconds or even hours. The duration of the visible emitted energy depends on the rapidity with which the electrons return to their normal energy state.

Fluorescent radiation generally is of a longer wavelength than the absorbed radiation that causes it; that is, the emitted photons are less energetic than the absorbed ones. This rule, known as Stokes' law, normally holds because some of the absorbed energy usually is lost to other processes; however, there are some exceptions to this law.

In many cases information about the energy levels of a system can be obtained only by luminescence studies. This type of study pointed the way for the development of the modern theories of the structure of atoms, molecules, and solids. Studies of electronic distributions, energies, and transitions between states by luminescence measurements continue to provide insights in the fields of chemistry, physics, and biology.

Temperature affects both the shape and the intensity of emission peaks in measured spectra. These effects arise by the changes in populations of the available rotational and vibrational levels with increase in temperature. At low temperature, peaks are sharper and more intense. The transitions that occur are primarily electronic and not vibrational or rotational in nature. Electronic transitions require much larger amounts of energy in discrete quanta than rotational or vibrational transitions. They show up as a single wavelength emission or absorption, and not as a near continuous spectrum as for rotational and vibrational transitions.

Ultraviolet (UV) light is frequently used to excite luminescence. Many minerals give characteristic emissions when illuminated with such light. Many organic molecules in solution at low temperatures show both fluorescence and phosphorescence when excited with ultraviolet light. The phosphorescence in this case has been shown to occur when the excited electron reverses its spin to give what is called a triplet state. The electron must then reverse its spin again to return to the lowest state. This process takes place only slowly.

The luminescence of a material can be studied using a fluorometer, which measures the light emitted at right angles to the path of the incident or excitation beam. A typical fluorometer consists of four basic parts: a radiation source, a monochromator, a sample cell and a detector.[56] A block diagram of such fluorimeters is given in Figure. 5

The most common source employed in these fluorometers is a low-pressure xenon or mercury arc lamp, which are the most powerful and brightest sources of UV radiation. The first one has the advantage of a relatively broad continuum, extending into the UV region. The second one is preferred for greater excitation energy at selected wavelengths. However, for the mercury arc lamp, the excitation spectra are often distorted, because the mercury arc consists of sharp mercury lines superimposed on a continuum.

A wave selection device (usually a monochromator) is used both before and after the sample chamber. Such devices are used to maximize the florescence signal and to minimize the background signal. The beam of light is separated into a band of narrow wavelengths by the monochromators using gratings or prisms.

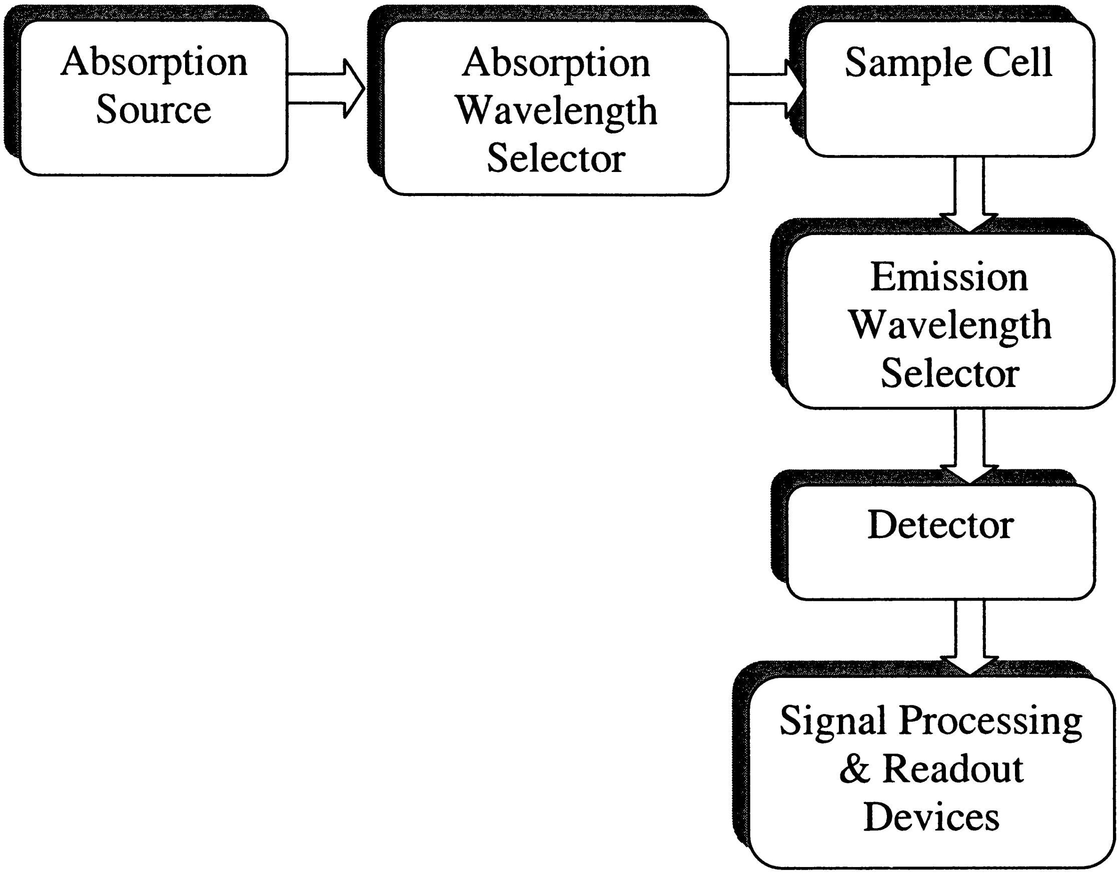


Figure. 5 Block Diagram of a Typical Fluorimeter.

The sample cell is placed in a sample chamber and the luminescence is viewed at 90° with respect to the excitation beam. The material used for making the cell windows must not fluoresce and must be transparent to the wavelength of interest. Although normal glass can be used, high quality fused synthetic silica is the best construction material.

The final component of the fluorimeter is the detector, which is placed at the exit slit of the emission-wavelength selection system. Since the radiant power in luminescence is low, a photomultiplier tube (PMT) is usually used as a detector, which has the advantage of a high gain and relatively broad spectral sensitivity to low radiation levels.

The output (current) from the PMT is first converted to voltage with an operational amplifier. After further voltage amplification, the readout voltage signal is digitized and stored in memory for later manipulation and display on computer screen.

CHAPTER IV

EXPERIMENTAL

SYNTHESIS

Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and 1, 10-phenanthroline (0.2366 g, 1.31 x 10^{-3} mol) were added to 30 ml of acetonitrile. The mixture was refluxed for 24 hours. After filtering the solution, the filtrate was left to stand. After 4 days, Black rhombic crystals formed. A crystal of appropriate dimensions was glued onto a glass fiber for use in X-ray diffraction studies.

$Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

CuI (0.25 g, 1.31 x 10^{-3} mol) and tri-*m*-tolylphosphine (0.1994 g, 6.55 x 10^{-4} mol) were added to 30 ml of acetonitrile. The mixture was refluxed for 24 hours. Then, the solution was filtered. White rhombic crystals formed in the filtrate after 5 days. A crystal was mounted on a glass fiber for X-ray structural analysis.

$Cu_2I_2(P(C_6H_5)_3)_3$

Triphenylphosphine (0.7171 g, 6.55 x 10^{-4} mol) and copper iodide (0.25 g, 1.31 x 10^{-3} mol) were dissolved in 30 ml of acetone. After refluxing the mixture for 1 day, the hot solution was filtered. Colorless irregular crystals were observed to form on the filtrate after one day. Thus, a re-crystallization process was performed after which a colorless nice cubic crystals started to form. Then, a crystal was mounted on a glass fiber for molecular structural determination by X-ray diffraction.

$CuI(P(C_6H_{11})_3)_2$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and tricyclohexylphosphine (0.1837 g, 6.55 x 10^{-4} mol) were mixed in 30 ml of hexane. After refluxing for 24 hours, the solution was filtered. Colorless needle-like crystals formed after 4 days. A crystal was selected and mounted on a glass fiber for X-ray structure determination.

$Cu_4I_4(P(C_6H_5)_2CH_3)_4$

CuI (0.25 g, 1.31 x 10^{-3} mol) and methyldiphenylphosphine (0.131 g, 6.55 x 10^{-4} mol) were dissolved in 30 ml of acetone. The mixture was heated under reflux for 24 hours and then filtered. White rhombic crystals formed after severeal days. A crystal with appropriate dimensions was chosen and mounted on a glass fiber for X-ray diffraction work.

$Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

CuI (0.25 g, 1.31 x 10^{-3} mol) and tri-*m*-tolylphosphine (0.1994 g, 6.55 x 10^{-4} mol) were added to hexane (30 ml). The resulting mixture was refluxed for 24 hrs. After filtering, the solution was left standing for 2 days whereupon crystal formation was observed. A colorless crystal was mounted on a glass fiber for X- ray diffraction study.

$Cu_2I_2(P(o\text{-}C_7H_7)_3)_2$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and tri-*o*-tolylphosphine (0.1994 g, 6.55 x 10^{-4} mol) were added to 30 ml of hexane. The mixture was refluxed for 24 hours. After filtering the solution, it was left to stand at ambient temperature. After 9 days, white rhombic crystals formed. A crystal was mounted on a glass fiber for X-ray structure determination.

$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Tri-*p*-tolylphosphine (0.1994 g, 6.55 x 10^{-4} mol) and copper iodide (0.25 g, 1.31 x 10^{-3} mol) were mixed in 30 ml of ethanol. After refluxing the mixture for 1 day, the solution was filtered. Colorless rhombic crystals were observed after a few days. A crystal was mounted on a glass fiber for molecular structural determination by the X-ray diffraction method.

$CuI(P(C_6H_5)_2CH_3)_3$

CuI (0.25 g, 1.31 x 10^{-3} mol) and methyldiphenylphosphine (0.131 g, 6.55 x 10^{-4} mol) were dissolved in 30 ml of ethanol. After refluxing the solution for 24 hours, the solution was filtered. White cubic crystals formed in the filtrate after several days. A crystal was selected and mounted on a glass fiber for X-ray structure determination.

$Cu_4I_4(PC_6H_5(CH_3)_2)_4$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and dimethylpheylphosphine (0.0905 g, 6.55 x 10^{-4} mol) were added to 30 ml of acetonitrile. The mixture was refluxed for 24 hours. Then, the solution was filtered. White rhombic crystals formed after a couple of days. A crystal with appropriate dimensions was chosen and then mounted on a glass fiber for X-ray diffraction work.

$Cu_2I_2(P(C_6H_{11})_3)_2$

CuI (0.25 g, 1.31 x 10^{-3} mol) and tricyclohexylphosphine (0.0905 g, 1.965 x 10^{-3} mol) were added to 30 ml of benzene. Then, the mixture was refluxed for 24 hours. After filtering the solution, it was left standing for 5 days, whereupon colorless cubic crytstals were observed. A crystal was mounted on a glass fiber for structural determination by the X-ray diffraction technique.

$CuI(P(C_6H_{11})_3)_2.C_6H_6$

Tricyclohexylphosphine (1.022 g, 3.93 x 10^{-3} mol) and copper iodide (0.25 g, 1.31 x 10^{-3} mol) were dissolved in 30 ml of benzene. The mixture was refluxed for 1 day. Then, the solution was filtered. After 7 days, white rhombic crystals were observed. A crystal was mounted on a glass fiber for molecular structural determination by the X-ray diffraction method.

$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and tri-*p*-tolylphosphine (0.1994 g, 6.55 x 10^{-4} mol) were added to 30 ml of acetone. The mixture was refluxed for 24 hours. After filtering the solution, it was left standing on the bench. After 4 days, black rhombic crystals formed. A crystal with appropriate dimensions was glued onto a glass fiber for use in X-ray diffraction studies.

$Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

CuI (0.25 g, 1.31×10^{-3} mol) and tri-*m*-tolylphosphine (0.1994 g, 6.55×10^{-4} mol) were added to 30 ml of acetone. The mixture was refluxed for 24 hours. Then, the solution was filtered. White rhombic crystals formed after 5 days. A crystal was mounted on a glass fiber for X-ray structural analysis.

$Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

Copper iodide (0.25 g, 1.31×10^{-3} mol) and methyldiphenylphosphine (0.524 g, 2.62×10^{-3} mol) were dissolved in 30 ml of a mixture of tetrahydrofuran and pentane (50%/50%). After refluxing the solution for 24 hours, the solution was filtered. Colorless needles-like crystals formed after 4 days. A suitable crystal was selected and mounted on a glass fiber for X-ray structure determination.

$Cu_2I_2(P(C_6H_5)_3)_3$

CuI (0.25 g, 1.31×10^{-3} mol) and triphenylphosphine (0.6868 g, 2.62×10^{-3} mol) were dissolved in 30 ml of toluene. The mixture was refluxed for 24 hours and then the solution was filtered. White rhombic crystals formed after several days. A crystal with appropriate dimensions was chosen and mounted on a glass fiber for X-ray diffraction work.

$CuI(P(C_6H_{11})_3)_2.C_7H_8$

Copper iodide (0.25 g, 1.31 x 10^{-3} mol) and tricyclohexylphosphine (0.7348 g, 2.62 x 10^{-3} mol) were added to 30 ml of toluene. Then, the mixture was refluxed for 24 hours. After filtering the solution, it was left standing for 2 days whereupon the formation of colorless cubic crystals were observed. A crystal was mounted on a glass fiber for X-ray structure diffraction study.

CRYSTALLOGRAPHY

Crystals with appropriate dimensions (<0.2 mm in all dimensions) of each compound were chosen for X-ray diffraction. A single crystal of good quality was mounted on a glass fiber held in a brass support. Then, the brass pin was placed in a goniometer head and mounted on a Siemens P4 automated four-circle diffractometer equipped with a PC-486DX computer. The crystals were irradiated with monochromated molybdenum radiation at a wavelength of 0.71073 A (a weighted average of $k_{\alpha 1}$ and $k_{\alpha 2}$). Unit cell dimensions were determined using the centered angles from 25 - 50 independent strong reflections which were refined by least-squares methods using the automated procedure in XSCANS[57]. Intensity data were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan range of 0.60 below $k_{\alpha 1}$ and 0.60 above $k_{\alpha 2}$ to a maximum 2θ value (normally 60.00°). Backgrounds were measured at the ends of the scan range for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections to monitor crystal decomposition. The raw intensity data collected were corrected for Lorentz, polarization, absorption, decomposition, centering and background effects, after which redundant and space group forbidden data were removed. The profile fitting technique for data reduction was employed. Observed reflections ($F>4.0\ F(l)$) were used to arrive at the non-hydrogen atom positions by direct methods[58-60]. Refinement of the scale factor, positional and anisotropic thermal parameters for all atoms was carried out using either XLS (refinement on F)[50] or SHELXL[61] (refinement on F^2) to convergence. Scattering factors were taken from the International Tables for Crystallography[62]. Hydrogen atom positions were calculated using idealized geometry. A weighting scheme ($w = (\sigma^2(F) + \mathrm{abs}(g)(F^2)^{-1})$ and extinction correction were applied at the last stages of refinement. Final refinement led to the agreement factor, R ($R = \sum(|F_o| - |F_c|) / \sum|F_o|$).

FLUORESCENCE

Emission spectra of all the synthesized complexes were measured using a Fluorolog-3 spectrofluorometer (ISA, inc.). Finely divided samples of these complexes were spread on double-sided tape attached to a 0.5 inch x 1.5 inch piece of non-emitting black cardboard. The light source was a xenon lamp. Measurements were made, from 340-700 nm at 0.5 nm intervals with integration time of 0.1 s, at room temperature. Both the excitation and emission slits were 1 mm in width. A blank sample showed no signal in the area of interest.

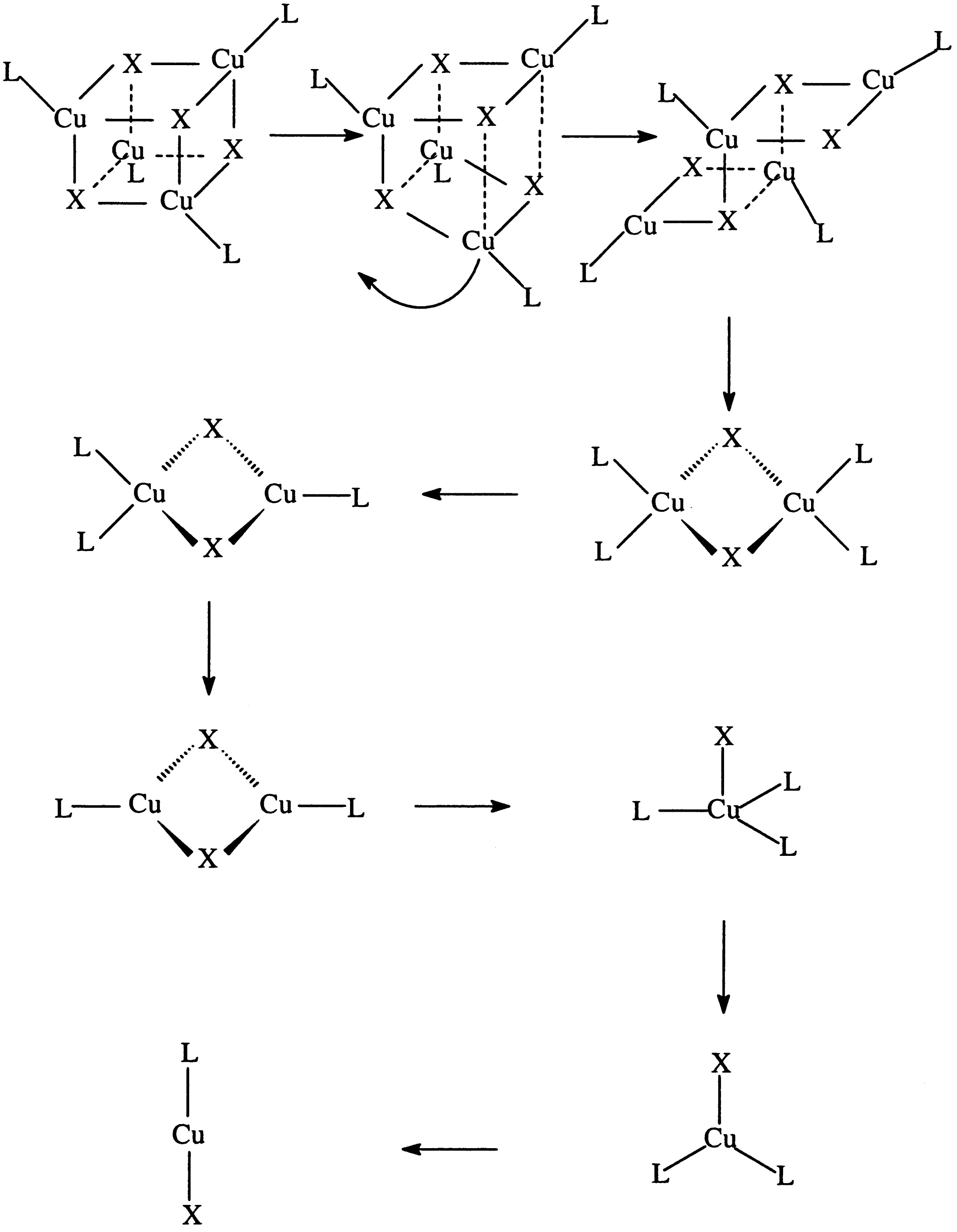
The emission spectrum was obtained by irradiating the sample at the wavelength of maximum absorption (300 nm) and observing the emitted fluorescence to give a plot of intensity versus wavelength in relative units.

CHAPTER V

RESULTS AND DISCUSSION

In this work, 19 copper halide complexes were synthesized and their crystal structures were determined by single crystal X-ray diffraction, followed by measurement of their luminescent spectra. Of these nineteen complexes, sixteen were not known before. Then, a correlation between the wavelength of maximum emission and the crystallographic symmetry was sought. *Ab initio* calculations were employed to support the correlation. The structures prepared can be grouped into four classes: i) hexaiodohexacopper(I) ($Cu_6I_6L_4L'_2$ (L= trisubstituted phosphine and L'= acetonitrile)), ii) cubanes ($Cu_4X_4L_4$), iii) rhombs ($Cu_2X_2L_4$, $Cu_2X_2L_3$ and $Cu_2X_2L_2$) and iv) monomers ($CuXL_3$ and $CuXL_2$). Tables 7-74 present the crystallographic data and the derived results for the different complexes. Projection views and emission spectra of the complexes are shown in Figures 6-39.

The reason for the structural variety observed is believed to be due to steric factors imposed by the size of ligands. Instead of the cubane structure in which Cu is tetrahedrally coordinated to three iodide atoms and additional fourth ligand, one can get step, rhomb and monomer motifs. A suggested scheme for such transformation is given in scheme I below. Each step reduces steric stress at copper.



Scheme I

It is important to respect the role of solvents in the syntheses. Carrying out the same type of synthesis (same reactants and same stoichiometry) in different solvents may lead to different products. For instance, reacting CuI with tri-*m*-tolylphosphine in hexane gives $Cu_2I_2(P(m\text{-tolyl})_3)_3$, which has a rhombic motif. On the other hand, carrying out the same reaction in acetone will result in $Cu_4I_4(P(m\text{-tolyl})_3)_4$, which exhibits a cubic form. Repeating the same thing in acetonitrile results in $Cu_6I_6(P(m\text{-tolyl})_3)_4(\text{acetonitrile})_2$. If the solvent is not included in the unit cell, it does not affect the luminescent behavior directly. Its effect on luminescence is indirect, i. e., by leading to different structures, materials of different luminescent behavior are prepared. However, it should be noted that this is not always the case. Many times, the same product can be obtained from different solvents, especially if the solvents are similar. This phenomenon was observed repeatedly during this study.

Internal symmetry elements, Cu-X distances, Cu-Cu distances, Cu-I-Cu angles and wavelengths of maximum emission (λ_{max}) for the complexes are given in Table 3.

To understand the emission behavior of the CuX phosphine complexes and to find a correlation of emission with crystallographic symmetry, *Ab initio* calculations were performed. The calculations were carried out using the Gaussian 94 software package[63]. To obtain a description of frontier molecular orbitals for the different solids, a Hartree-Fock method of calculation was employed[64]. The chosen basis set was LANL1DZ, representing core orbitals (non-valent) for heavy atoms (I, Cu and P) in the form of primitive Gaussian type orbitals. The Z-matrix for each structure was constructed on the basis of the crystallographic coordinates; i.e. using bond lengths, bond angles and torsional (dihedral) angles derived from the crystallographic results. Owing to

Table 3 Structural and Emission Data for the Copper Halide Phosphine Complexes

Motif	Space group	Symmetry	Cu-X (Å)	Cu-Cu (Å)	Cu-I-Cu angle (°)	λ_{max}, nm
Cu_6I_6						
$Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$	*F*d-3	1	2.6188-2.7278	2.985	67.83-111.50	585
Cubanes [$Cu_4I_4L_4$]						
$Cu_4I_4(P(C_6H_5)_2CH_3)_4$	*C*2/c	2	2.635-2.794	2.871-3.043	63.4-67.2	570
$Cu_4I_4(PC_6H_5(CH_3)_2)_4$	*C*2/c	2	2.653-2.810	2.848-2.941	61.75-65.88	592
$Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$	*I*-42d	1	2.729-2.802	3.348-3.667	74.85-83.30	385
Rhombs [$Cu_2I_2L_4$]						
$Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$	*C*2/c	$\bar{1}$	2.698-2.795	3.170	70.45	547
Rhombs [$Cu_2I_2L_3$]						
$Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$	$P\bar{1}$	1	2.583-2.819	3.059	68.8-68.9	479
$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$	$P\bar{1}$	1	2.579-2.817	2.947	65.59-66.44	478
$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$	$P2_1/a$	1	2.563-2.786	2.927	65.91-66.19	473
$Cu_2I_2(P(C_6H_5)_3)_3$	$P2_1$	1	2.537-2.854	3.077	69.3-70.3	472
$Cu_2I_2(P(C_6H_5)_3)_3$	$P2_1/c$	1	2.569-2.779	3.137	71.7-72.1	472
Rhombs [$Cu_2I_2L_2$]						
$Cu_2I_2(P(o\text{-}C_7H_7)_3)_2$	$P\bar{1}$	$\bar{1}$	2.581-2.604	3.135	74.4	426
$Cu_2I_2(P(C_6H_{11})_3)_2$	$P\bar{1}$	$\bar{1}$	2.604-2.618	3.062	71.8	450
Monomer [$CuIL_3$]						
$CuI(P(C_6H_5)_2CH_3)_3$	*P*na2$_1$	1	2.881	-----	-----	403
Monomer [$CuIL_2$]						
$CuI(P(C_6H_{11})_3)_2.C_6H_6$	$P\bar{1}$	1	2.626	-----	-----	377
$CuI(P(C_6H_{11})_3)_2.C_7H_8$	$P\bar{1}$	1	2.637	-----	-----	450
$CuI(P(C_6H_{11})_3)_2$ (hex)*	*C*2/c	2	2.587	-----	-----	364
$CuI(P(C_6H_{11})_3)_2$ (mix)#	$P\bar{1}$	1	2.591	-----	-----	350

* This compound was crystallized from hexane

\# This compound was crystallized from a mixture of *n*-pentane and terahydrofuran.

the size of the molecules under investigation (104 electrons for Cu, I and P in cubic cases) as well as to facilitate the comparative nature of the study, the calculations were performed with the alkyl and aryl phosphine ligands replaced by a PH_3 group. The major contributing atomic orbitals to HOMO and LUMO molecular orbitals of motifs observed for copper halide phosphine complexes are shown in Table 4.

Copper iodide has a perfect tetrahedral structure. The center of the tetrahedron is iodide, the other four attached atoms will be copper (or vise versa). The bond angles are all about 109.5^{o} and the Cu-I distance is 2.663Å[65]. However, the coordination geometry, Cu-I distances and bond angles change upon complexation with the different ligand as can be observed from Table 3 and from the discussion below.

Hexaiodohexacopper(I)

We have prepared a unique Cu_6I_6 cluster of a motif not previously observed in the literature with any ligand. The compound, $Cu_6I_6(P(m\text{-tolyl})_3)_4(\text{acetonitrile})_2$, crystallizes with disorder about a 3-fold axis. This motif is of unusually high nuclearity as copper iodide ligand complexes are normally tetracuprous or smaller.

Normally, Cu_4I_4 clusters are at the upper limit of nuclearity observed in the structure for both neutral and anionic complexes[66-69]. However, there are several known clusters of higher nuclearity. For example, $(Cu_8I_{13}^{-5})$[70], $(Cu_{19}I_{27}^{-8})$[71], and $(Cu_{36}I_{56}^{-20})$[72] are reported but these are unusual. Polymeric clusters of both neutral and anionic types have been also identified[73-74].

Table 4 Major Contributing Atomic Orbitals to HOMO and LUMO Molecular Orbitals of Motifs in CuX Phosphine Complexes

Motif	Atom	HOMO		LUMO & LUMO+n					
Monomer [CuXL$_2$]		HOMO 17		LUMO 18		LUMO 19		LUMO 20	
Case #1:	Cu	0.16194	5D-2	1.08286	4Pz	1.15411	4P$_x$	1.34104	4P$_x$
* X=I								-0.35193	3P$_y$
* Symmetry: No	I	0.52828	4P$_y$	-0.29483	4Pz	-0.33698	4P$_x$	-0.27257	4P$_y$
Examples:		0.50273	3P$_y$			0.14415	2S		
CuI(P(C_6H_{11})$_3$)$_2$ (mix)	P1					-0.53701	2S	0.38883	2S
CuI(P(C_6H_{11})$_3$)$_2$.C_6H_6						-0.14634	1S	-0.23601	4P$_y$
CuI(P(C_6H_{11})$_3$)$_2$.C_7H_8								0.14851	4P$_x$
								0.11440	1S
	P2					-0.53674	2S	-0.38919	2S
						-0.14626	1S	-0.23597	4P$_y$
								-0.14848	4P$_x$
								-0.1149	1S
		HOMO 17 B		LUMO 18 B		LUMO 19 A		LUMO 20 B	
Case #2:	Cu	-0.16200	5D-1	1.08265	4P$_x$	1.15431	4P$_z$	1.34071	4P$_y$
* X=I						-0.74011	2S	-0.35157	3P$_y$
* Symmetry: Yes	I	0.52825	4P$_y$	-0.29480	4P$_x$	-0.33716	4Pz	-0.27254	4P$_y$
{2-fold symmetry axis}		0.50273	3P$_y$			-0.14419	2S		
Example:	P1					0.53750	2S	-0.38893	2S
CuI(P(C_6H_{11})$_3$)$_2$ (hex)						0.14643	1S	-0.23563	4P$_y$
								0.14859	4P$_z$
								-0.11439	1S
	P2					0.53750	2S	0.38893	2S
						0.14643	1S	-0.23563	4P$_y$
								-0.14859	4P$_z$
								0.11439	1S

Case #3:		**HOMO**	**17**	**LUMO**	**18**	**LUMO**	**19**	**LUMO**	**20**
* X=Br	Cu	0.20876	5D-2	0.99068	$4P_z$	1.11895	$4P_x$	1.33665	$4P_y$
* Symmetry: No						0.77454	2S	-0.38523	$3P_y$
Example:						-0.15045	$3P_x$		
$CuBr(P(C_6H_{11})_3)_2$ (benzene)						0.10033	1S		
	Br	0.53257	$4P_y$	-0.23389	$4P_z$	-0.29000	$4P_x$	-0.20150	$4P_y$
		0.49530	$3P_y$						
	P1	-0.10414	2S	0.16955	$4P_z$	-0.51868	2S	-0.33937	2S
						-0.14210	1S	-0.26199	$4P_y$
						0.12080	$4P_x$	-0.12944	$4P_x$
	P2	0.10441	2S	0.16538	$4P_z$	-0.49183	2S	0.37943	2S
						-0.13431	1S	-0.24895	$4P_y$
						0.12645	$4P_x$	-0.12840	$4P_x$
Case #4:		**HOMO**	**17 B**	**LUMO**	**18 B**	**LUMO**	**19 A**	**LUMO**	**20 B**
* X=Br	Cu	-0.20797	5D-1	1.03108	$4P_x$	1.12414	$4P_z$	1.33525	$4P_y$
* Symmetry: Yes						-0.74798	2S	-0.39449	$3P_y$
{2-fold symmetry axis}						-0.16802	$3P_z$		
Example:	Br	0.53270	$4P_y$	-0.23744	$4P_x$	-0.29123	$4P_z$	-0.20089	$4P_y$
$CuBr(P(C_6H_{11})_3)_2$ (hexane)		0.49517	$3P_y$						
	P1	-0.10775	2S	0.11280	$4P_x$	0.50841	2S	-0.35615	2S
						0.13911	1S	-0.24552	$4P_y$
						0.12240	$4P_z$	0.10481	1S
	P2	0.10775	2S	0.11280	$4P_x$	0.50841	2S	0.35615	2S
						0.13911	1S	-0.24552	$4P_y$
						0.12240	$4P_z$	0.10481	1S
Monomer [$CuXL_3$]									
* X=I									

* Symmetry: No		**HOMO 21**		**LUMO 22**		**LUMO 23**		**LUMO 24**	
Example:	Cu	0.11462	5D-2	1.08349	$4P_z$	1.16702	$4P_y$	1.15622	$4P_x$
$CuI(P(C_6H_5)_2CH_3)_3$				-0.66838	$4P_y$	0.74361	$4P_z$	-0.83530	2S
				0.44748	$4P_x$	-0.24691	$3P_y$	-0.40263	$4P_z$
				-0.32272	2S	-0.17157	$3P_z$	0.32050	$4P_y$
								0.15417	$3P_x$
	I	0.42925	$4P_y$	-0.22378	$4P_z$	-0.24307	4Py	0.28740	$4P_x$
		0.40167	$3P_y$	0.13584	$4P_y$	-0.15145	4Pz	-0.15386	2S
		0.31432	$4P_z$	-0.1077	$4P_x$				
		0.29494	$3P_z$						
	P1	0.11521	2S	0.22028	2S	0.37697	2S	0.38168	2S
						-0.21315	4Py		
						-0.18108	4Pz		
						0.10494	1S		
	P2			0.42854	2S			0.26753	2S
								0.18472	$4P_y$
	P3			-0.27317	$4P_z$			0.52523	2S
Rhombs [$Cu_2X_2L_2$]								0.13405	1S
Case #1:		**HOMO 26**		**LUMO 27**		**LUMO 28**		**LUMO 29**	
* X=I	Cu1			1.05111	$4P_x$	0.57110	2S	0.52128	$4P_z$
* Symmetry: No				0.45082	2S	0.54861	$4P_z$	0.49919	$4P_x$
Example:				-0.38140	$4P_z$	-0.30766	$4P_x$	0.30319	2S
$Cu_2I_2(P(C_6H_{11})_3)_2$						0.15458	1S	-0.17339	$3P_x$
								-0.12399	$3P_z$
	Cu2			-0.42771	2S	0.58475	2S	0.57924	$4P_z$
				-0.41241	$4P_z$	-0.52377	4Pz	0.55098	$4P_x$
						0.25944	$4P_x$	-0.29220	2S
						0.15274	1S	-0.18630	$3P_x$
								-0.12830	$3P_z$
	I1	0.57414	$4P_y$					-0.16283	$4P_z$
		0.41426	$3P_y$						

		0.26043	2S						
	I2	0.57420	$4P_y$					-0.16278	$4P_z$
		0.41444	$3P_y$						
		-0.26023	2S						
	P1			0.24231	2S	-0.22293	2S	-0.19573	$4P_x$
						-0.17032	$4P_x$	0.19023	2S
								-0.12166	$4P_z$
	P2			-0.24903	2S	-0.21016	2S	-0.21314	2S
Case #2:						0.17804	4Px	-0.19413	$4P_x$
* X=I								-0.14364	$4P_z$
* Symmetry: Yes		**HOMO 26**	**A_u**	**LUMO 27**	**A_u**	**LUMO 28**	**A_g**	**LUMO 30**	**A_g**
{center of symmetry}	Cu1	0.16929	$4P_z$	1.10230	$4P_x$	1.13075	$4P_y$	0.85958	$4P_x$
Examples:				1.05026	2S	0.35557	$4P_x$	0.78718	2S
$Cu_2I_2(P(o\text{-}C_7H_7)_3)_2$				0.82594	$4P_z$	0.33437	2S	0.66702	$4P_z$
$Cu_2I_2(P(C_6H_{11})_3)_2$				-0.12877	$3P_x$	-0.26647	$4P_z$	0.53815	$4P_y$
								-0.11771	$3P_x$
	Cu2	-0.16929	$4P_z$	1.10230	$4P_x$	-1.13075	$4P_y$	-0.85958	$4P_x$
				-1.05026	2S	0.35557	$4P_x$	-0.78718	2S
				0.82594	$4P_z$	0.33437	2S	-0.66702	$4P_z$
				-0.12877	$3P_x$	0.26647	$4P_z$	-0.53815	$4P_y$
								0.11771	$3P_x$
	I1	0.28567	$3P_z$					-0.17073	$4P_z$
		0.27734	$4P_z$					0.12534	$4P_x$
		-0.23491	$3P_x$						
		-0.22996	$4P_x$						
	I2	0.28567	$3P_z$					0.17073	$4P_z$
		0.27734	$4P_z$					-0.12534	$4P_x$
		-0.23491	$3P_x$						
		-0.22996	$4P_x$						
	P1			0.10778	2S			0.25432	2S
Rhombs [$Cu_2X_2L_3$]	P2			-0.10778	2S			0.25432	2S

* X=I									
* Symmetry: No		**HOMO 30**		**LUMO 31**		**LUMO 32**		**LUMO 33**	
Examples:	Cu1	0.12175	$4P_z$	0.93560	$3P_x$	1.14357	$4P_x$	-0.53173	$4P_x$
$Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$		-0.10540	$3P_z$	0.62217	2S	-0.47725	$4P_y$	0.38815	2S
$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$				-0.10819	$4P_y$	-0.17168	$3P_x$	0.23017	$4P_y$
$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$						-0.12128	2S	0.10159	$3P_x$
$Cu_2I_2(P(C_6H_5)_3)_3$	Cu2	0.11670	$4P_z$	1.20446	$4P_x$	-0.93647	2S	0.93436	$4P_y$
$Cu_2I_2(P(C_6H_5)_3)_3$				-0.29657	$4P_y$	0.58396	$4P_y$	0.60337	$4P_x$
				0.16365	2S	0.36896	$4P_x$	0.37850	2S
				-0.11788	$3P_y$	-0.15232	1S	-0.19018	$3P_x$
								-0.10283	$3P_y$
	I1	0.61493	$4P_z$					-0.17505	$4P_y$
		0.41351	$3P_z$						
		0.31132	2S						
	I2	0.61448	$4P_z$					-0.17189	$4P_y$
		0.41345	$3P_z$					0.10454	$4P_z$
		-0.31126	2S						
	P1			0.13499	2S	0.25780	2S	-0.15469	2S
				0.10195	$4P_x$				
	P2					0.41483	2S	0.26066	2S
						0.11803	1S		
	P3			-0.32562	2S	-0.28448	$4P_x$	-0.49381	2S
				-0.10856	1S	-0.13545	$4P_y$	-0.13504	1S
Rhombs [$Cu_2X_2L_4$]								-0.12009	$4P_y$
* X=I									
* Symmetry: Yes		**HOMO 34**	**A_u**	**LUMO 35**	**A_u**	**LUMO 36**	**A_g**	**LUMO 38**	**A_g**
{center of symmetry}	Cu1	-0.16674	5D+1	1.13961	2S	0.91359	$4P_x$	1.74075	$4P_y$
Examples:		0.12060	5D+2	1.13539	$4P_x$	0.75138	$4P_z$	-0.19812	$3P_y$
$Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$				0.78517	$4P_z$	-0.73310	2S	-0.13404	$4P_z$
						0.15879	$4P_y$	0.12041	2S
						-0.12000	$3P_x$		

	Cu2	0.16674	5D+1	1.13961	2S	-0.91359	$4P_x$	-1.74075	$4P_y$
		-0.12060	5D+2	1.13539	$4P_x$	-0.75138	$4P_z$	0.19812	$3P_y$
				0.78517	$4P_z$	-0.73310	2S	0.13404	$4P_z$
						-0.15879	$4P_y$	0.12041	2S
						0.12000	$3P_x$		
	I1	0.34445	$4P_x$			-0.11566	$4P_z$		
		0.33193	$3P_x$						
	I2	0.34445	$4P_x$			0.11566	$4P_z$		
		0.33193	$3P_x$						
	P1	0.11199	$4P_y$			0.14271	2S		
	P2	0.11199	$4P_y$			0.14271	2S		
	P3					0.13028	2S	-0.11467	2S
	P4					0.13028	2S	-0.11467	2S
Cubane * X=I * Symmetry: No Example: $Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$		**HOMO 52**		**LUMO 53**		**LUMO 54**		**LUMO 55**	
	Cu1			-0.70645	2S	0.55614	$4P_x$	1.20240	$4P_x$
				0.53555	$4P_z$	0.50880	$4P_z$	-1.00473	2S
				0.28264	$3P_x$	-0.35158	2S	0.89819	$4P_z$
				0.22276	$3P_z$	0.21777	$4P_y$		
	Cu2			0.84194	$4P_y$	1.27291	$4P_y$	0.18458	$4P_x$
				-0.61235	2S	1.08010	2S	-0.11229	$4P_y$
				-0.29997	$3P_y$	0.87311	$4P_z$	-0.10584	2S
				-0.21698	$3P_z$				
	Cu3			-0.78470	2S	0.20847	$4P_z$	0.75429	$4P_x$
				0.64626	$4P_x$	0.18867	$4P_y$	0.41101	2S
				-0.40423	$4P_z$	-0.14460	$4P_x$	-0.25405	$4P_z$
				-0.29745	$3P_x$				
				0.18656	$3P_z$				
	Cu4			-0.77686	2S	0.84175	$4P_y$	-0.78216	$4P_y$
				-0.62564	$4P_y$	-0.43422	2S	0.58788	$4P_z$

				0.45347	$4P_z$	-0.34470	$4P_z$	0.53817	2S
				0.29225	$3P_y$			0.18943	$4P_x$
				-0.19649	$3P_z$				
	I1	0.14520	$4P_x$						
		0.12935	$3P_x$						
	I2	0.47250	$4P_x$						
		0.39405	$3P_x$						
		0.25387	$4P_z$						
		0.20946	$3P_z$						
		-0.19103	2S						
	I3	0.15312	$4P_x$						
		0.13624	$3P_x$						
		-0.11147	$4P_z$						
	I4	0.31525	$4P_x$						
		0.26725	$3P_x$						
		0.10377	2S						
	P1			0.27960	2S	-0.20019	2S	-0.38341	2S
				0.10072	$4P_x$	-0.10456	$4P_x$	-0.21077	$4P_x$
								-0.16267	$4P_z$
								-0.11295	1S
	P2			0.31880	2S	0.39339	2S		
				-0.12473	$4P_y$	-0.22329	$4P_y$		
				0.10317	1S	-0.15963	$4P_z$		
						0.11555	1S		
	P3			0.24760	2S			0.20174	2S
								-0.11661	$4P_x$
	P4			0.24986	2S	-0.23410	2S	0.25490	2S
						-0.12960	$4P_y$	0.14202	$4P_y$
Cubane * X=I									

* Symmetry: Yes		**HOMO 52**	**B**	**LUMO 53**	**A**	**LUMO 54**	**B**	**LUMO 55**	**B**
{2-fold symmetry axis}	Cu1	-0.16169	5D+2	0.92792	$4P_y$	0.12486	2S	1.32620	2S
Example:		0.11725	5D-1	0.75385	2S	-0.11993	$4P_y$	-1.29435	$4P_y$
$Cu_4I_4(PC_6H_5(CH_3)_2)_4$				0.53461	$4P_z$			-0.48457	$4P_z$
$Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$				-0.10966	$3P_y$			0.11215	$3P_y$
	Cu2	0.16169	5D+2	-0.92792	$4P_y$	-0.12486	2S	-1.32620	2S
		0.11725	5D-1	0.75385	2S	-0.11993	$4P_y$	-1.29435	$4P_y$
				0.53461	$4P_z$			0.48457	$4P_z$
				0.10966	$3P_y$			0.11215	$3P_y$
	Cu3			-0.90748	$4P_x$	1.30578	$4P_x$	-0.16390	$4P_x$
				0.72993	2S	1.25559	2S	-0.12634	2S
				-0.55553	$4P_z$	0.47646	$4P_z$	-0.10167	$4P_y$
				0.11834	$3P_x$	-0.12675	$3P_x$		
				0.10714	$4P_y$				
	Cu4			0.90748	$4P_x$	1.30578	$4P_x$	-0.16390	$4P_x$
				0.72993	2S	-1.25559	2S	0.12634	2S
				-0.55553	$4P_z$	-0.47646	$4P_z$	-0.10167	$4P_y$
				-0.11834	$3P_x$	-0.12675	$3P_x$		
				-0.10714	$4P_y$				
	I1	0.24160	$4P_y$			-0.11985	$4P_x$		
		0.23510	$3P_y$						
	I2	0.24160	$4P_y$			-0.11985	$4P_x$		
		0.23510	3P						
		0.19375	$4P_y$						
	I3	0.19263	$3P_y$					0.12440	$4P_y$
		-0.12461	$4P_z$						
		-0.11864	$3P_z$						
	I4	0.19375	$4P_y$					0.12440	$4P_y$
		0.19263	$3P_y$						
		0.12461	$4P_z$						
		0.11864	$3P_z$						

	P1	0.17017	$4P_y$	-0.12606	2S			0.12907	$4P_y$
		0.15660	$3P_y$						
		-0.10282	2S						
	P2	0.17017	$4P_y$	-0.12606	2S			0.12907	$4P_y$
		0.15660	$3P_y$						
		0.10282	2S						
	P3			-0.12725	2S	-0.12947	$4P_x$		
	P4			-0.12725	2S	-0.12947	$4P_x$		
Cubane * X=I * Symmetry: Yes {3-fold symmetry axis} Example: $Cu_4I_4(P(p\text{-}C_7H_7)_3)_4$		HOMO 52	E	LUMO 53	A	LUMO 54	A	LUMO 55	E
	Cu1	0.13625	5D+2	1.09902	$4P_z$	1.62556	$4P_z$	0.21211	$4P_x$
				0.65633	2S	1.49076	2S	0.10277	$4P_y$
				-0.17431	$3P_z$	-0.16426	$3P_z$		
	Cu2	0.11783	5D+1	0.80932	$4P_x$	-0.44851	$4P_x$	-0.84215	$4P_x$
				-0.78464	2S	0.40514	$4P_z$	-0.80363	2S
				0.46000	$4P_y$	-0.43672	2S	-0.26203	$4P_y$
				-0.30335	$4P_z$	-0.25137	$4P_y$	0.25005	$4P_z$
				-0.12020	$3P_x$				
	Cu3	-0.12248	5D+1	-0.80303	$4P_x$	0.44195	$4P_x$	1.40965	2S
				-0.78464	2S	-0.43673	2S	-1.31082	$4P_x$
				0.47089	$4P_y$	0.40514	$4P_z$	0.75390	$4P_y$
				-0.30335	$4P_z$	-0.26274	$4P_y$	-0.43636	$4P_z$
				0.11941	$3P_x$			0.13126	$3P_x$
	Cu4	0.12927	5D-1	-0.93089	$4P_y$	0.51410	$4P_y$	0.65182	$4P_y$
		-0.12713	5D+2	-0.78464	2S	-0.43672	2S	-0.60602	2S
				-0.30335	$4P_z$	0.40514	$4P_z$	-0.19667	$4P_x$
				0.13834	$3P_y$			0.18630	$4P_z$
	I1	0.24276	$4P_y$						
		0.23788	$3P_y$						

	I2	0.23664	$4P_y$						
		0.23404	$3P_y$						
	I3	0.25315	$4P_y$						
		0.24673	$3P_y$						
	I4	0.25071	$4P_y$						
		0.24501	$3P_y$						
	P1			0.13068	2S				
	P2			0.13068	2S			0.14615	$4P_x$
								0.11299	2S
	P3	0.17586	$4P_y$	0.13068	2S				
		0.15607	$3P_y$						
	P4			0.13335	2S	0.10895	2S		

Tri-*m*-tolylphosphine has previously[32] been observed to form two complexes with copper iodide, $Cu_2I_2L_3$ is prepared by warming a 1:1 CuI/P ligand mixture in acetonitrile or toluene. The tetramer, $[CuIP(m\text{-tolyl})_3]_4$ is prepared by briefly boiling a 4:10 CuI/P ligand mixture until dissolution in acetone or acetone/toluene[11]. We have prepared a third form, $Cu_6I_6(P(m\text{-tolyl})_3)_4(\text{acetonitrile})_2$ by refluxing a 2:1 mixture of CuI/ tri-*m*-tolylphosphine for 24 hrs in acetonitrile.

Copper iodide complexes often exhibit structural disorders. It is common to see Cu_4I_6 complexes (which may be visualized as a tetrahedron of copper(I) atoms bridged on all edges by iodine atoms), with a disorder about a center of symmetry and, thus, appearing as a cube of copper atoms with face bridging iodide atoms. Distances between adjacent copper atoms are too short - 2.0Å and each of the eight copper sites refines to half occupancy indicating 2 half occupancy $Cu_4I_6^{2-}$ motif with superimposed tetrahedra of Cu atoms, edge bridged by iodide atoms[66].

In $Cu_6I_6(P(m\text{-tolyl})_3)_4(\text{acetonitrile})_2$, a cube of eight copper atoms appears with symmetry versions of Cu(3) at one set of four alternating corners of the cube and Cu(2) atoms at the other four corners. Cu(3) is a full occupancy position. Cu(2) refines to half occupancy. All Cu(2)-Cu(3) separations are noninteractive distances (2.986Å). Cu(3) and its three symmetrical equivalents are present in all molecules in the solid but only two of the Cu(2) atoms are present at any one time (Figure 6). There are thus a total of six Cu atoms in the cluster. Six iodide atoms balance the charge of four Cu(3)(I) atoms plus two Cu(2)(I) atoms. Copper atoms are three coordinate to iodide and also bound to $P(m\text{-tolyl})_3$(Cu(3)) or to CH_3CN(Cu(2)).

In the disordered cube, a 3-fold axes pass through P, Cu(2),Cu(3), C/N and C at opposite corners and a two fold axis passes through the iodine atoms on opposite faces of the cube. Only a single twofold axis describes the ordered cluster.

The base of the ordered cluster may be described as four Cu_2I_2 rhombs which share a single iodine vertice and which also share two contiguous sides with each of two adjacent rhombs. Two additional copper atoms [C(3) atoms] are found 2.986Å above two basal copper atoms at opposite corners of the basal unit. Each is bound to two iodide atoms of the nearest sides. These two copper(I) atoms are bridged by the sixth atom. Cu(3) and Cu(2) are bound to three iodide atoms [Cu(2)-I, 2.7280Å, Cu(3)-I, 2.619Å] and to a Lewis base ligand.

The acetonitrile molecules are disordered about their central carbon atom. At first sight, they appear to bridge neighboring Cu_6I_6 clusters, however, the N atom of the acetonitrile molecule is bonded to one cluster and the neighboring cluster is missing the Cu atoms which appear to be bonded to the methyl end of that acetonitrile molecule.

Cubanes

Four previously unknown compounds of this category; Cu_4I_4(P(diphenylmethyl))$_4$, Cu_4I_4(P(phenyldimethyl))$_4$, Cu_4I_4(P(*m*-tolyl)$_3$)$_4$ and Cu_4I_4(P(triphenyl))$_4$ were synthesized, crystallized and identified in the solid state by single crystal X-ray diffraction.

The cuprous halide cluster consists of discrete tetrameric molecular units of stoichiometry $[CuIL]_4$. The coordination number of copper is four. As Table 3 reveals, the Cu-I-Cu angles (61.75°-83.30°) in these complexes are smaller than the usual tetrahedral angle (109.5°). This has to do with the van der Waals repulsion between the I atoms. To keep reasonable X-X separation, the angles at copper open, causing angles at halide to become smaller.

Since some comparison data for analogous Cu bromide complexes exists[11], it is useful to compare data for cuprous iodide and cuprous bromide complexes. Comparison between the Cu-I-Cu and Cu-Br-Cu angles reveals that the compression in the latter is lesser. The Cu-Br-Cu angle is normally compressed only to values like 72.4°, whereas the Cu-I-Cu angle is compressed to values like 61.75°. This can be related to the smaller van der Waals radius in Br. This may also help explain the increased irregularity of the cubane structure as the halide changes from bromide to iodide.

The Cu-Cu distances (2.871Å - 3.667Å) in these complexes are large enough to suggest that there is no significant direct metal-metal interaction.

It was generally perceived that working with large ligands (triphenylphosphine) and large halides (iodide) would favor formation of smaller motifs (such as step or rhombs structures). This work confirms the conclusion reached by Barron et. al[22] that this is not the case. $Cu_4I_4(P(triphenyl))_4$ was isolated with sterically crowded motif. It seems solvent plays a significant role here that can not be ignored. This complex was synthesized and reported by Durand[11], and was identified a second time in this study.

The *Ab Initio* calculations for $Cu_4I_4(P(m\text{-tolyl})_3)_4$ show that the HOMO orbital is dominated by p orbitals on the iodide whereas the LUMO level has major contribution from p and s orbitals on copper. LUMO level also has appreciable contribution from the p and s orbitals on phosphorus. *Ab initio* results for $Cu_4I_4(P(diphenylmethyl))_4$ and $Cu_4I_4(P(phenyldimethyl))_4$ are similar to the above case except that the phosphorus contribution is smaller but also present in the HOMO orbital.

As can be seen from Table 3, λ_{max} for $Cu_4I_4(P(m\text{-tolyl})_3)_4$, which exhibits no symmetry element, is 385 nm. However, the wavelength maxima for $Cu_4I_4(P(\text{diphenylmethyl}))_4$ (2-fold axis), $Cu_4I_4(P(\text{phenyldimethyl}))_4$ (2-fold axis) and $Cu_4I_4(P(p\text{-tolyl})_3)_4$[11] (3-fold axis) are 570, 592 and 520 nm, respectively. The λ_{max} for these compounds are longer than that observed for the solid state cluster without symmetry elements. The imposition of a symmetry elements (2- or 3-fold axis) results in a shift of emission to lower energy. This correlates with a forbiddance of the transition between normal HOMO and LUMO levels resulting in transition from HOMO to LUMO+n followed by emission to an intermediate LUMO level and radiationless decay to the ground state. *Ab initio* results here were used to identify the major atomic contribution to the molecular orbitals and the characters of the frontier orbitals.

The following points show that there are cases when forbidden transition do take place in reality although classic theory can not explain them.

* For noncenterosymmetric complexes, selection rules do not impose forbiddances in most cases. But this does not mean that all the forbidden transitions are mandated by the selection rules. The presence of 2-fold symmetry axis in the cubes and in monomers (discussed in separate section) should not inhibit transitions between HOMO and LUMO levels but it does so.

* These selection rules were derived based on assuming zero electron-electron repulsions. However, in reality and especially in more complicated molecular systems as in our case, such repulsions do exist. Such repulsions could also change both the HOMO and the LUMO arrangement in unexpected ways.

* Sometimes, a forbidden transition may take place with an appreciable intensity since it can borrows intensity from another allowed transition due to vibronic mixing[75]. In some other cases, forbidden transitions occur as a result of the perturbation effects brought about by certain types of ligands[14].

The difference between Cu_4I_4(P(diphenylmethyl))$_4$ ($\lambda_{max=}$ 570 nm), Cu_4I_4(P(phenyldimethyl))$_4$ ($\lambda_{max=}$ 592 nm) can be rationalized on the basis of the latter being more basic than the former. This increased ability for electron donation will let the HOMO-LUMO energy separation smaller in the latter, thus it emits at longer wavelength.

It is interesting to note that λ_{max} for Cu_4I_4(P(*p*-tolyl)$_3$)$_4$ and Cu_4Br_4(P(*p*-tolyl)$_3$)$_4$[11] are 520 nm and 490 nm, respectively. These two compounds crystallize in same space group (*R*-3) and both exhibit 3-fold symmetry axis. They are isostructural. A change of halide from iodide to bromide results in a change of emission from a lower energy to higher energy by about 30 nm. The emission is due to one electron moving from an orbital (HOMO) primarily dominated by the halogen to a new orbital (LUMO) that is dominated by copper. Because the electronegativity of Br is greater than that of I, the HOMO-LUMO separation is bigger in the bromide complex than in the iodide complex. Thus, it is expected that a change from bromide to iodide, results in the shift of the wavelength maxima to higher wavelength.

Rhombs

There are three subgroups of this group. Rhombs with 4 phosphorus ligands, 3 phosphorus ligands and 2 phosphorus ligands. Cu_2I_2(P(diphenylmethyl))$_4$.tetrahydrofuran belongs to the first subgroup. The structure consists of a dinuclear

Cu_2I_2(P(diphenylmethyl))$_4$ molecule with two bridging iodide ions, and with a solvent molecule (tetrahydrofuran) included in the unit cell.

The following three compounds belongs to the second subgroup (rhombs with 3 ligands): Cu_2I_2(P(*m*-tolyl)$_3$)$_3$, Cu_2I_2(P(*p*-tolyl)$_3$)$_3$ (Space group $P\bar{1}$), Cu_2I_2(P(*p*-tolyl)$_3$)$_3$ (Space group $P2_1$/a), Cu_2I_2(P(triphenyl))$_3$ (Space group $P2_1$) and Cu_2I_2(P(triphenyl))$_3$ (Space group $P2_1$/c). In these complexes, two copper atoms are bridged by two iodide ions, and one phosphine ligand is bonded to one Cu atom (roughly trigonal planar) whereas two ligands are bound to the other Cu atom (distorted tetrahedral geometry). It can be seen from Table 8 that these compounds all emit at very similar λ_{max}. Thus, emission may be considered to be arising from the same mechanism within each solid.

Cu_2I_2(P(*o*-tolyl)$_3$)$_2$ and Cu_2I_2(P(cyclohexyl)$_3$)$_2$ belongs to the third group (rhombs with 2 ligands). The structure is dinuclear with two copper atoms joined by two iodide bridges. Coordination around copper is close to trigonal planar. It can be noted that in the latter case that the tricyclohexylphosphine ligands are orienting themselves in a way as not to interfere with the rhombic motif (Figure 26, 28). Also, it can be observed that tricyclohexylphosphine probably can not form a cubane form with CuI since tricyclohexylphosphine is considered to be among the bulkiest of the phosphine ligands.

An interesting observation has to do with the series, para-, meta- and ortho- tri-tolylphosphines. Whereas both meta and para ligands, upon reacting with CuI, form complexes of either cubane or rhombic motifs with three ligands, the use of ortho-tolyl ligand only leads to rhombs with two ligands. That can be explained on the basis of steric bulkiness. To quantify this bulkiness, one can use the concept of Tolman's cone angle (θ)[76]. This steric parameter was introduced after it became clear that the ability of phosphorus ligands to compete for coordination positions on a metal could not be explained in terms of electronic character. Rather, correlation existed with the angle at metal of the cone swept out by the van der Waals radii of the groups attached to phosphorus. The theoretical cone angles in the para, meta and ortho complexes are 145°, 165° and 194°, respectively[76].

The *Ab Initio* calculations for Cu_2I_2(P(diphenylmethyl))$_4$.tetrahydrofuran show that the HOMO orbital is dominated by p orbitals on the halide whereas the LUMO has major contributions from p and s orbitals on copper. Both HOMO and LUMO also have appreciable contribution from the p and s orbitals on phosphorus. Calculations performed for rhombs with 2 phosphorous ligands (with and without symmetry elements) and 3 phosphorous ligands show that the contribution is similar to the case with 4 phosphorous ligands except that the phosphorus contribution is limited to the LUMO level.

The λ_{max} for Cu_2I_2(P(cyclohexyl)$_3$)$_2$[10] (non-centrosymmetric motif), which exhibits no symmetry element, is 375 nm. However, the wavelength maxima for Cu_2I_2(P(*o*-tolyl)$_3$)$_2$ (centrosymmetric motif) and Cu_2I_2(P(cyclohexyl)$_3$)$_2$ (centrosymmetric motif) are 426 and 450 nm, respectively (Table 3). The λ_{max} for these compounds are longer than the case without symmetry elements. Again, the imposition of a symmetry elements results in a shift of emission to lower energy. This correlates with a forbidden character of the transition between normal HOMO and LUMO levels resulting in transition from HOMO to LUMO+n followed by emission to an intermediate level and radiationless decay to the ground state. The *Ab initio* results support this observation. For the first case (no symmetry), the transition HOMO (26) → LUMO (27) and to higher MO's (28, 29), is allowed, however, the transition HOMO (26) $A_u \rightarrow$ LUMO (27) A_u is not allowed when a center of symmetry is present in the cluster. From the selection rules, only gerade (g) to ungerade (u), or the reverse, transitions are allowed. So, in this case, only the transition HOMO (26) $A_u \rightarrow$ LUMO (28, 30) A_g is allowed.

The difference between $Cu_2I_2(P(o\text{-tolyl})_3)_2$ ($\lambda_{max=}$ 426 nm), $Cu_2I_2(P(\text{cyclohexyl})_3)_2$ ($\lambda_{max=}$ 450 nm) can be rationalized on the basis of the latter being more basic than the former. This increased ability for electron donation will let the HOMO-LUMO energy separation smaller in the latter, thus it emits at longer wavelength.

There is another interesting correlation that can be observed for the rhombs in general. From Table 3, it can be seen that there is a progressive increase in the wavelength maxima as one goes from motifs with 2 ligands (λ_{max} = 426 nm) to motifs with 3 ligands (473 nm) to motifs with 4 ligands (547 nm). So, as more phosphorus atoms are attached to the rhomb, the more there is a shift of emission to lower energy. If one resorts to results of *ab initio* calculations for these complexes (Table 4), one may relate this behavior to the following difference in contributing atomic orbitals to HOMO and LUMO levels of these complexes. The HOMO orbitals for all 3 rhombs have p orbitals on bridging iodides pointing at each other across the rhombs. The difference in the frontier orbitals is more pronounced in the LUMO level. For $Cu_2I_2L_2$, a copper encompassing orbital is major with involvement of the adjacent phosphorus and the two bridging iodides.

For $Cu_2I_2L_3$, the trigonal planer copper shows major involvement along with its attached phosphorus atoms and one bridging iodide. For $Cu_2I_2L_4$, LUMO involves only one tetrahedral copper atom and the attached phosphorus atom. The halides are not involved. Apparently, Cu-P overlap is of lower energy than Cu-I overlap and the $Cu_2I_2L_4$ LUMO is of lower energy.

Monomers

There are two groups of monocopper complexes, monomers with 3 phosphorous ligands and monomers with 2 phosphorous ligands. $CuI(P(diphenylmethyl))_3$ belongs to the former. The angles at the copper are nearly tetrahedral. This complex was the single example of this type prepared and was not further studied. The following complexes belong to the latter group: $CuI(P(cyclohexyl)_3)_2$.benzene, $CuI(P(cyclohexyl)_3)_2$.toluene, $CuI(P(cyclohexyl)_3)_2$ (from hexane), $CuI(P(cyclohexyl)_3)_2$ (from a mixture of tetrahydrofuran and *n*-pentane), $CuBr(P(cyclohexyl)_3)_2$ (from hexane) and $CuBr(P(cyclohexyl)_3)_2$ (from benzene)[11]. Coordination around the copper atom is nearly trigonal planar. In the first two cases, a benzene and toluene molecules, respectively, were co-crystallized within the unit cell. These structures may have 2-fold symmetry axis or no symmetry element at all. For the first case, the Cu-X bond lies on a crystallographic 2-fold symmetry axis and one half of the molecule compromises the asymmetric unit.

$CuX(P(cyclohexyl)_3)_2$ complexes have interesting structural and catalytic properties.[77-78] The complex $CuBr(P(cyclohexyl)_3)_2$ was synthesized from both hexane and benzene. The bromide form crystallized from benzene lacks an internal crystallographic symmetry element within the cluster and emits at 400 nm. The bromide form crystallized from hexane crystallizes with a two fold axis passing through the copper and bromine atoms and relating the two tricyclohexylphosphine groups. This solid state form emits at 460 nm.

The iodide form crystallized from hexane similarly has a two fold axis passing through the copper and iodide atoms. It emits at 364 nm. The iodide form crystallized from a mixture of tetrahydrofuran and *n*-pentane (like the bromide) has no crystallographic symmetry element within the $CuI(P(cyclohexyl)_3)_2$ cluster. We recorded the emission spectrum for this solid (λ_{max} = 350 nm), but were unable to complete X-ray data collection due to decomposition of the crystal. However, the unit cell parameters correspond exactly to those published in a paper by Soloveichik et. al[79]. To facilitate the comparison between the tricyclohexylphosphine allotropes, their crystal data is given in Table 5. Comparison of the structural details of the four structures shows that they display very similar bond lengths and angles (Table 6). Thus, the emission may be considered to be arising from the same species ($CuX(P(cyclohexyl)_3)_2$) within each solid.

The *Ab Initio* calculations for the different monomers show that the HOMO orbital is dominated by p orbitals on the halide whereas the LUMO has major contribution from p and s orbitals on copper. The LUMO level also has appreciable contribution from the p and s orbitals on phosphorus. But in general there is no huge difference in the *ab initio* calculated contribution between the iodide (with and without symmetry) and bromide cases (with and without symmetry).

Within the bromide and the iodide series, the imposition of a symmetry element results in a shift of emission to lower energy. This correlates with a forbidden character of the transition between normal HOMO and LUMO levels resulting in transition from HOMO to LUMO+n followed by emission to an intermediate level and radiationless

Table 5 Crystal Data of the [$CuXL_2$] Allotropes

Compound	Empirical formula	Formula Weight (g/mol)	Crystal system/ space group	Symmetry	Unit Cell Dimensions	Z
$CuBr(P(C_6H_{11})_3)_2$ *(Crystallized from hexane)*	$C_{18}H_{30}CuBrP_2$	263.4	monoclinic, *C2/c*	2	a = 18.084(2) Å b = 9.1150(10) Å c = 22.327(2) Å α = 90.0 deg. β = 96.710(10) deg. γ = 90.0 deg.	8
$CuBr(P(C_6H_{11})_3)_2$ *(Crystallized from benzene)*	$C_{36}H_{66}CuBrP_2$	704.3	monoclinic, $P2_1/c$	1	a = 9.982(2) Å b = 15.571(3) Å c = 24.074(3) Å α = 90.0 deg. β = 97.830(0) deg. γ = 90.0 deg.	4
$CuI(P(C_6H_{11})_3)_2$ *(Crystallized from hexane)*	$C_{18}H_{33}Cu_{0.5}I_{0.5}P$	375.6	monoclinic, *C2/c*	2	a = 18.441(9) Å b = 9.276 (6) Å c = 22.51(2) Å α = 90.0 deg. β = 97.03(5) deg. γ = 90.0 deg.	8
$CuI(P(C_6H_{11})_3)_2$ *(Crystallized from mixture)*[79]	$C_{36}H_{66}CuIP_2$	751.32	triclinic, $P\bar{1}$	1	a = 9.534(2) Å b = 22.975(5) Å c = 9.058(2) Å α = 97.38(1) deg. β = 114.49(1) deg. γ = 93.40(1) deg.	2

decay to the ground state. As stated in the cubane motif discussion, the cause behind forbiddance was not identified. However, the possible reasons for this were discussed.

Table 6 Structural Data in the [$CuXL_2$] Allotropes

Compound	Cu-X (Å)	Cu-P (Å)	P-C (Å)	P-Cu-X angle (°)	P-Cu-P angle (°)
$CuBr(P(C_6H_{11})_3)_2$ (Crystallized from hexane)	2.390(4)	2.263(3)	1.843(14)-1.853(14)	112.4(1)	135.1(2)
$CuBr(P(C_6H_{11})_3)_2$ (Crystallized from benzene)	2.384(6)	2.276(8)-2.287(8)	1.821(30)-1.935(32)	107.3(3)-115.7(3)	136.5(4)
$CuI(P(C_6H_{11})_3)_2$ (Crystallized from hexane)	2.587(3)	2.285(3)	1.864(9)-1.871(9)	112.2(1)	135.5(1)
$CuI(P(C_6H_{11})_3)_2$ (Crystallized from mixture)[79]	2.5913(7)	2.2753(12)-2.2846(12)	1.855(4)-1.865(4)	110.99(3)-114.79(3)	134.06(4)

A change of halide from bromide to iodide results in a change of emission from a lower energy to higher energy. This is not consistent with what was seen for the cubanes. The bromo and iodo monomers have LUMO levels which are very similar in orbital population. Both show a major contribution from copper P_z orbitals but with involvement also of the $4P_z$ orbitals of the halide which are pointing in the direction of copper. In the case of Br, there is also contribution from P_z orbitals on both P atoms.

For these monomers, the change of halide is apparent more specifically in the orbital population at the HOMO level. For the iodide, d orbitals on copper are slightly populated and the 3 and $4P_y$ orbitals on iodide make the major contribution. For bromide, there is a further contribution from the s orbitals on phosphorous. One can postulate that the energy transition from HOMO to LUMO for the iodide is a more difficult transition (and thus of higher energy) on the basis of greater differences of copper and iodide orbital size making electron excitation more difficult. The overlap efficiency for a bromide to copper excitation will be greater and thus the transition is of lower energy.

Cu_4I_6-nitrogen based ligand

Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$ belongs to this group. It is the only ionic complex that was prepared in this study. Also, it is the only complex with nitrogen based ligand. The copper atoms form a tetrahedron with six edges, each bridged by an iodide atom. Copper is three coordinate with Cu-I distances (2.525-2.684Å). The Cu-Cu distances are nonbonding (2.914Å).

CONCLUSIONS

The main objective of this work was to understand the relationship between solid state emission characteristics and the structural symmetry of crystalline complexes of copper(I), iodine and Lewis base ligands with phosphorus donor atoms. Nineteen copper(I) halide phosphine complexes have been synthesized, crystallized and characterized by single crystal X-ray diffraction. These complexes can be grouped into four classes: i) hexaiodohexacopper, $Cu_6I_6L_4L'_2$ (L= trisubstituted phosphine and L'= acetonitrile) ii) cubanes $Cu_4I_4L_4$, iii) rhombs, $Cu_2I_2L_4$, $Cu_2I_2L_3$ and $Cu_2I_2L_2$ plus iv) monomers, $CuIL_3$ and $CuXL_2$. The solid forms crystallize with a variety of internal symmetry elements including centers of symmetry and 2- or 3-fold rotation axes. The emission spectra of these solid complexes show that groups of complexes, identical in structural motif, but differing in internal crystallographic symmetry element display emission at wavelengths of different λ_{max}.

Ab initio calculations allowed the identification of major atomic contributions to HOMO, LUMO and LUMO+n orbitals and also the identification of allowed and forbidden transitions. Complexes of all motifs show the HOMO orbitals to be dominated by contribution from halide p orbitals and LUMO levels to be dominated by copper based orbitals. Thus the excitation mechanism involves excitation of halide based electron density into copper orbitals. Differences in emission maxima for identical clusters which differ in solid state symmetry may be understood in terms of the influence of the symmetry element present on the choice of frontier orbitals involved in the radiative process.

Examination of three families of copper(I) halide complexes has allowed a correlation of structural and emission characteristics. For the cubanes, the effects of 2- and 3-fold axes have been observed to lead to a shift in the wavelength maxima to lower energy compared with the wavelength maximum observed for a complex with no internal symmetry. For instance, λ_{max} for $Cu_4I_4(P(m\text{-tolyl})_3)_4$, which exhibits no symmetry element, is 385 nm. However, the wavelength of maximum emission for $Cu_4I_4(P(\text{diphenylmethyl}))_4$ (2-fold axis), $Cu_4I_4(P(\text{phenyldimethyl}))_4$ (2-fold axis) and $Cu_4I_4(P(p\text{-tolyl})_3)_4$ (3-fold axis) are 570, 592 and 520 nm, respectively. The λ_{max} for these compounds are thus of lower energy than those observed for a similar solid state cluster without symmetry elements. The imposition of a symmetry element (2- or 3-fold axis) results in a shift of emission to lower energy, which correlates with a forbiddance of the transition between normal HOMO and LUMO levels representing a transition from

HOMO to LUMO+n followed by emission to an intermediate LUMO level and radiationless decay to the ground state.

In the rhombs, the presence of center of symmetry affects the position of the wavelength maxima. For example, The λ_{max} for $Cu_2I_2(P(cyclohexyl)_3)_2$ (non-centrosymmetric motif), which exhibits no symmetry element, is 375 nm. However, the wavelength maxima for $Cu_2I_2(P(o\text{-tolyl})_3)_2$ (centrosymmetric motif) and $Cu_2I_2(P(cyclohexyl)_3)_2$ (centrosymmetric motif) are 426 and 450 nm, respectively. The λ_{max} for these compounds are longer than for the case without symmetry elements. Again, the imposition of a symmetry elements results in a shift of emission to lower energy. This correlates with a forbidden character of the transition between normal HOMO and LUMO levels resulting in excitation from HOMO to LUMO+n followed by emission to an intermediate LUMO level and radiationless decay to the ground state. The *Ab initio* results support this observation. For the first case (no symmetry), the transition HOMO (26) → LUMO (27) and to higher MO's (28, 29), is allowed, however, the transition HOMO (26) A_u→ LUMO (27) A_u is not allowed when a center of symmetry is present in the cluster. From the selection rules, only gerade (g) to ungerade (u), or the reverse, transitions are allowed. So, in this case, only the transition HOMO (26) A_u → LUMO (28, 30) A_g is allowed and emission occurs from LUMO (28) to MO (27) followed by radiationless transition to HOMO (26).

Comparison of emission maxima for the series of increasing phosphine content: $Cu_2I_2L_2$, $Cu_2I_2L_3$ and $Cu_2I_2L_4$ showed that increased phosphine ligation resulted in a progressive increase in the wavelength maxima.

Ab initio calculations for these complexes, one may relate this behavior to the following difference in contributing atomic orbitals to HOMO and LUMO levels of these complexes. The HOMO orbitals for all 3 rhombs have p orbitals on bridging iodides pointing at each other across the rhombs. The difference in the frontier orbitals is more pronounced in the LUMO level.

For $Cu_2I_2L_2$, a copper encompassing orbital is major with involvement of the adjacent phosphorus and the two bridging iodides. For $Cu_2I_2L_3$, the trigonal planer copper shows major involvement along with its attached phosphorus atoms and one bridging iodide. For $Cu_2I_2L_4$, LUMO involves only one tetrahedral copper atom and the attached phosphorus atom. The halides are not involved. Apparently, Cu-P overlap is of lower energy than Cu-I overlap and the $Cu_2I_2L_4$LUMO is of lower energy.

The effect of 2-fold axis was observed again in the monomer family. With both the analogues bromide and the iodide complexes, the imposition of the 2-fold rotational axis results in a shift of emission to lower energy. The change from iodide to bromide resulted in a shift of observed emission to lower energy.

Thus, this work has shown that alkyl and aryl phosphine substituted complexes of copper iodide adopt a variety of forms and stoichiometries yet all emit in the visible when excited in the ultraviolet. Comparison of the emission characteristics of formulas of isostructural complexes which differ only in intra cluster symmetry element has confirmed that center of symmetry, 3-fold symmetry axis perturbs the wavelength of maximum emission. This work has shown for the first time that 2-fold axes are capable of similar influence.

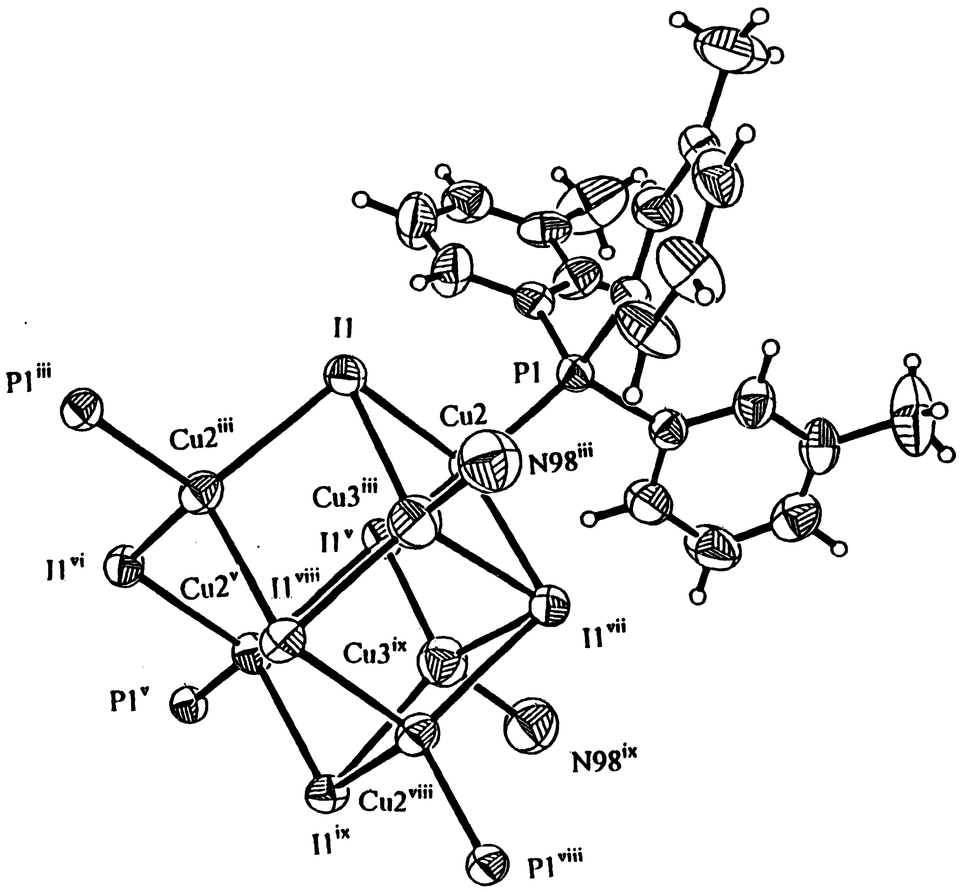


Figure 6 Projection View of $Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

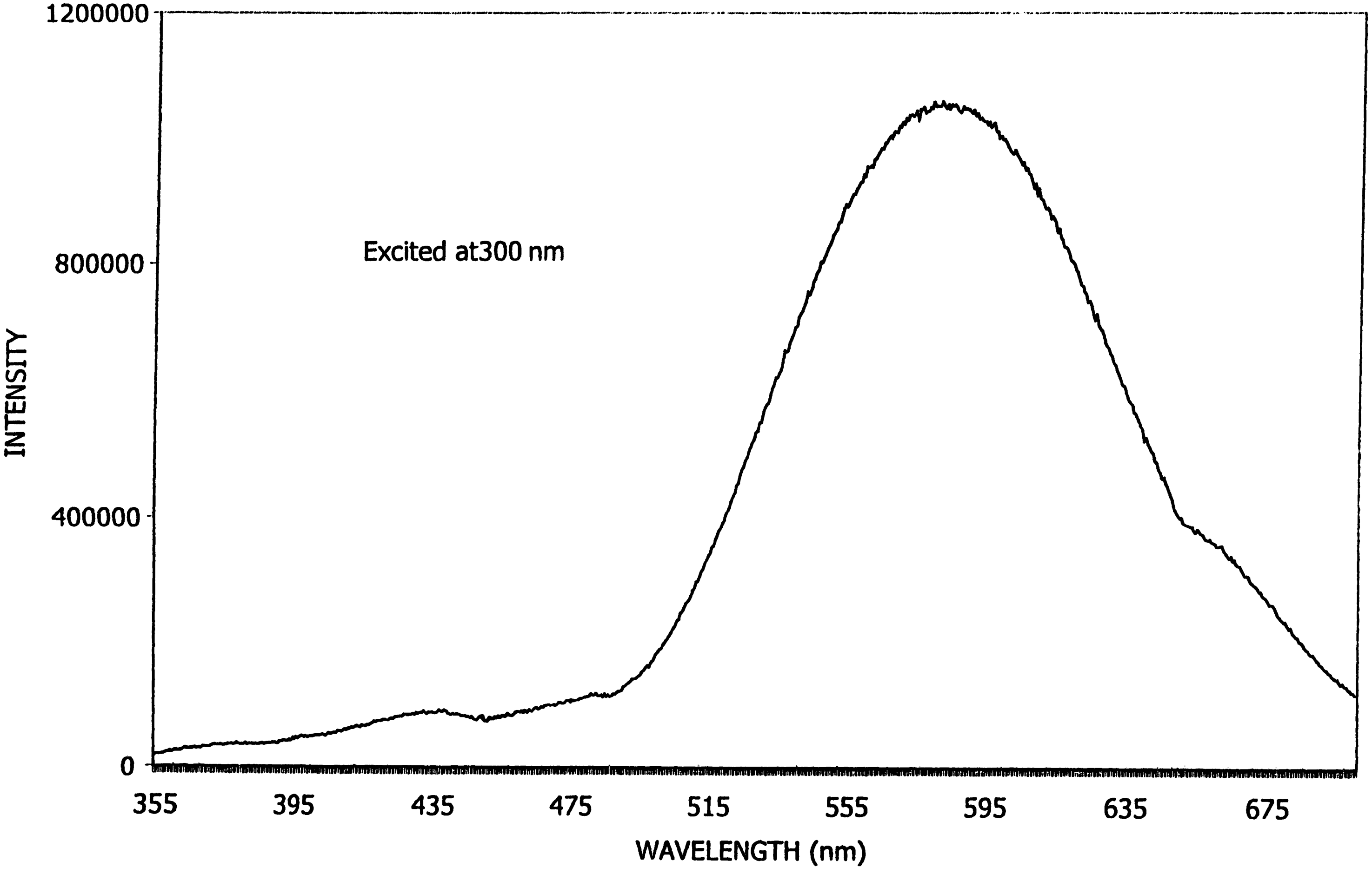


Figure 7 Emission Spectrum of $Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

Table 7. Crystal Data and Structure Refinement for $Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

Empirical formula	$C_{88}H_{90}Cu_6I_6N_2P_4$
Formula weight	2442.14
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Cubic, *F*d-3
Unit cell dimensions	a = 26.874(4) Å α = 90.0 deg. b = 26.874(4) Å β = 90.0 deg. c = 26.874(4) Å γ = 90.0 deg.
Volume	19409(5) $Å^3$
Z, Calculated density	8, 1.672 Mg/m^3
Absorption coefficient	3.306 mm^{-1}
F(000)	9472
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	2.14 to 29.98 deg.
Index ranges	$-1 \leq h \leq 37, -37 \leq k \leq 1, -1 \leq l \leq 37$
Reflections collected / unique	8008 / 2385 [R(int) = 0.0849]
Goodness-of-fit	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1322
R indices (all data)	R1 = 0.1558, wR2 = 0.1778
Extinction coefficient	0.000022(11)
Largest diff. peak and hole	1.003 and -0.601e. $Å^{-3}$

Table 8. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

	x	y	z	U(eq)
I(1)	5085(1)	6250	1250	64(1)
Cu(2)	5657(1)	6843(1)	657(1)	67(1)
P(1)	5168(1)	7332(1)	168(1)	58(1)
Cu(3)	5739(1)	5739(1)	739(1)	102(1)
C(1)	5511(3)	7837(3)	-150(3)	65(2)
C(2)	5329(4)	8314(3)	-237(3)	87(3)
C(3)	5605(4)	8687(3)	-475(3)	90(3)
C(4)	6076(4)	8575(4)	-628(4)	101(3)
C(5)	6276(4)	8114(5)	-542(4)	134(5)
C(6)	5983(3)	7744(4)	-307(4)	107(4)
C(7)	5406(5)	9193(4)	-579(5)	175(7)
C(99)	5000	5000	0	83(6)
N(98)	5288(4)	5288(4)	288(4)	126(6)
C(98)	5288(4)	5288(4)	288(4)	126(6)
H(2A)	4992	8390	-146	80
H(4A)	6279	8830	-773	80
H(5A)	6605	8034	-654	80
H(6A)	6108	7412	-268	80
H(7A)	5651	9400	-737	80
H(7B)	5121	9161	-792	80
H(7C)	5307	41	-269	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 9. Bond Lengths [Å] and Angles [deg] for
$Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

I(1)-Cu(3)#1	2.6188(12)
I(1)-Cu(3)	2.6188(12)
I(1)-Cu(2)	2.7278(8)
I(1)-Cu(2)#1	2.7278(8)
Cu(2)-P(1)	2.274(3)
Cu(2)-I(1)#2	2.7278(8)
Cu(2)-I(1)#3	2.7278(8)
Cu(2)-Cu(3)	2.985(2)
Cu(2)-Cu(3)#1	2.985(2)
Cu(2)-Cu(3)#4	2.985(2)
P(1)-C(1)#3	1.851(7)
P(1)-C(1)#5	1.851(7)
P(1)-C(1)	1.851(7)
Cu(3)-N(98)	2.097(18)
Cu(3)-I(1)#2	2.6188(12)
Cu(3)-I(1)#6	2.6188(12)
Cu(3)-Cu(2)#4	2.985(2)
Cu(3)-Cu(2)#1	2.985(2)
C(1)-C(6)	1.360(11)
C(1)-C(2)	1.390(10)
C(2)-C(3)	1.402(11)
C(3)-C(4)	1.363(13)
C(3)-C(7)	1.488(11)
C(4)-C(5)	1.370(13)
C(5)-C(6)	1.417(13)
C(99)-N(98)	1.341(18)
C(99)-C(98)#7	1.341(18)
C(99)-N(98)#7	1.341(18)
Cu(3)#1-I(1)-Cu(3)	95.8(2)
Cu(3)#1-I(1)-Cu(2)	67.83(5)
Cu(3)-I(1)-Cu(2)	67.83(5)
Cu(3)#1-I(1)-Cu(2)#1	67.83(5)
Cu(3)-I(1)-Cu(2)#1	67.83(5)
Cu(2)-I(1)-Cu(2)#1	111.50(6)
P(1)-Cu(2)-I(1)#2	110.48(3)
P(1)-Cu(2)-I(1)	110.48(3)
I(1)#2-Cu(2)-I(1)	108.44(3)
P(1)-Cu(2)-I(1)#3	110.48(3)
I(1)#2-Cu(2)-I(1)#3	108.44(3)
I(1)-Cu(2)-I(1)#3	108.44(3)
P(1)-Cu(2)-Cu(3)	131.25(8)
I(1)#2-Cu(2)-Cu(3)	54.346(18)

Table 9. (Continued)

C(1)#3-P(1)-C(1)#5	104.8(3)
C(1)#3-P(1)-C(1)	104.8(3)
C(1)#5-P(1)-C(1)	104.8(3)
C(1)#3-P(1)-Cu(2)	113.8(2)
C(1)#5-P(1)-Cu(2)	113.8(2)
C(1)-P(1)-Cu(2)	113.8(2)
N(98)-Cu(3)-I(1)#2	102.65(10)
N(98)-Cu(3)-I(1)	102.64(10)
I(1)#2-Cu(3)-I(1)	115.35(7)
C(6)-C(1)-C(2)	116.5(8)
C(6)-C(1)-P(1)	118.2(6)
C(2)-C(1)-P(1)	125.3(6)
C(1)-C(2)-C(3)	123.3(9)
C(4)-C(3)-C(2)	118.1(8)
C(4)-C(3)-C(7)	118.5(9)
C(2)-C(3)-C(7)	123.3(10)
C(3)-C(4)-C(5)	120.8(9)
C(4)-C(5)-C(6)	119.5(10)
C(1)#3-P(1)-C(1)#5	104.8(3)
C(1)#3-P(1)-C(1)	104.8(3)
C(1)#5-P(1)-C(1)	104.8(3)
C(1)#3-P(1)-Cu(2)	113.8(2)
C(1)#5-P(1)-Cu(2)	113.8(2)
C(1)-P(1)-Cu(2)	113.8(2)
N(98)-Cu(3)-I(1)#2	102.65(10)
N(98)-Cu(3)-I(1)	102.64(10)
I(1)#2-Cu(3)-I(1)	115.35(7)
N(98)-Cu(3)-I(1)#6	102.65(10)
C(6)-C(1)-C(2)	116.5(8)
C(6)-C(1)-P(1)	118.2(6)
C(2)-C(1)-P(1)	125.3(6)
C(1)-C(6)-C(5)	121.7(9)
N(98)-C(99)-C(98)#7	180.000(6)
N(98)-C(99)-N(98)#7	180.000(6)
C(99)-N(98)-Cu(3)	180.0(17)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+5/4,-z+1/4 #2 y,z+1/2,x-1/2 #3 z+1/2,-x+5/4,-y+3/4 #4 -x+5/4,-y+5/4,z
#5 -y+5/4,-z+3/4,x-1/2 #6 z+1/2,x,y-1/2 #7 -x+1,-y+1,-z

Table 10. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_6I_6(P(m\text{-}C_7H_7)_3)_4(CH_3CN)_2$

	U11	U22	U33	U23	U13	U12
I(1)	58(1)	68(1)	65(1)	10(1)	0	0
Cu(2)	67(1)	67(1)	67(1)	8(1)	-8(1)	8(1)
P(1)	58(1)	58(1)	58(1)	3(1)	-3(1)	3(1)
Cu(3)	102(1)	102(1)	102(1)	0(2)	0(2)	0(2)
C(1)	68(5)	64(5)	63(4)	8(4)	-9(4)	0(4)
C(2)	104(7)	69(5)	89(6)	8(5)	18(5)	5(5)
C(3)	144(9)	63(5)	65(5)	13(4)	11(5)	3(6)
C(4)	100(7)	101(7)	101(7)	31(6)	6(6)	-15(6)
C(5)	79(7)	159(11)	165(11)	76(10)	24(7)	8(7)
C(6)	79(6)	99(7)	143(9)	56(7)	21(6)	12(6)
C(7)	260(18)	91(8)	173(13)	41(9)	95(13)	31(10)
C(99)	83(6)	83(6)	83(6)	27(9)	27(9)	27(9)
N(98)	126(6)	126(6)	126(6)	-11(7)	-11(7)	-11(7)
C(98)	126(6)	126(6)	126(6)	-11(7)	-11(7)	-11(7)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

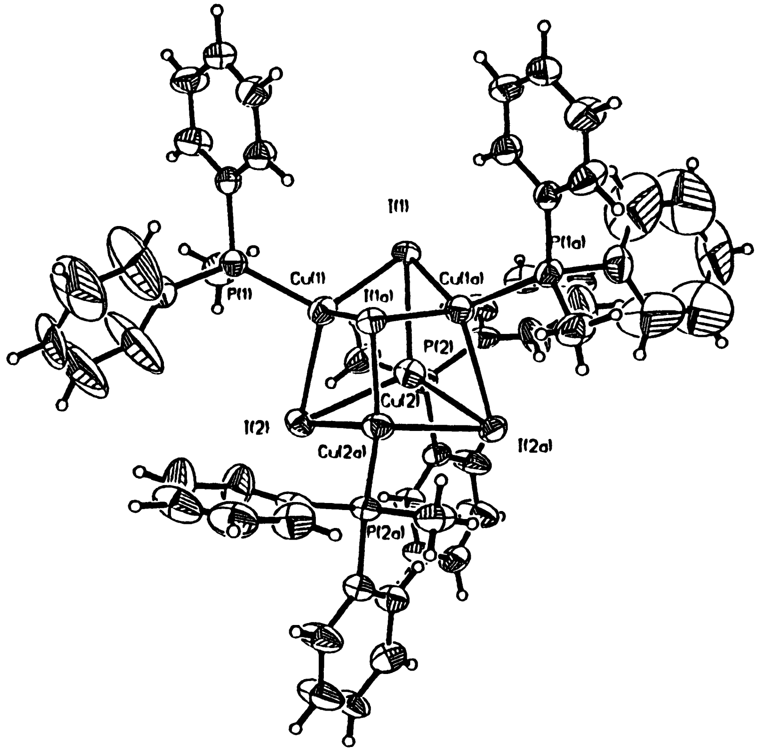


Figure 8 Projection View of $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

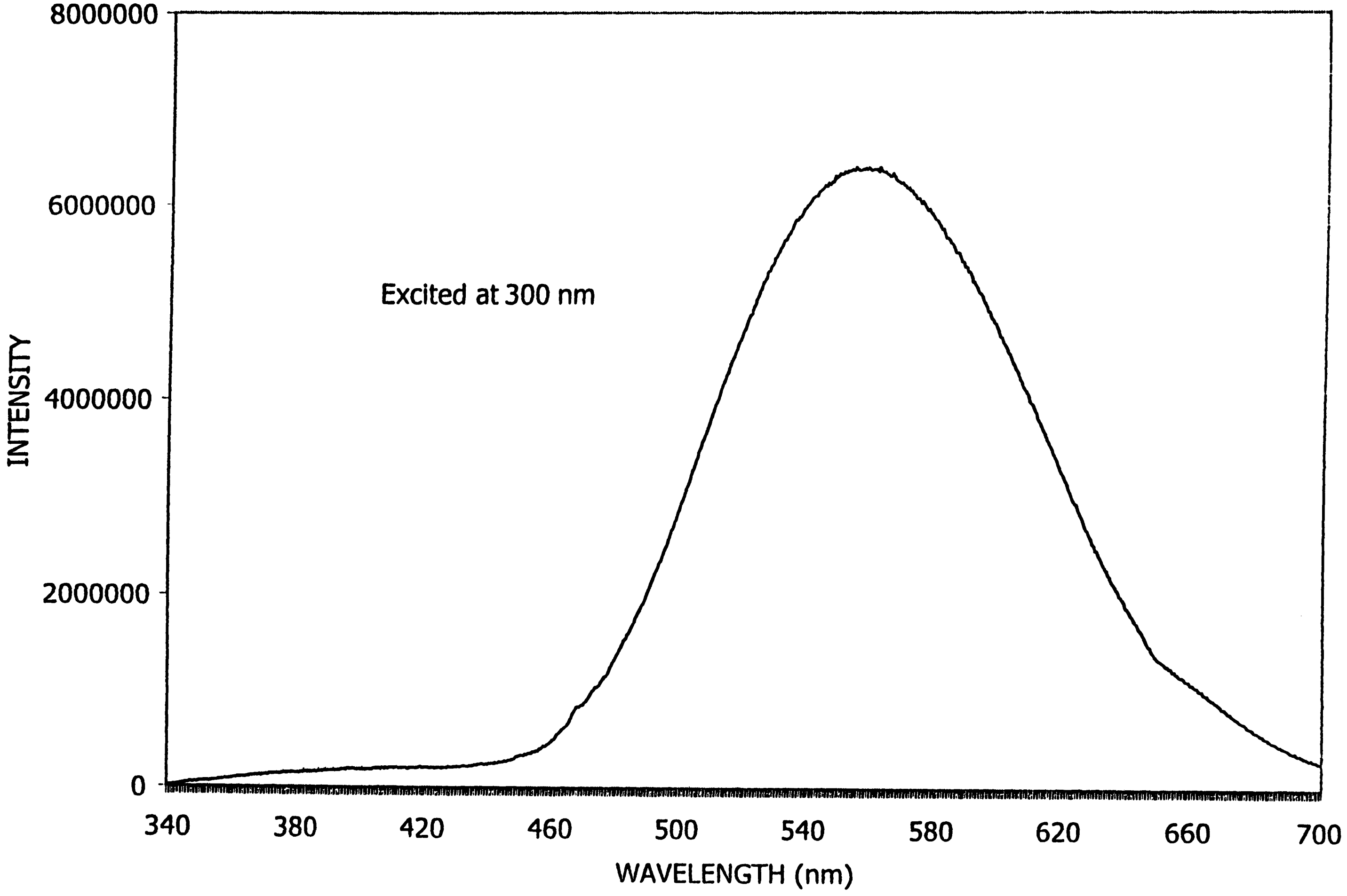


Figure 9 Emission Spectrum of $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

Table 11. Crystal Data and Structure Refinement for $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

Empirical formula	$C_{26}H_{26}Cu_2I_2P_2$
Formula weight	781.3
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C2/c*
Unit cell dimensions	a = 25.958(10) Å α = 90.0 deg.
	b = 12.130(6) Å β = 110.710 (10) deg.
	c = 19.822(7) Å γ = 90.0 deg.
Volume	5842(4) $Å^3$
Z, Calculated density	8, 1.777 Mg/m^3
Absorption coefficient	3.691 mm^{-1}
F(000)	3008
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	2.14 to 29.98 deg.
Index ranges	$-1 \le h \le 36$, $-17 \le k \le 1$, $-27 \le l \le 26$
Reflections collected / unique/ observed	9839 / 8526 [R(int) = 0.0225]/ 3668(5.0>σ(F))
Goodness-of-fit	1.25
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.0581
R indices (all data)	R1 = 0.1200, wR2 = 0.0774
Extinction coefficient	-0.000019(5)
Largest diff. peak and hole	0.81 and –0.52 $eÅ^{-3}$

Table 12. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

	x	y	z	U(eq)
I(1)	-647(1)	1952(1)	1446(1)	57(1)
I(2)	596(1)	4663(1)	1954(1)	65(1)
Cu(1)	447(1)	2434(1)	2189(1)	70(1)
Cu(2)	-465(1)	4154(1)	1808(1)	70(1)
P(1)	908(1)	1606(2)	1545(1)	63(1)
P(2)	-1057(1)	4997(2)	810(1)	59(1)
C(2)	-838(6)	4829(9)	44(6)	98(6)
C(111)	-1138(4)	6515(7)	842(4)	60(4)
C(112)	-689(4)	7150(8)	1218(5)	72(4)
C(113)	-751(5)	8310(9)	1233(6)	83(5)
C(114)	-1235(5)	8825(9)	898(7)	89(6)
C(115)	-1663(5)	8199(10)	516(9)	132(8)
C(116)	-1639(5)	7061(9)	478(8)	114(7)
C(1)	645(6)	2188(10)	626(5)	102(6)
C(212)	2002(5)	986(9)	2224(8)	313(23)
C(213)	2570	1162	2475	360(28)
C(214)	2780	2158	2332	239(18)
C(215)	2423	2977	1937	367(31)
C(216)	1855	2801	1686	356(28)
C(211)	1645	1805	1830	95(6)
C(221)	846(4)	105(8)	1415(4)	57(4)
C(222)	790(5)	-558(9)	1961(5)	74(5)
C(223)	770(5)	-1714(9)	1886(6)	84(5)
C(224)	788(4)	-2199(9)	1295(6)	77(5)
C(225)	829(6)	-1587(9)	748(6)	97(6)
C(226)	863(5)	-432(9)	804(5)	91(6)
C(121)	-1767(4)	4490(7)	512(6)	72(4)
C(122)	-2083(6)	4275(10)	-199(7)	102(6)
C(123)	-2633(7)	3922(12)	-410(9)	115(8)
C(124)	-2849(6)	3835(12)	97(11)	132(8)
C(125)	-2556(6)	3975(16)	798(10)	158(11)
C(126)	-1998(5)	4319(13)	1017(8)	114(7)
H(2A)	-1091	5189	-373	80
H(2B)	-479	5147	161	80
H(2C)	-823	4057	-54	80
H(11A)	-340	6804	1463	80
H(11B)	-434	8747	1489	80
H(11C)	-1273	9608	935	80
H(11D)	-2006	8555	255	80
H(11E)	-1959	6641	207	80
H(1A)	834	1846	343	80

Table 12. (Continued)

H(1B)	257	2046	410	80
H(1C)	708	2969	645	80
H(21A)	1858	301	2323	80
H(21B)	2816	598	2747	80
H(21C)	3171	2279	2505	80
H(21D)	2568	3662	1839	80
H(21E)	1609	3364	1415	80
H(22A)	764	-226	2388	80
H(22B)	747	-2157	2275	80
H(22C)	770	-2987	1249	80
H(22D)	836	-1932	315	80
H(22E)	899	-13	412	80
H(12A)	-1925	4381	-565	80
H(12B)	-2840	3762	-906	80
H(12C)	-3232	3652	-43	80
H(12D)	-2719	3833	1155	80
H(12E)	-1786	4426	1519	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 13. Bond Lengths [Å] and Angles [deg] for $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

I(1)-Cu(1)	2.761 (2)
I(1)-Cu(2)	2.763 (2)
I(1)-Cu(1A)	2.635 (2)
I(2)-Cu(1)	2.794 (2)
I(2)-Cu(2)	2.737 (2)
I(2)-Cu(2A)	2.667 (2)
Cu(1)-Cu(2)	3.043 (2)
Cu(1)-P(1)	2.270 (4)
Cu(1)-I(1A)	2.635 (2)
Cu(1)-Cu(1A)	2.987 (3)
Cu(1)-Cu(2A)	2.871 (2)
Cu(2)-P(2)	2.273 (3)
Cu(2)-I(2A)	2.667 (2)
Cu(2)-Cu(1A)	2.871 (2)
Cu(2)-Cu(2A)	2.945 (2)
P(1)-C(1)	1.846 (10)
P(1)-C(211)	1.809 (13)
P(1)-C(221)	1.837 (10)
P(2)-C(2)	1.810 (14)
P(2)-C(111)	1.857 (9)
P(2)-C(121)	1.832 (10)
C(111)-C(112)	1.374 (13)
C(111)-C(116)	1.409 (14)
C(112)-C(113)	1.417 (14)
C(113)-C(114)	1.349 (16)
C(114)-C(115)	1.336 (16)
C(115)-C(116)	1.386 (16)
C(221)-C(222)	1.397 (15)
C(221)-C(226)	1.390 (15)
C(222)-C(223)	1.410 (15)
C(223)-C(224)	1.325 (17)
C(224)-C(225)	1.350 (18)
C(225)-C(226)	1.405 (16)
C(121)-C(122)	1.381 (15)
C(121)-C(126)	1.355 (21)
C(122)-C(123)	1.405 (22)
C(123)-C(124)	1.316 (30)
C(124)-C(125)	1.339 (24)
C(125)-C(126)	1.419 (20)
Cu(1)-I(1)-Cu(2)	66.9(1)
Cu(1)-I(1)-Cu(1A)	67.2(1)
Cu(2)-I(1)-Cu(1A)	64.2(1)

Table 13. (Continued)

Cu(1)-I(2)-Cu(2)	66.8(1)
Cu(1)-I(2)-Cu(2A)	63.4(1)
Cu(2)-I(2)-Cu(2A)	66.0(1)
I(1)-Cu(1)-I(2)	107.1(1)
I(1)-Cu(1)-Cu(2)	56.6(1)
I(2)-Cu(1)-Cu(2)	55.7(1)
I(1)-Cu(1)-P(1)	104.7(1)
I(2)-Cu(1)-P(1)	101.7(1)
Cu(2)-Cu(1)-P(1)	133.1(1)
I(1)-Cu(1)-I(1A)	107.1(1)
I(2)-Cu(1)-I(1A)	113.4(1)
Cu(2)-Cu(1)-I(1A)	105.1(1)
P(1)-Cu(1)-I(1A)	121.8(1)
I(1)-Cu(1)-Cu(1A)	54.4(1)
I(2)-Cu(1)-Cu(1A)	104.0(1)
Cu(2)-Cu(1)-Cu(1A)	56.8(1)
P(1)-Cu(1)-Cu(1A)	150.8(1)
I(1A)-Cu(1)-Cu(1A)	58.4(1)
I(1)-Cu(1)-Cu(2A)	106.6(1)
I(2)-Cu(1)-Cu(2A)	56.2(1)
Cu(2)-Cu(1)-Cu(2A)	59.6(1)
P(1)-Cu(1)-Cu(2A)	145.9(1)
I(1A)-Cu(1)-Cu(2A)	60.1(1)
Cu(1A)-Cu(1)-Cu(2A)	62.6(1)
I(1)-Cu(2)-I(2)	108.6(1)
I(1)-Cu(2)-Cu(1)	56.5(1)
I(2)-Cu(2)-Cu(1)	57.5(1)
I(1)-Cu(2)-P(2)	102.0(1)
I(2)-Cu(2)-P(2)	109.6(1)
Cu(1)-Cu(2)-P(2)	138.7(1)
I(1)-Cu(2)-I(2A)	113.4(1)
I(2)-Cu(2)-I(2A)	107.6(1)
Cu(1)-Cu(2)-I(2A)	105.8(1)
P(2)-Cu(2)-I(2A)	115.4(1)
I(1)-Cu(2)-Cu(1A)	55.7(1)
I(2)-Cu(2)-Cu(1A)	108.7(1)
Cu(1)-Cu(2)-Cu(1A)	60.6(1)
P(2)-Cu(2)-Cu(1A)	140.4(1)
I(2A)-Cu(2)-Cu(1A)	60.5(1)
I(1)-Cu(2)-Cu(2A)	104.5(1)
I(2)-Cu(2)-Cu(2A)	55.9(1)
Cu(1)-Cu(2)-Cu(2A)	57.3(1)
P(2)-Cu(2)-Cu(2A)	152.8(1)
I(2A)-Cu(2)-Cu(2A)	58.1(1)

Table 13. (Continued)

Cu(1A)-Cu(2)-Cu(2A)	63.1(1)
Cu(1)-P(1)-C(1)	107.5(5)
Cu(1)-P(1)-C(211)	118.4(5)
C(1)-P(1)-C(211)	103.8(7)
Cu(1)-P(1)-C(221)	118.7(4)
C(1)-P(1)-C(221)	104.9(5)
C(211)-P(1)-C(221)	101.9(5)
Cu(2)-P(2)-C(2)	111.3(4)
Cu(2)-P(2)-C(111)	117.8(3)
C(2)-P(2)-C(111)	102.3(5)
Cu(2)-P(2)-C(121)	115.0(3)
C(2)-P(2)-C(121)	105.6(6)
C(111)-P(2)-C(121)	103.4(4)
P(2)-C(111)-C(112)	119.3(7)
P(2)-C(111)-C(116)	122.9(7)
C(112)-C(111)-C(116)	117.8(9)
C(111)-C(112)-C(113)	119.1(9)
C(112)-C(113)-C(114)	122.8(10)
C(113)-C(114)-C(115)	117.2(11)
C(114)-C(115)-C(116)	123.6(11)
C(111)-C(116)-C(115)	119.4(10)
P(1)-C(211)-C(212)	120.0(4)
P(1)-C(211)-C(216)	119.9(4)
P(1)-C(221)-C(222)	119.3(7)
P(1)-C(221)-C(226)	124.0(8)
C(222)-C(221)-C(226)	116.7(9)
C(221)-C(222)-C(223)	120.0(10)
C(222)-C(223)-C(224)	121.6(11)
C(223)-C(224)-C(225)	120.2(11)
C(224)-C(225)-C(226)	120.3(12)
C(221)-C(226)-C(225)	121.1(11)
P(2)-C(121)-C(122)	124.1(11)
P(2)-C(121)-C(126)	118.1(8)
C(122)-C(121)-C(126)	117.8(11)
C(121)-C(122)-C(123)	122.4(15)
C(122)-C(123)-C(124)	117.4(14)
C(123)-C(124)-C(125)	122.9(15)
C(124)-C(125)-C(126)	119.9(18)
C(121)-C(126)-C(125)	119.3(13)

Table 14. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_4I_4(P(C_6H_5)_2CH_3)_4$

	U11	U22	U33	U23	U13	U12
I(1)	61(1)	52(1)	52(1)	-8(1)	10(1)	-6(1)
I(2)	63(1)	56(1)	74(1)	-5(1)	21(1)	12(1)
Cu(1)	77(1)	71(1)	65(1)	6(1)	30(1)	1(1)
Cu(2)	66(1)	64(1)	70(1)	7(1)	12(1)	11(1)
P(1)	73(2)	63(2)	59(1)	-6(1)	32(1)	0(1)
P(2)	62(2)	46(1)	61(1)	6(1)	12(1)	2(1)
C(2)	148(12)	66(7)	84(7)	22(8)	46(8)	13(6)
C(111)	64(6)	53(5)	57(5)	7(5)	13(4)	-2(4)
C(112)	69(7)	60(6)	74(6)	1(5)	9(5)	1(5)
C(113)	102(9)	56(7)	83(7)	-24(6)	23(6)	-14(5)
C(114)	85(8)	53(7)	128(9)	25(6)	35(7)	-5(6)
C(115)	73(8)	56(8)	223(17)	6(7)	-4(10)	9(9)
C(116)	66(7)	47(7)	191(14)	-1(6)	-1(8)	2(8)
C(1)	149(12)	93(9)	74(7)	8(8)	51(8)	13(6)
C(212)	75(13)	432(51)	358(37)	-57(22)	-16(17)	100(38)
C(213)	65(13)	350(46)	580(59)	-29(20)	9(22)	2(43)
C(214)	58(11)	337(37)	332(32)	-76(17)	81(16)	-107(28)
C(215)	90(15)	235(31)	707(72)	-80(19)	57(28)	34(37)
C(216)	85(14)	219(26)	688(65)	-52(16)	42(24)	171(34)
C(211)	77(8)	104(10)	114(9)	-20(8)	47(7)	-27(8)
C(221)	57(5)	63(6)	53(5)	1(5)	21(4)	2(4)
C(222)	92(8)	71(7)	66(6)	-1(6)	36(5)	-2(5)
C(223)	105(9)	67(7)	87(7)	11(7)	43(7)	20(6)
C(224)	85(8)	57(6)	90(7)	-4(6)	32(6)	-6(6)
C(225)	147(12)	68(8)	88(8)	-23(8)	58(8)	-25(6)
C(226)	142(11)	79(8)	62(6)	-27(8)	49(7)	-9(6)
C(121)	59(6)	45(6)	87(7)	11(5)	-5(5)	-6(5)
C(122)	97(9)	87(9)	100(9)	-16(8)	8(7)	-4(7)
C(123)	121(14)	83(10)	112(11)	5(9)	5(10)	-11(9)
C(124)	62(8)	86(10)	184(16)	2(7)	-34(10)	-27(12)
C(125)	88(11)	238(23)	155(15)	-41(13)	52(11)	-12(15)
C(126)	64(7)	162(14)	109(9)	-37(9)	21(7)	-4(9)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2$ [h^2a^{*2} U_{11} + ... + 2 h k a* b* U_{12}]

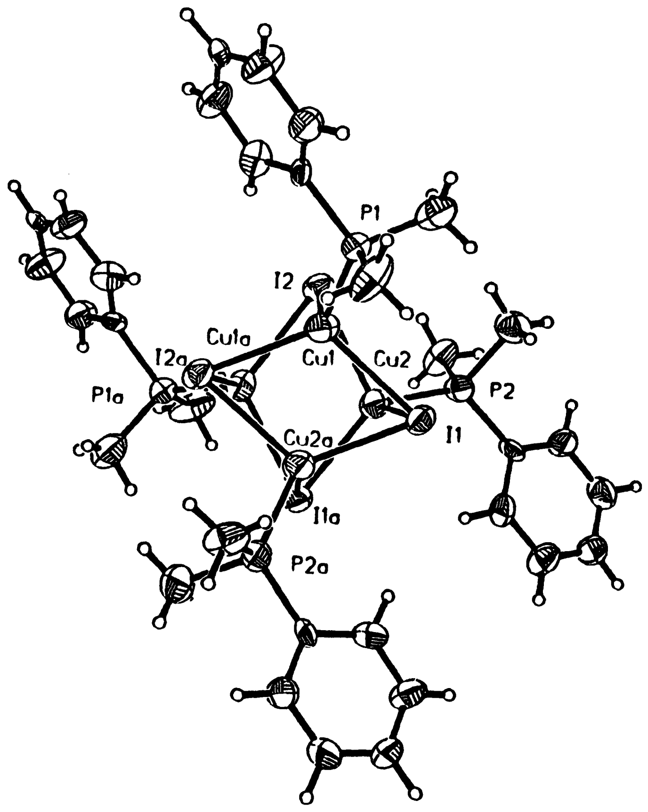


Figure 10 Projection View of $Cu_4I_4(PC_6H_5(CH_3)_2)_4$

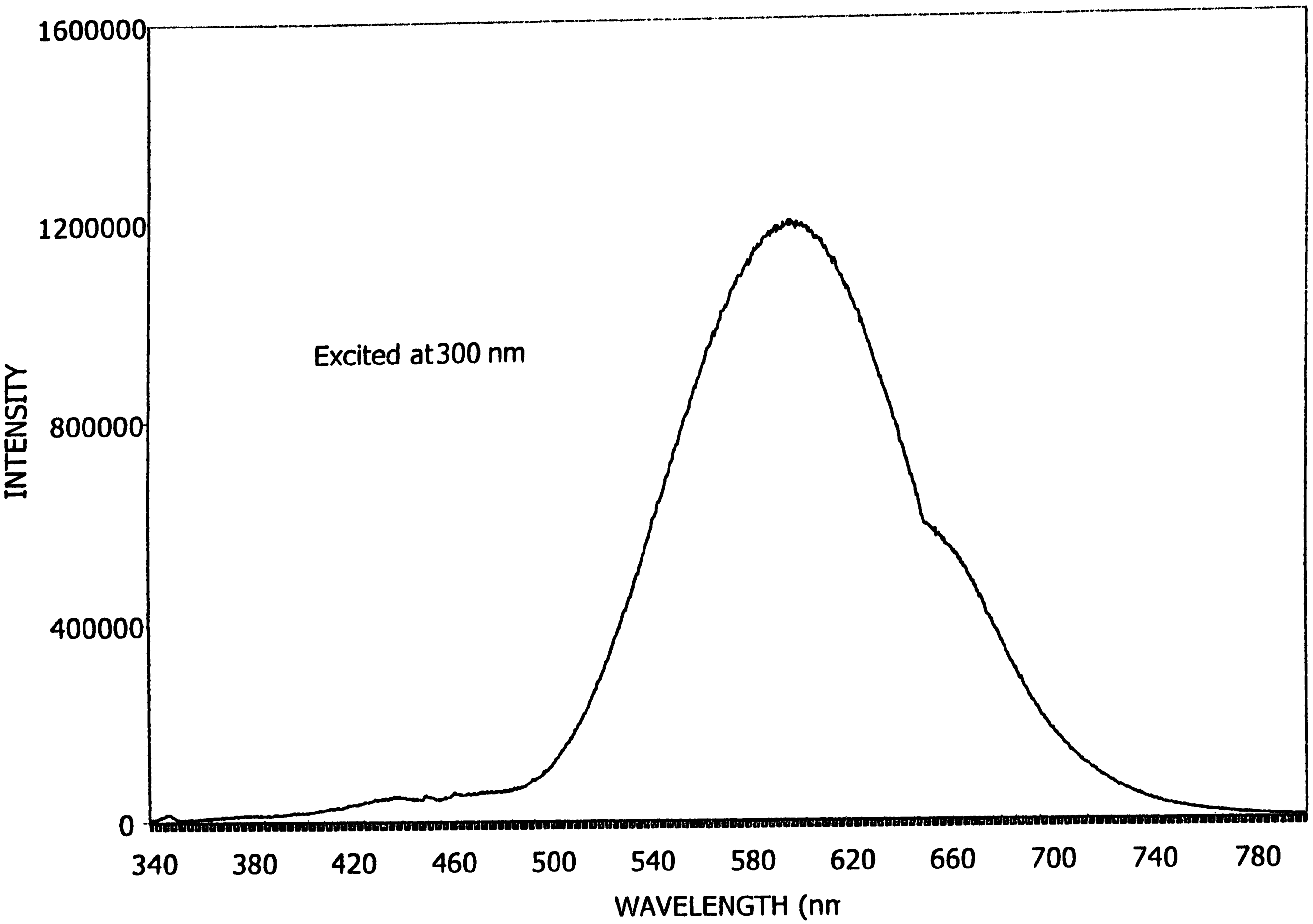


Figure 11 Emission Spectrum of $Cu_4I_4(PC_6H_5(CH_3)_2)_4$

Table 15. Crystal Data and Structure Refinement for $Cu_4I_4(PC_6H_5(CH_3)_2)_4$

Empirical formula	$C_{16}H_{22}Cu_2I_2P_2$
Formula weight	657.16
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C2/c*
Unit cell dimensions	a = 26.116(10) Å α = 90.0 deg.
	b = 11.899(4) Å β = 131.87(2) deg.
	c = 19.524(9) Å γ = 90.0 deg.
Volume	4518(3) $Å^3$
Z, Calculated density	8, 1.932 Mg/m^3
Absorption coefficient	4.752 mm^{-1}
F(000)	2496
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	2.01 to 30.01 deg.
Index ranges	$-1 \leq h \leq 36, -1 \leq k \leq 16, -27 \leq l \leq 1$
Reflections collected / unique/	3997 / 3652 [R(int) = 0.0785]
Goodness-of-fit	0.925
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.1599
R indices (all data)	R1 = 0.1497, wR2 = 0.2101
Extinction coefficient	0.00037(8)
Largest diff. peak and hole	0.973 and –0.606 $eÅ^{-3}$

Table 16. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_4I_4(PC_6H_5(CH_3)_2)_4$

	x	y	z	U(eq)
I(1)	4458(1)	-513(1)	1050(1)	65(1)
I(2)	4032(1)	2353(1)	2213(1)	69(1)
Cu(1)	4615(2)	1750(2)	1544(2)	75(1)
Cu(2)	4357(2)	71(2)	2321(2)	75(1)
P(1)	4108(3)	2505(3)	151(3)	58(2)
P(2)	3349(3)	-653(3)	1807(4)	63(2)
C(1)	3230(2)	2192(16)	-720(2)	120(16)
C(2)	4430(15)	1941(13)	-347(17)	107(11)
C(3)	3038(13)	-63(14)	2325(18)	95(11)
C(4)	2631(16)	-279(16)	588(15)	99(11)
C(11)	4141(11)	4055(11)	84(12)	52(6)
C(12)	4270(13)	4731(14)	745(14)	75(8)
C(13)	4274(15)	5911(13)	698(17)	86(9)
C(14)	4155(14)	6374(13)	-45(15)	69(8)
C(15)	4059(16)	5726(12)	-714(15)	96(10)
C(16)	4023(14)	4564(13)	-658(14)	78(8)
C(21)	3258(12)	-2161(12)	1837(13)	54(6)
C(22)	3818(13)	-2885(13)	2178(13)	71(8)
C(23)	3755(14)	-4054(14)	2171(15)	81(9)
C(24)	3167(16)	-4541(15)	1881(16)	86(10)
C(25)	2624(16)	-3860(18)	1542(16)	91(10)
C(26)	2659(14)	-2662(13)	1516(17)	77(9)
H(1A)	3038	2527	-1293	80
H(1B)	3168	1392	-791	80
H(1C)	3000	2484	-525	80
H(2A)	4200	2286	-933	80
H(2B)	4915	2085	55	80
H(2C)	4350	1145	-427	80
H(3A)	2613	-423	2064	80
H(3B)	3368	-184	2978	80
H(3C)	2962	729	2201	80
H(4A)	2214	-597	394	80
H(4B)	2584	523	515	80
H(4C)	2720	-582	220	80
H(12A)	4380	4392	1276	80
H(13A)	4303	6372	1127	80
H(14A)	4200	7175	-45	80
H(15A)	3994	6070	-1212	80
H(16A)	3903	4089	-1145	80
H(22A)	4252	-2569	2432	80
H(23A)	4121	-4531	2344	80

Table 16. (Continued)

H(24A)	3138	-5336	1933	80
H(25A)	2197	-4194	1304	80
H(26A)	2263	-2211	1269	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 17. Bond Lengths [Å] and Angles [deg] for
$Cu_4I_4(PC_6H_5(CH_3)_2)_4$

I(1)-Cu(2)#1	2.653(4)
I(1)-Cu(2)	2.754(2)
I(1)-Cu(1)	2.796(2)
I(2)-Cu(1)	2.683(2)
I(2)-Cu(1)#1	2.728(4)
I(2)-Cu(2)	2.810(2)
Cu(1)-P(1)	2.270(5)
Cu(1)-I(2)#1	2.728(4)
Cu(1)-Cu(1)#1	2.820(5)
Cu(1)-Cu(2)	2.848(3)
Cu(1)-Cu(2)#1	2.857(4)
Cu(2)-P(2)	2.269(6)
Cu(2)-I(1)#1	2.653(4)
Cu(2)-Cu(1)#1	2.857(4)
Cu(2)-Cu(2)#1	2.941(6)
P(1)-C(2)	1.788(15)
P(1)-C(1)	1.76(4)
P(1)-C(11)	1.854(13)
P(2)-C(3)	1.810(14)
P(2)-C(21)	1.816(15)
P(2)-C(4)	1.85(2)
C(11)-C(12)	1.358(19)
C(11)-C(16)	1.403(19)
C(12)-C(13)	1.41(2)
C(13)-C(14)	1.38(2)
C(14)-C(15)	1.39(2)
C(15)-C(16)	1.39(2)
C(21)-C(26)	1.37(3)
C(21)-C(22)	1.42(3)
C(22)-C(23)	1.40(2)
C(23)-C(24)	1.36(3)
C(24)-C(25)	1.36(3)
C(25)-C(26)	1.43(3)

Cu(2)#1-I(1)-Cu(2)	65.88(12)
Cu(2)#1-I(1)-Cu(1)	63.18(8)
Cu(2)-I(1)-Cu(1)	61.75(6)
Cu(1)-I(2)-Cu(1)#1	62.81(9)
Cu(1)-I(2)-Cu(2)	62.41(6)
Cu(1)#1-I(2)-Cu(2)	62.09(9)
P(1)-Cu(1)-I(2)	114.20(16)
P(1)-Cu(1)-I(2)#1	109.59(17)
I(2)-Cu(1)-I(2)#1	108.42(9)

Table 17. (Continued)

P(1)-Cu(1)-I(1)	97.73(12)
I(2)-Cu(1)-I(1)	115.13(9)
I(2)#1-Cu(1)-I(1)	111.43(10)
P(1)-Cu(1)-Cu(1)#1	156.37(12)
I(2)-Cu(1)-Cu(1)#1	59.37(8)
I(2)#1-Cu(1)-Cu(1)#1	57.82(11)
I(1)-Cu(1)-Cu(1)#1	105.50(5)
P(1)-Cu(1)-Cu(2)	139.4(2)
I(2)-Cu(1)-Cu(2)	60.97(7)
I(2)#1-Cu(1)-Cu(2)	109.74(12)
I(1)-Cu(1)-Cu(2)	58.39(6)
Cu(1)#1-Cu(1)-Cu(2)	60.53(8)
P(1)-Cu(1)-Cu(2)#1	134.51(14)
I(2)-Cu(1)-Cu(2)#1	110.79(8)
I(2)#1-Cu(1)-Cu(2)#1	60.36(9)
I(1)-Cu(1)-Cu(2)#1	55.96(8)
Cu(1)#1-Cu(1)-Cu(2)#1	60.22(9)
Cu(2)-Cu(1)-Cu(2)#1	62.06(12)
P(2)-Cu(2)-I(1)#1	120.81(14)
P(2)-Cu(2)-I(1)	106.58(15)
I(1)#1-Cu(2)-I(1)	106.04(11)
P(2)-Cu(2)-I(2)	97.53(15)
I(1)#1-Cu(2)-I(2)	113.31(10)
I(1)-Cu(2)-I(2)	112.46(8)
P(2)-Cu(2)-Cu(1)	130.37(19)
I(1)#1-Cu(2)-Cu(1)	108.65(13)
I(1)-Cu(2)-Cu(1)	59.85(6)
I(2)-Cu(2)-Cu(1)	56.61(6)
P(2)-Cu(2)-Cu(1)#1	145.17(13)
I(1)#1-Cu(2)-Cu(1)#1	60.86(9)
I(1)-Cu(2)-Cu(1)#1	105.63(9)
I(2)-Cu(2)-Cu(1)#1	57.54(8)
Cu(1)-Cu(2)-Cu(1)#1	59.24(10)
P(2)-Cu(2)-Cu(2)#1	155.35(12)
I(1)#1-Cu(2)-Cu(2)#1	58.71(12)
I(1)-Cu(2)-Cu(2)#1	55.41(7)
I(2)-Cu(2)-Cu(2)#1	104.93(6)
Cu(1)-Cu(2)-Cu(2)#1	59.12(8)
Cu(1)#1-Cu(2)-Cu(2)#1	58.83(10)
C(2)-P(1)-C(1)	100.4(13)
C(2)-P(1)-C(11)	105.9(7)
C(1)-P(1)-C(11)	103.7(9)
C(2)-P(1)-Cu(1)	113.1(9)
C(1)-P(1)-Cu(1)	114.5(7)
C(11)-P(1)-Cu(1)	117.5(5)

Table 17. (Continued)

C(3)-P(2)-C(21)	104.3(7)
C(3)-P(2)-C(4)	100.3(13)
C(21)-P(2)-C(4)	103.7(9)
C(3)-P(2)-Cu(2)	115.2(7)
C(21)-P(2)-Cu(2)	120.0(7)
C(4)-P(2)-Cu(2)	111.0(8)
C(12)-C(11)-C(16)	118.0(14)
C(12)-C(11)-P(1)	121.0(11)
C(16)-C(11)-P(1)	120.9(10)
C(11)-C(12)-C(13)	122.5(15)
C(14)-C(13)-C(12)	117.4(15)
C(13)-C(14)-C(15)	122.7(15)
C(16)-C(15)-C(14)	117.2(14)
C(15)-C(16)-C(11)	121.9(14)
C(26)-C(21)-C(22)	116.9(15)
C(26)-C(21)-P(2)	123.2(16)
C(22)-C(21)-P(2)	119.8(14)
C(23)-C(22)-C(21)	121(2)
C(24)-C(23)-C(22)	121(2)
C(23)-C(24)-C(25)	118.0(17)
C(24)-C(25)-C(26)	123(2)
C(21)-C(26)-C(25)	120(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table 18. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_4I_4(PC_6H_5(CH_3)_2)_4$

	U11	U22	U33	U23	U13	U12
I(1)	71(2)	50(1)	75(1)	-10(1)	49(1)	-3(1)
I(2)	73(2)	53(1)	90(1)	1(1)	58(1)	9(1)
Cu(1)	86(4)	65(1)	74(2)	8(1)	53(2)	10(1)
Cu(2)	64(4)	65(1)	95(2)	0(1)	53(3)	-3(2)
P(1)	60(6)	52(2)	62(3)	0(2)	40(4)	0(3)
P(2)	58(6)	61(2)	75(3)	5(2)	47(5)	3(3)
C(1)	140(6)	67(11)	120(2)	7(13)	70(4)	6(19)
C(2)	180(4)	69(9)	160(2)	-31(12)	150(3)	-32(15)
C(3)	100(3)	75(10)	170(3)	-23(13)	110(3)	-22(14)
C(4)	100(4)	95(12)	86(17)	28(12)	50(3)	6(17)
C(11)	30(2)	43(6)	64(11)	-12(7)	27(16)	-13(9)
C(12)	80(3)	78(10)	77(13)	-12(10)	59(19)	-13(13)
C(13)	100(3)	54(8)	117(18)	-14(11)	80(3)	-6(14)
C(14)	20(3)	53(8)	84(16)	2(10)	10(2)	-7(12)
C(15)	160(4)	55(8)	104(17)	0(9)	100(2)	-8(13)
C(16)	90(3)	65(8)	76(13)	-2(9)	50(2)	-6(13)
C(21)	20(2)	63(8)	57(12)	12(9)	19(17)	7(10)
C(22)	60(3)	70(9)	81(15)	-17(9)	50(2)	-21(12)
C(23)	90(3)	56(8)	110(2)	-1(11)	80(3)	-10(13)
C(24)	90(4)	55(9)	83(16)	16(11)	50(3)	-7(15)
C(25)	60(4)	91(14)	87(18)	11(13)	30(3)	-15(17)
C(26)	60(3)	62(9)	110(2)	-10(11)	50(3)	1(13)

The anisotropic displacement factor exponent takes the form:
$-2\,pi^2\,[\,h^2a^{*2}\,U_{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U_{12}\,]$

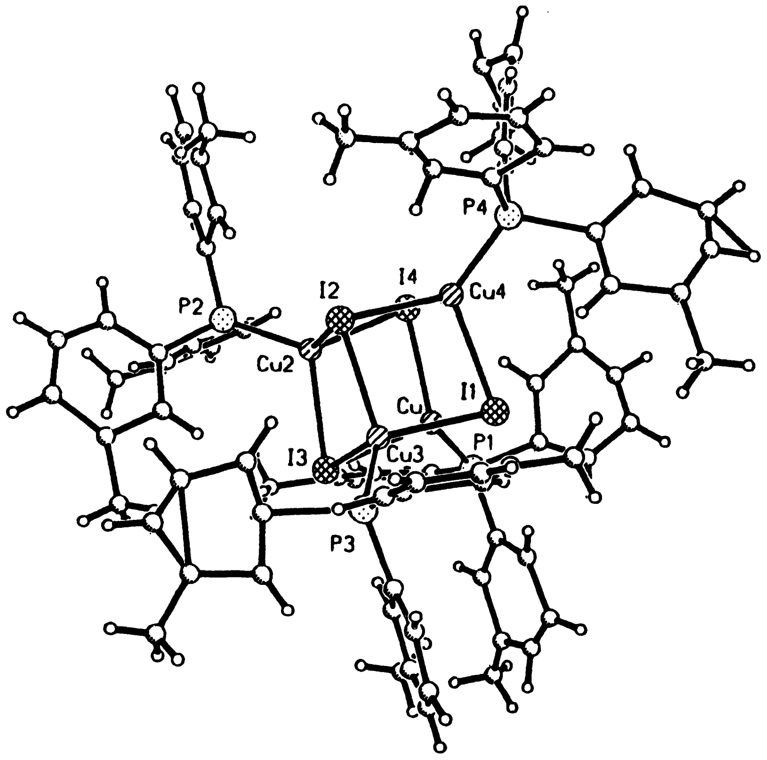


Figure 12 Projection View of $Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

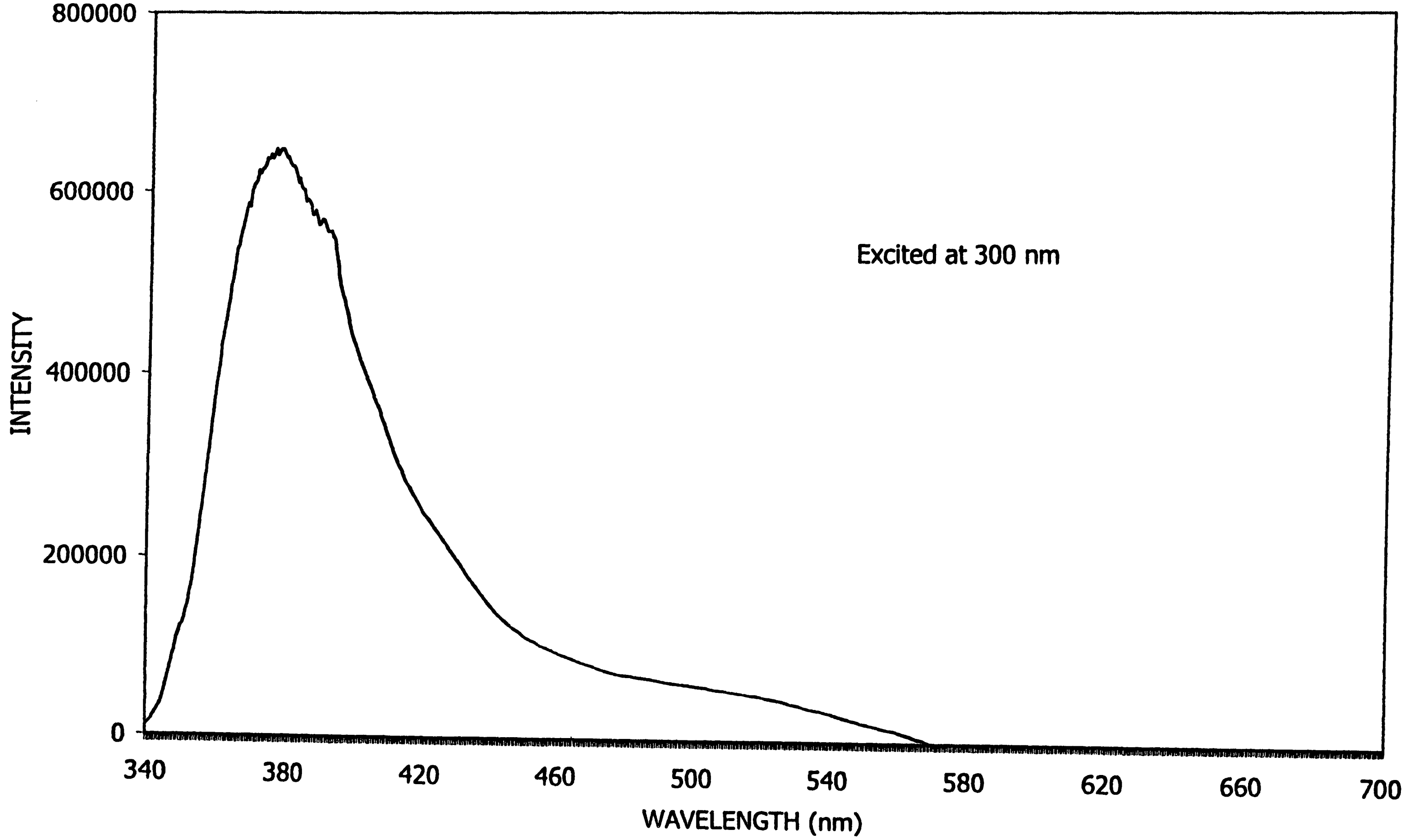


Figure 13 Emission Spectrum of $Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

Table 19. Crystal Data and Structure Refinement for
$Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

Empirical formula	$C_{84.25}H_{84.25}Cu_4I_4P_4$
Formula weight	1982.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, *I*-42d
Unit cell dimensions	a = 32.248(16) Å α = 90.0 deg.
	b = 32.248(16) Å β = 90.0 deg.
	c = 32.174(14) Å γ = 90.0 deg.
Volume	33459(28) $Å^3$
Z, Calculated density	8, 0.787 Mg/m^3
Absorption coefficient	1.298 mm^{-1}
F(000)	7822
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	1.79 to 30.07 deg.
Index ranges	$-1 \leq h \leq 45$, $-1 \leq k \leq 45$, $-45 \leq l \leq 1$
Reflections collected / unique/	27816 / 13990 [R(int) = 0.5427]
Goodness-of-fit	0.900
Final R indices [I>2sigma(I)]	R1 = 0.1210, wR2 = 0.1115
R indices (all data)	R1 = 0.4715, wR2 = 0.1903
Extinction coefficient	0.0000014(13)
Largest diff. peak and hole	0.572 and –0.566 $eÅ^{-3}$

Table 20. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

	x	y	z	U(eq)
I(1)	2664(1)	1179(1)	372(1)	67(1)
I(2)	3378(1)	161(1)	73(1)	68(1)
I(3)	2596(1)	94(1)	1155(1)	69(1)
I(4)	3677(1)	878(1)	1089(1)	68(1)
Cu(1)	2827(2)	917(2)	1162(2)	85(2)
Cu(2)	3417(2)	90(2)	924(1)	83(2)
Cu(3)	2592(2)	333(2)	334(2)	85(2)
Cu(4)	3502(2)	1002(2)	248(2)	73(2)
P(1)	2570(5)	1287(4)	1696(4)	73(4)
P(2)	3794(4)	-445(4)	1186(3)	65(4)
P(3)	2043(4)	63(4)	-39(4)	66(4)
P(4)	3907(4)	1405(4)	-150(3)	58(4)
C(111)	2020(2)	1358(15)	1687(17)	110(2)
C(112)	1783(17)	1462(16)	1335(15)	130(2)
C(113)	1325(17)	1563(16)	1430(3)	220(5)
C(114)	1160(3)	1450(2)	1660(3)	400(10)
C(115)	1300(2)	1328(12)	2025(15)	160(4)
C(116)	1798(11)	1278(18)	2036(19)	110(2)
C(117)	1097(15)	1304(14)	2367(12)	120(2)
C(121)	2703(12)	1844(14)	1755(9)	64(16)
C(122)	3130(2)	1897(10)	1729(11)	150(3)
C(123)	3405(14)	2282(19)	1760(18)	90(2)
C(124)	3140(14)	2560(3)	1836(15)	230(8)
C(125)	2760(2)	2596(12)	1822(13)	140(3)
C(126)	2543(16)	2205(12)	1798(12)	110(2)
C(127)	3892(12)	2303(13)	1786(14)	103(19)
C(131)	2685(11)	1107(17)	2238(13)	70(16)
C(132)	2757(14)	668(18)	2268(12)	94(19)
C(133)	2843(12)	478(17)	2663(14)	100(2)
C(134)	2882(17)	676(15)	3048(18)	120(2)
C(135)	2842(14)	1080(2)	2953(12)	110(2)
C(136)	2721(11)	1312(12)	2585(10)	52(13)
C(137)	2846(10)	-55(12)	2688(12)	95(19)
C(211)	3575(14)	-965(13)	1061(11)	67(16)
C(212)	3846(11)	-1290(13)	1012(8)	44(14)
C(213)	3726(12)	-1670(2)	929(17)	130(3)
C(124)	3330(2)	-1766(16)	884(13)	120(3)
C(215)	2998(14)	-1430(2)	928(13)	90(2)
C(216)	3141(11)	-1012(13)	996(13)	79(18)
C(217)	2503(13)	-1425(12)	881(12)	110(2)
C(221)	4289(15)	-509(13)	998(13)	71(15)

Table 20. (Continued)

C(222)	4663(13)	-523(15)	1210(2)	110(3)
C(223)	5040(2)	-559(14)	1090(2)	120(2)
C(224)	5070(2)	-581(170	640(2)	120(3)
C(225)	4773(19)	-540(2)	401(17)	130(3)
C(226)	4393(12)	-465(18)	550(15)	120(3)
C(227)	4794(16)	-531(14)	-68(13)	160(3)
C(231)	3840(3)	-850(5)	1970(6)	430(9)
C(232)	3886(17)	-190(3)	1878(18)	210(6)
C(233)	4045(19)	-39(14)	2380(3)	210(4)
C(234)	3965(18)	-340(2)	2560(2)	130(3)
C(235)	3820(14)	-782(14)	2410(3)	220(5)
C(236)	3740(3)	-800(3)	1945(19)	400(10)
C(237)	3830(2)	-1102(11)	2652(14)	270(5)
C(311)	2111(14)	-610(3)	-61(18)	130(3)
C(312)	1710(3)	-680(2)	-29(16)	240(6)
C(313)	1771(16)	-1160(5)	-93(19)	330(9)
C(314)	2130(2)	-1350(2)	-196(18)	180(4)
C(315)	2360(2)	-1143(16)	-300(12)	140(3)
C(316)	2440(16)	-679(17)	-190(16)	101(19)
C(317)	1420(2)	-1433(18)	-34(16)	170(3)
C(321)	2022(11)	223(16)	-575(14)	73(17)
C(322)	1940(3)	20(3)	-926(11)	240(6)
C(323)	1933(17)	159(19)	-1270(2)	130(3)
C(324)	1961(14)	553(19)	-1354(16)	140(3)
C(325)	1984(13)	-1074(19)	-1074(19)	87(19)
C(326)	2003(13)	740(2)	-645(15)	160(3)
C(327)	1987(13)	1243(18)	-1065(17)	170(3)
C(331)	1515(9)	205(9)	167(14)	56(15)
C(332)	1172(14)	232(11)	-87(11)	54(12)
C(333)	794(13)	294(12)	95(13)	60(14)
C(334)	738(13)	360(2)	497(17)	90(3)
C(335)	1030(2)	330(2)	720(3)	140(3)
C(336)	1439(18)	267(14)	631(15)	110(2)
C(337)	1088(13)	377(14)	1236(16)	120(2)
C(411)	4024(13)	1186(13)	-682(12)	59(14)
C(412)	4071(15)	1466(10)	-1048(13)	73(16)
C(413)	4166(15)	1220(2)	-1415(14)	120(2)
C(414)	4230(13)	848(14)	-1406(17)	120(2)
C(415)	4210(16)	574(16)	-1093(16)	140(3)
C(416)	4119(12)	789(16)	-730(13)	120(3)
C(417)	4261(17)	154(15)	-1146(12)	140(3)
C(421)	3678(13)	1953(12)	-264(12)	77(16)
C(422)	3936(9)	2329(14)	312(12)	70(16)
C(423)	3680(3)	2703(11)	-447(12)	-180(4)
C(424)	3390(4)	2640(3)	-500(3)	750(17)

Table 20. (Continued)

C(425)	3113(15)	2379(14)	-474(10)	71(17)
C(426)	3262(11)	1947(12)	-361(10)	66(15)
C(427)	2620(14)	2434(16)	-479(14)	170(3)
C(431)	4466(14)	1519(9)	44(12)	75(15)
C(432)	4466(12)	1636(10)	462(13)	60(14)
C(433)	4840(2)	1780(3)	620(2)	110(3)
C(434)	5230(5)	1600(3)	440(3)	570(16)
C(435)	5182(12)	1749(13)	120(3)	250(6)
C(436)	4830(2)	1566(18)	-180(12)	180(4)
C(437)	4918(15)	1828(19)	1104(15)	180(3)
H(11A)	1927	1437	1074	80
H(11B)	1177	1712	1214	80
H(11C)	882	1353	1628	80
H(11D)	1942	1181	2278	80
H(11F)	825	1378	2272	80
H(11G)	1098	1019	2456	80
H(11H)	1174	1479	2595	80
H(12A)	3321	1672	1671	80
H(12C)	3250	2834	1835	80
H(12D)	2583	2835	1830	80
H(12E)	2253	2187	1859	80
H(12F)	4013	2570	1834	80
H(12G)	3978	2115	2001	80
H(12H)	3981	2199	1521	80
H(13A)	2781	487	2032	80
H(13B)	2974	552	3303	80
H(13C)	2875	1264	3187	80
H(13E)	2672	1602	2540	80
H(13F)	2767	-157	2419	80
H(13G)	3130	-128	2742	80
H(13H)	2671	-177	2896	80
H(21A)	4141	-1273	1046	80
H(21B)	3918	-1898	920	80
H(21C)	3235	-2046	857	80
H(21D)	2954	-785	1047	80
H(21F)	2398	-1693	804	80
H(21G)	2427	-1366	1163	80
H(21H)	2388	-1218	701	80
H(22A)	4628	-468	1505	80
H(22B)	5266	-615	1277	80
H(22C)	5343	-636	528	80
H(22D)	4274	-433	350	80
H(22F)	5074	-565	-164	80
H(22G)	4627	-758	-167	80
H(22H)	4683	-275	-172	80

Table 20. (Continued)

H(23A)	3933	33	1685	80
H(23C)	4152	201	2523	80
H(23D)	3959	-322	2853	80
H(23B)	3687	-1056	1806	80
H(23G0	3867	-1042	2943	80
H(23H)	3563	-1217	2605	80
H(23I)	4041	-1298	2567	80
H(31A)	1453	-544	45	80
H(31C)	2140	-1640	-232	80
H(31B)	2612	-1299	-334	80
H(31D)	2654	-489	-272	80
H(31H)	1486	-1716	-92	80
H(31I)	1319	-1410	247	80
H(31J)	1203	-1343	-221	80
H(32A)	1906	-270	-878	80
H(32B)	1921	-18	-1510	80
H(32C)	1869	679	-1621	80
H(32D)	2024	933	-421	80
H(32F)	2059	1314	-793	80
H(32G)	2163	1372	-1268	80
H(32H)	1703	1311	-1123	80
H(33A)	1221	196	-379	80
H(33B)	575	326	-104	80
H(33C)	469	414	613	80
H(33D)	1677	239	809	80
H(33G)	812	431	1332	80
H(33H)	1190	127	1362	80
H(33I)	1265	604	1310	80
H(41A)	4018	1759	-1047	80
H(41B)	4205	1369	-1673	80
H(41C)	4287	709	-1663	80
H(41D)	3875	651	-630	80
H(41E)	4337	736	-535	80
H(41F)	4338	114	-1432	80
H(41G)	4473	44	-969	80
H(41H)	4004	14	-1092	80
H(42A)	4232	2312	-287	80
H(42B)	3823	2963	-448	80
H(42C)	3267	2892	-610	80
H(42D)	3092	1703	-375	80
H(42E)	2534	2714	-530	80
H(42F)	2557	2265	-717	80
H(42G)	2477	2327	-241	80
H(43A)	4225	1655	636	80
H(43B)	5510	1622	544	80

Table 20. (Continued)

H(43C)	5406	1817	-62	80
H(43D)	4821	1521	-474	80
H(43E)	5195	1885	1197	80
H(43F)	4737	2048	1192	80
H(43G)	4825	1571	1222	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 21. Bond Lengths [Å] and Angles [deg] for $Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

I(1)-Cu(1)	2.729(6)
I1-Cu3	2.743(7)
I1-Cu4	2.791(7)
I2-Cu3	2.725(7)
I2-Cu2	2.751(6)
I2-Cu4	2.802(7)
I3-Cu3	2.753(7)
I3-Cu2	2.750(7)
I3-Cu1	2.757(7)
I4-Cu2	2.729(7)
I4-Cu1	2.754(7)
I4-Cu4	2.793(6)
Cu1-P1	2.253(14)
Cu2-P2	2.272(13)
Cu3-P3	2.309(14)
Cu4-P4	2.244(12)
P1-C111	1.79(7)
P1-C121	1.85(4)
P1-C131	1.87(5)
P2-C221	1.72(4)
P2-C211	1.86(4)
P2-C231	2.58(19)
P3-C321	1.80(4)
P3-C331	1.89(4)
P3-C311	2.18(8)
P4-C411	1.89(4)
P4-C431	1.94(4)
P4-C421	1.95(4)
C111C116	1.35(6)
C111-C112	1.40(6)
C112-C113	1.54(7)
C113-C114	1.00(10)
C114-C115	1.30(11)
C115-C117	1.28(4)
C115-C116	1.63(8)
C121-C126	1.28(5)
C121-C122	1.40(7)
C122-C123	1.52(6)
C123-C124	1.26(11)
C123-C127	1.57(5)
C124-C125	1.23(7)
C125-C126	1.44(6)
C131-C136	1.30(4)

Table 21. (Continued)

C131-C132	1.44(6)
C132-C133	1.44(5)
C133-C134	1.40(7)
C133-C137	1.72(6)
C134-C135	1.35(6)
C135-C136	1.45(5)
C211-C212	1.37(5)
C211-C216	1.42(5)
C212-C213	1.31(6)
C213-C214	1.31(7)
C214-C215	1.53(6)
C215-C216	1.45(6)
C215-C217	1.60(5)
C221-C222	1.39(6)
C221-C226	1.49(5)
C222-C223	1.29(7)
C223-C224	1.47(7)
C224-C225	1.23(6)
C225-C226	1.34(6)
C225-C227	1.51(6)
C231-C236	0.8(2)
C231-C232	1.29(18)
C231-C235	1.54(19)
C232-C233	1.77(10)
C233-C234	1.16(7)
C234-C235	1.56(10)
C235-C237	1.30(5)
C235-C236	1.51(10)
C311-C316	1.16(6)
C311-C312	1.32(9)
C312-C313	1.57(16)
C313-C314	1.34(12)
C313-C317	1.46(10)
C314-C315	1.08(8)
C315-C316	1.56(6)
C321-C322	1.33(7)
C321-C326	1.68(7)
C322-C323	1.19(8)
C323-C324	1.30(7)
C324-C325	1.27(5)
C325-C327	1.36(6)
C325-C326	1.41(7)
C331-C332	1.38(4)
C331-C336	1.53(5)
C332-C333	1.37(4)

Table 21. (Continued)

C333-C334	1.32(6)
C334-C335	1.18(8)
C335-C336	1.36(7)
C335-C337	1.69(9)
C411-C416	1.32(5)
C411-C412	1.49(5)
C412-C413	1.45(5)
C413-C414	1.23(6)
C414-C415	1.34(6)
C415-C416	1.39(6)
C415-C417	1.38(5)
C421-C426	1.38(5)
C421-C422	1.48(5)
C422-C423	1.52(6)
C423-C424	0.97(16)
C424-C425	1.23(12)
C425-C426	1.52(5)
C425-C427	1.60(5)
C431-C432	1.40(5)
C431-C436	1.40(6)
C432-C433	1.40(7)
C433-C434	1.51(16)
C433-C437	1.57(7)
C434-C435	1.13(12)
C435-C436	1.60(8)
Cu1-I1-Cu3	75.5(2)
Cu1-I1-Cu4	83.24(18)
Cu3-I1-Cu4	82.6(2)
Cu3-I2-Cu2	75.68(19)
Cu3-I2-Cu4	82.73(18)
Cu2-I2-Cu4	82.73(18)
Cu3-I3-Cu2	75.25(18)
Cu3-I3-Cu1	74.85(18)
Cu2-I3-Cu1	75.28(19)
Cu2-I4-Cu1	75.7(2)
Cu2-I4-Cu4	83.30(17)
Cu1-I4-Cu4	82.77(19)
P1-Cu1-I1	118.3(4)
P1-Cu1-I4	117.1(4)
I1-Cu1-I4	97.3(2)
P1-Cu1-I3	114.6(4)
I1-Cu1-I3	103.9(2)
I4-Cu1-I3	103.0(2)
P2-Cu2-I4	118.1(4)

Table 21. (Continued)

P2-Cu2-I2	117.2(4)
I4-Cu2-I2	97.5(2)
P2-Cu2-I3	114.7(4)
I4-Cu2-I3	103.9(2)
I2-Cu2-I3	103.0(2)
P3-Cu3-I2	118.4(4)
P3-Cu3-I1	117.6(4)
I2-Cu3-I1	98.0(2)
P3-Cu3-I3	113.4(4)
I2-Cu3-I3	103.6(2)
I1-Cu3-I3	103.6(2)
P4-Cu4-I1	121.8(4)
P4-Cu4-I4	121.2(4)
I1-Cu4-I4	95.01(19)
P4-Cu4-I2	122.0(4)
I1-Cu4-I2	95.1(2)
I4-Cu4-I2	94.85(18)
C111-P1-C121	96(2)
C111-P1-C131	105(2)
C121-P1-C131	99(2)
C111-P1-Cu1	115(2)
C121-P1-Cu1	120.4(11)
C131-P1-Cu1	118.2(17)
C221-P2-C211	100(2)
C221-P2-Cu2	117.2(16)
C211-P2-Cu2	113.7(17)
C221-P2-C231	106(3)
C211-P2-C231	95(4)
Cu2-P2-C231	122(4)
C321-P3-C331	103.5(19)
C321-P3-C311	105(2)
C331-P3-C311	110.1(16)
C321-P3-Cu3	114.7(15)
C331-P3-Cu3	114.7(13)
C311-P3-Cu3	108.4(16)
C411-P4-C431	100.2(17)
C411-P4-C421	104.3(18)
C431-P4-C421	103.9(15)
C411-P4-Cu4	114.6(15)
C431-P4-Cu4	117.8(13)
C421-P4-Cu4	114.3(14)
C116-C111-C112	116(6)
C116-C111-P1	119(4)
C112-C111-P1	125(5)
C111-C112-C113	115(6)

Table 21. (Continued)

C114-C113-C112	125(8)
C113-C114-C115	128(10)
C117-C115-C114	129(8)
C117-C115-C116	118(7)
C114-C115-C116	112(5)
C111-C116-C115	119(5)
C126-C121-C122	107(4)
C126-C121-P1	143(4)
C122-C121-P1	110(3)
C121-C122-C123	132(5)
C124-C123-C122	102(5)
C124-C123-C127	130(6)
C122-C123-C127	128(5)
C123-C124-C125	138(9)
C124-C125-C126	113(7)
C121-C126-C125	127(5)
C136-C131-C132	115(5)
C136-C131-P1	131(4)
C132-C131-P1	114(3)
C133-C132-C131	121(5)
C134-C133-C132	127(5)
C134-C133-C137	114(3)
C132-C133-C137	118(5)
C135-C134-C133	104(5)
C134-C135-C136	135(5)
C131-C136-C135	118(4)
C212-C211-C216	122(4)
C212-C211-P2	118(3)
C216-C211-P2	120(4)
C213-C212-C211	123(4)
C214-C213-C212	122(5)
C213-C214-C215	120(5)
C216-C215-C214	117(4)
C216-C215-C217	108(5)
C214-C215-C217	135(5)
C211-C216-C215	116(4)
C222-C221-C226	107(4)
C222-C221-P2	129(4)
C226-C221-P2	123(4)
C223-C222-C221	132(7)
C222-C223-C224	112(7)
C225-C224-C223	124(7)
C224-C225-C226	121(6)
C224-C225-C227	126(6)
C226-C225-C227	113(5)

Table 21. (Continued)

C225-C226-C221	122(4)
C236-C231-C232	151(10)
C236-C231-C235	73(10)
C232-C231-C235	130(10)
C236-C231-P2	90(10)
C232-C231-P2	67(10)
C235-C231-P2	163(10)
C231-C232-C233	94(9)
C234-C233-C232	98(6)
C233-C234-C235	133(9)
C237-C235-C234	121(8)
C237-C235-C236	125(8)
C234-C235-C236	113(6)
C237-C235-C231	152(10)
C234-C235-C231	83(6)
C236-C235-C231	30(8)
C231-C236-C235	77(10)
C316-C311-C312	154(8)
C316-C311-P3	107(6)
C312-C311-P3	94(5)
C311-C312-C313	92(5)
C314-C313-C317	115(10)
C314-C313-C312	126(10)
C317C313-C312	119(8)
C315C314-C313	113(10)
C314-C315-C316	128(7)
C311-C316-C315	96(6)
C322-C321-C326	111(5)
C322-C321-P3	133(5)
C326-C321-P3	114(4)
C323-C322-C321	128(9)
C322-C323-C324	124(7)
C325-C324-C323	121(6)
C324-C325-C327	134(7)
C324-C325-C326	125(6)
C327-C325-C326	100(6)
C325-C326-C321	109(5)
C332-C331-C336	116(4)
C332-C331-P3	122(4)
C336-C331-P3	121(3)
C331-C332-C333	118(4)
C334-C333-C332	124(4)
C335-C334-C333	118(6)
C334-C335-C336	131(8)
C334-C335-C337	132(6)

Table 21. (Continued)

C336-C335-C337	96(6)
C335-C336-C331	112(5)
C416-C411-C412	118(4)
C416-C411-P4	121(4)
C412-C411-P4	121(3)
C413-C412-C411	110(3)
C414-C413-C412	123(5)
C413-C414-C415	131(5)
C416-C415-C414	108(5)
C416-C415-C417	129(5)
C414-C415-C417	123(5)
C411-C416-C415	129(5)
C426-C421-C422	122(4)
C426-C421-P4	113(3)
C422-C421-P4	123(3)
C421-C422-C423	112(4)
C424-C423-C422	115(8)
C423-C424-C425	145(10)
C424-C425-C426	115(7)
C424-C425-C427	130(7)
C426-C425-C427	115(4)
C421-C426-C425	110(4)
C432-C431-C436	118(4)
C432-C431-P4	111(3)
C436-C431-P4	130(4)
C433-C432-C431	117(5)
C432-C433-C434	117(8)
C432-C433-C437	122(6)
C434-C433-C437	108(6)
C435-C434-C433	94(10)
C434-C435-C436	119(8)
C431-C436-C435	109(4)

Table 22. Anisotropic Displacement Parameters (A^2 x 10^3) for
$Cu_4I_4(P(m\text{-}C_7H_7)_3)_4$

	U11	U22	U33	U23	U13	U12
I(1)	66(1)	67(1)	38(1)	11(1)	6(1)	17(1)
I(1)	71(2)	62(2)	70(2)	-3(2)	-9(2)	3(2)
I(2)	75(2)	67(2)	61(2)	-11(2)	2((2)	10(2)
I(3)	74(2)	69(2)	65(2)	-6(2)	-(2)	7(2)
I(4)	75(2)	69(2)	61(2)	-6(2)	-7(2)	-1(2)
Cu(1)	103(5)	71(4)	81(4)	-6(4)	7(4)	15(4)
Cu(2)	92(5)	78(5)	78(4)	2(4)	-5(4)	9(4)
Cu(3)	78(5)	91(5)	86(5)	-4(4)	-9(4)	-5(4)
Cu(4)	83(5)	69(4)	68(4)	-1(3)	-7(3)	3(4)
P(1)	81(11)	67(10)	73(9)	-7(8)	-24(8)	12(9)
P(2)	65(9)	81(10)	50(7)	-15(7)	-6(7)	2(8)
P(3)	58(9)	74(10)	66(8)	7(8)	6(7)	-1(8)
P(4)	63(9)	57(8)	53(7)	-23(7)	-1(7)	10(7)
C(111)	210(8)	40(3)	90(4)	50(3)	20(5)	20(4)
C(112)	160(6)	150(6)	70(4)	-70(4)	-20(4)	80(5)
C(113)	90(4)	90(5)	480(14)	20(7)	-200(7)	50(4)
C(114)	560(18)	160(8)	470(13)	-160(8)	420(13)	350(11)
C(115)	370(10)	0(2)	100(4)	40(2)	210(5)	50(4)
C(116)	0(2)	170(6)	150(5)	0(5)	10(3)	10(3)
C(117)	190(6)	100(5)	80(3)	20(3)	10(4)	-80(5)
C(121)	80(3)	100(4)	12(19)	-40(2)	80(2)	-50(3)
C(122)	400(10)	0(19)	40(2)	-16(2)	60(4)	-150(4)
C(123)	50(4)	130(5)	100(4)	60(4)	30(4)	-50(4)
C(124)	50(4)	600(2)	40(3)	120(8)	-40(3)	-220(8)
C(125)	350(10)	0(2)	80(4)	-20(3)	-110(5)	-10(4)
C(126)	180(5)	50(3)	90(3)	-10(3)	160(4)	30(4)
C(127)	60(4)	110(5)	130(4)	-10(4)	-40(3)	-20(4)
C(131)	0(2)	130(5)	80(3)	-10(4)	0(2)	-40(3)
C(132)	100(4)	150(5)	30(3)	40(3)	30(3)	0(4)
C(133)	40(3)	190(6)	90(3)	140(3)	40(4)	-70(3)
C(134)	130(5)	100(4)	130(5)	60(4)	-20(4)	100(4)
C(135)	50(3)	250(7)	20(2)	-10(4)	-10(2)	30(4)
C(136)	60(3)	60(3)	40(2)	-60(2)	-10(2)	-10(2)
C(137)	20(3)	130(4)	130(4)	110(4)	-20(3)	-20(3)
C(211)	90(4)	90(4)	30(2)	-50(2)	60(2)	-30(3)
C(212)	30(2)	90(3)	8(16)	-20(2)	38(17)	-70(3)
C(213)	0(2)	170(7)	210(6)	80(5)	-70(3)	20(3)
C(214)	210(8)	70(4)	70(4)	-60(3)	0(5)	60(5)
C(215)	40(3)	180(6)	50(3)	80(4)	-20(2)	-80(4)
C(216)	10(2)	80(4)	150(4)	80(3)	50(3)	20(2)
C(217)	70(4)	70(3)	190(5)	-60(4)	50(4)	-10(3)

Table 22. (Continued)

C(121)	70(4)	70(3)	70(3)	-20(3)	30(3)	50(3)
C(222)	10(2)	110(5)	220(7)	-80(5)	70(4)	-60(3)
C(223)	160(7)	10(3)	200(7)	-20(4)	-60(7)	-20(4)
C(224)	70(5)	80(4)	230(8)	-70(5)	0(6)	-20(4)
C(225)	70(4)	240(8)	80(4)	120(5)	20(4)	40(5)
C(226)	0(2)	260(8)	100(4)	10(5)	0(3)	-50(4)
C(227)	190(8)	120(5)	160(5)	-20(4)	150(5)	-4(5)
C(231)	80(6)	300(2)	900(3)	200(2)	200(11)	-40(10)
C(232)	40(4)	490(14)	110(5)	300(8)	40(3)	30(6)
C(233)	120(5)	0(2)	500(13)	40(5)	-30(7)	-10(3)
C(234)	110(5)	160(7)	130(6)	10(6)	0(5)	-40(5)
C(235)	20(3)	50(3)	590(12)	260(5)	0(5)	-10(2)
C(236)	420(15)	620(19)	150(6)	-350(10)	-250(8)	420(14)
C(237)	610(14)	0(3)	200(6)	-60(4)	-170(8)	80(6)
C(311)	10(3)	250(9)	120(5)	-80(5)	30(3)	0(4)
C(312)	400(13)	280(9)	50(4)	-20(5)	-150(6)	310(10)
C(313)	0(3)	900(3)	50(4)	70(9)	30(3)	30(8)
C(314)	200(7)	250(10)	90(5)	70(5)	40(4)	-170(7)
C(315)	320(9)	90(4)	20(3)	-40(3)	-70(4)	190(5)
C(316)	60(40	120(5)	120(5)	10(4)	10(4)	-20(4)
C(317)	270(9)	170(7)	80(4)	-30(4)	10(6)	20(8)
C(321)	0(2)	130(5)	90(3)	50(3)	30(2)	-40(3)
C(322)	480(14)	230(9)	0(2)	50(4)	40(5)	0(9)
C(323)	90(5)	110(5)	200(7)	-80(6)	100(5)	-20(4)
C(324)	100(4)	170(6)	160(5)	-100(5)	-160(4)	0(4)
C(325)	20(3)	120(5)	120(5)	-30(4)	-20(3)	-60(3)
C(326)	30(3)	360(11)	70(4)	-40(6)	90(3)	-60(5)
C(327)	60(4)	320(9)	130(5)	10(6)	10(4)	-170(5)
C(331)	5(19)	0(18)	160(4)	50(2)	-60(2)	-42(16)
C(332)	70(3)	40(3)	40(2)	10(2)	10(3)	0(3)
C(333)	40(3)	90(4)	60(3)	-50(3)	10(3)	-10(3)
C(334)	0(2)	190(7)	90(5)	-40(5)	-10(3)	-20(4)
C(335)	80(5)	140(6)	190(9)	-10(6)	70(6)	-50(6)
C(336)	150(6)	90(4)	90(4)	20(3)	-120(4)	50(4)
C(337)	70(4)	90(5)	200(6)	-30(5)	60(5)	-20(3)
C(411)	70(3)	40(3)	70(3)	-50(2)	-60(3)	30(3)
C(412)	170(5)	0(19)	50(3)	10(2)	0(3)	-10(3)
C(413)	80(4)	270(7)	20(3)	40(4)	30(3)	60(5)
C(414)	60(3)	50(3)	250(6)	-150(4)	-20(4)	60(3)
C(415)	260(7)	30(4)	110(4)	50(4)	-80(5)	-20(5)
C(416)	0(2)	240(7)	130(4)	-150(5)	30(2)	-30(3)
C(417)	200(7)	150(6)	60(3)	-40(4)	-80(4)	-60(6)
C(421)	70(3)	60(3)	100(3)	-90(3)	-30(3)	-20(3)
C(422)	0(18)	110(4)	100(3)	50(3)	-30(2)	-70(2)
C(423)	520(13)	0(2)	30(3)	20(2)	50(5)	10(5)

Table 22. (Continued)

C(424)	1100(4)	800(2)	400(14)	-450(16)	-230(18)	-400(2)
C(425)	120(4)	70(3)	17(19)	-10(2)	-50(2)	100(3)
C(426)	50(3)	90(3)	60(3)	-70(2)	-70(2)	-30(3)
C(427)	130(5)	200(6)	160(5)	140(5)	-30(4)	90(5)
C(431)	150(4)	0(18)	70(3)	-32(19)	-30(3)	-80(2)
C(432)	60(3)	20(2)	100(3)	-60(2)	-60(3)	0(2)
C(433)	130(5)	120(7)	100(5)	20(5)	-100(4)	20(5)
C(434)	1200(5)	50(10)	440(16)	50(10)	-400(2)	-100(2)
C(435)	0(2)	20(3)	730(18)	220(6)	50(5)	20(2)
C(436)	300(8)	220(7)	30(3)	10(4)	140(4)	-130(7)
C(437)	90(5)	260(9)	200(6)	90(7)	-40(6)	-20(5)

The anisotropic displacement factor exponent takes the form:
$-2 \text{ pi}^2 [h^2 a^{*2} U_{11} + .. + 2 h k a^* b^* U_{12}]$

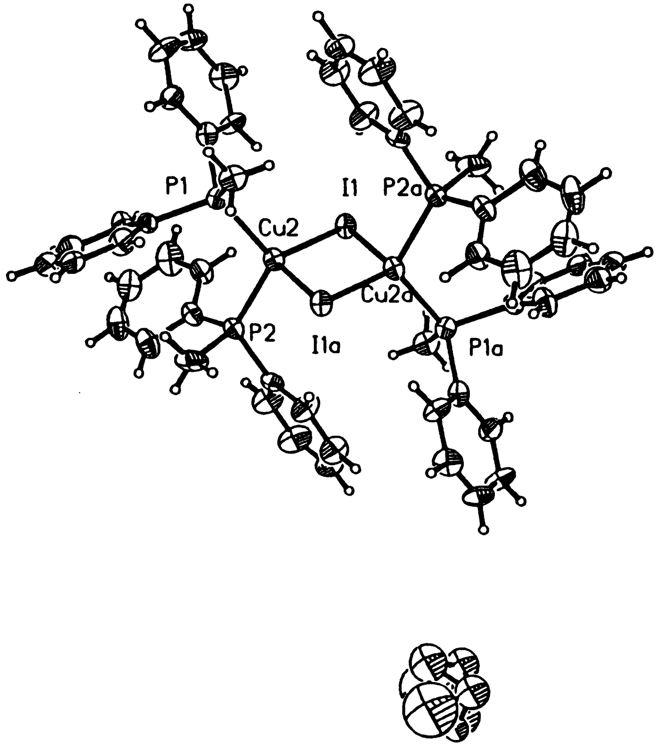


Figure 14 Projection View of $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

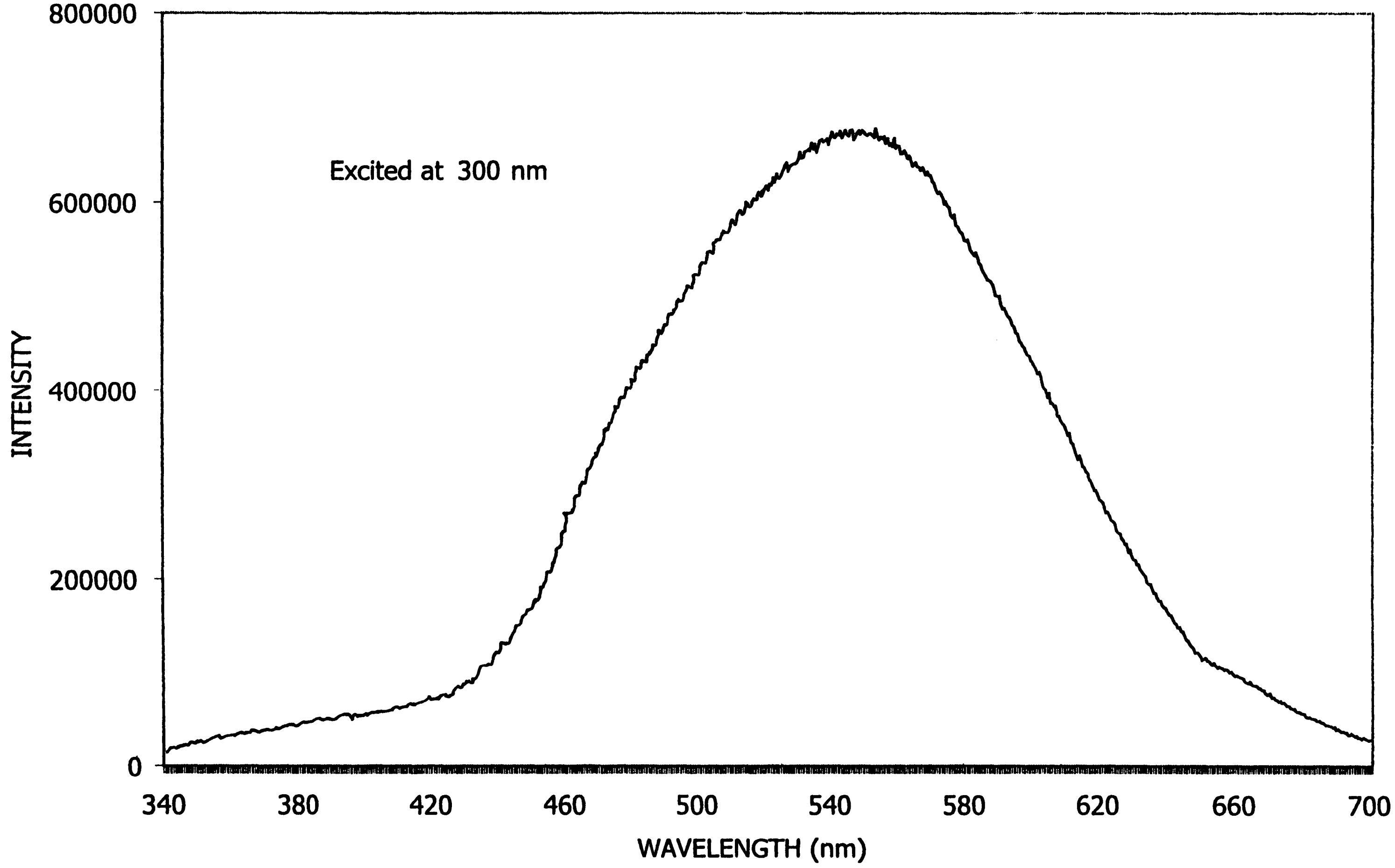


Figure 15 Emission Spectrum of $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

Table 23. Crystal Data and Structure Refinement for $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

Empirical formula	$C_{13}H_{13}CuIO_{0.11}P$
Formula weight	392.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C*2/c
Unit cell dimensions	a = 27.66(5) Å α = 90.0 deg.
	b = 13.08(2) Å β = 125.06(13) deg.
	c = 19.73(4) Å γ = 90.0 deg.
Volume	5844(17) Å^3
Z, Calculated density	18, 2.007 Mg/m^3
Absorption coefficient	4.152 mm^{-1}
F(000)	3400
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	1.80 to 30.11 deg.
Index ranges	$-1 \leq h \leq 38$, $-18 \leq k \leq 1$, $-27 \leq l \leq 23$
Reflections collected / unique/	9708 / 8499 [R(int) = 0.1878]
Goodness-of-fit	1.065
Final R indices [I>2sigma(I)]	R1 = 0.1433, wR2 = 0.3244
R indices (all data)	R1 = 0.2941, wR2 = 0.4237
Extinction coefficient	0.00000(15)
Largest diff. peak and hole	4.051 and –1.850 eÅ^{-3}

Table 24. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

	x	y	z	U(eq)
I(1)	3187(1)	8002(1)	1302(1)	51(1)
Cu(2)	2867(1)	6478(2)	199(1)	49(1)
P(2)	2590(2)	5077(3)	610(3)	47(1)
P(1)	3468(2)	6107(4)	-228(2)	48(1)
C(111)	3534(8)	4696(13)	-321(12)	52(4)
C(112)	3882(12)	4148(16)	438(15)	79(7)
C(113)	3911(12)	3021(19)	390(18)	85(7)
C(114)	3601(14)	2580(2)	-410(2)	105(10)
C(115)	3254(11)	3150(2)	-1130(2)	98(9)
C(116)	3231(9)	4178(18)	-1058(13)	76(7)
C(121)	3194(9)	6633(17)	-1269(11)	66(5)
C(131)	4258(8)	6479(14)	377(9)	52(4)
C(132)	4625(8)	6256(16)	116(12)	66(5)
C(133)	5221(8)	6550(2)	570(11)	75(6)
C(134)	5483(8)	7048(18)	1367(11)	72(6)
C(135)	5126(8)	7251(17)	1613(9)	71(6)
C(136)	4516(7)	6980(16)	1144(9)	59(5)
C(211)	2030(8)	5226(13)	832(9)	48(4)
C(212)	1497(9)	5610(19)	266(11)	76(7)
C(213)	1039(11)	5703(19)	379(14)	84(7)
C(214)	1149(10)	5396(18)	1140(13)	75(6)
C(215)	1701(11)	4970(2)	1720(14)	97(8)
C(216)	2131(10)	4880(2)	1589(12)	84(7)
C(221)	3194(9)	4376(13)	1516(11)	57(5)
C(222)	3720(8)	4899(16)	2094(11)	66(5)
C(223)	4204(12)	4380(2)	2780(12)	92(8)
C(224)	4190(11)	3350(2)	2880(12)	80(7)
C(225)	3715(13)	2826(19)	2324(15)	93(8)
C(226)	3164(12)	3273(17)	1606(15)	85(7)
C(231)	2226(10)	4140(19)	-254(14)	90(8)
C(1)	300(4)	5210(8)	8050(5)	190(5)
C(2)	550(3)	4420(6)	7810(6)	100(4)
C(3)	310(9)	4150(19)	8300(11)	510(15)
C(4)	-280(4)	4600(6)	7900(6)	240(6)
H(11A)	4089	4451	979	80
H(11B)	4141	2639	896	80
H(11C)	3653	1862	-423	80
H(11D)	3021	2802	-1649	80
H(11E)	2977	4535	-1572	80
H(12A)	3451	6481	-1437	80
H(12B)	2815	6327	-1652	80

Table 24. (Continued)

H(12C)	3150	7360	-1263	80
H(13A)	4463	5845	-372	80
H(13B)	5446	6403	351	80
H(13F)	5282	7611	2123	80
H(13D)	4274	7161	1329	80
H(21A)	1413	5834	-255	80
H(21B)	657	5947	-62	80
H(21C)	859	5490	1256	80
H(21D)	1775	4737	2233	80
H(21E)	2509	4603	2012	80
H(22A)	3740	5628	2060	80
H(22B)	4561	4752	3162	80
H(22C)	4519	2996	3344	80
H(22D)	3701	2103	2396	80
H(22E)	2822	2875	1217	80
H(23A)	2110	3556	-83	80
H(23B)	1883	4439	-736	80
H(23C)	2498	3930	-381	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 25. Bond Lengths [Å] and Angles [deg] for $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

I1-Cu2	2.698(4)
I1-Cu2	2.795(7)
Cu2-P2	2.305(5)
Cu2-P1	2.307(5)
Cu2-I1	2.795(7)
P2-C221	1.84(2)
P2-C211	1.844(16)
P2-C231	1.857(18)
P1-C131	1.855(19)
P1-C121	1.867(18)
P1-C111	1.873(18)
C111-C116	1.37(2)
C111-C112	1.42(3)
C112-C113	1.48(3)
C113-C114	1.41(4)
C114-C115	1.38(4)
C115-C116	1.36(3)
C131-C132	1.41(2)
C131-C136	1.41(2)
C132-C133	1.40(2)
C133-C134	1.45(3)
C134-C135	1.35(3)
C135-C136	1.43(2)
C211-C212	1.34(2)
C211-C216	1.42(2)
C212-C213	1.41(3)
C213-C214	1.41(3)
C214-C215	1.39(3)
C215-C216	1.36(3)
C221-C222	1.41(3)
C221-C226	1.46(3)
C222-C223	1.41(3)
C223-C224	1.37(3)
C224-C225	1.32(3)
C225-C226	1.48(3)
C4C2	1.18(10)
C4-C3	1.47(19)
C4-C1	1.64(11)
C4-C1	2.02(12)
C3-C1	1.5(2)
C3-C2	1.48(19)
C3-C2	2.1(2)
C2-C4	1.18(10)

Table 25. (Continued)

C2-C1	1.47(10)
C2-C3	2.1(2)
C1-C1	1.83(15)
C1-C4	2.02(12)
Cu2-I1-Cu2	70.45(15)
P2-Cu2-P1	114.6(2)
P2-Cu2-I1	108.98(18)
P1-Cu2-I1	118.60(18)
P2-Cu2-I1	102.23(18)
P1-Cu2-I1	101.2(2)
I1-Cu2-I1	109.55(15)
C221-P2-C211	103.9(7)
C221-P2-C231	105.8(11)
C211-P2-C231	101.7(8)
C221-P2-Cu2	115.9(6)
C211-P2-Cu2	119.5(6)
C231-P2-Cu2	108.4(8)
C131-P1-C121	101.2(8)
C131-P1-C111	100.1(8)
C121-P1-C111	104.8(9)
C131-P1-Cu2	122.7(5)
C121-P1-Cu2	113.8(7)
C111-P1-Cu2	112.0(5)
C116-C111-C112	119.9(19)
C116-C111-P1	123.9(17)
C112-C111-P1	115.9(14)
C111-C112-C113	118(2)
C114-C113-C112	117(3)
C115-C114-C113	123(3)
C116-C115-C114	118(3)
C115-C116-C111	124(3)
C132-C131-C136	117.5(16)
C132 C131-P1	122.8(13)
C136-C131-P1	119.7(12)
C133-C132-C131	122.6(17)
C132-C133-C134	119.0(16)
C135-C134-C133	117.6(16)
C134-C135-C136	123.6(15)
C131-C136-C135	119.5(15)
C212-C211-C216	116.8(16)
C212-C211P2	121.1(12)
C216 -C211-P2	122.0(15)
C211-C212-C213	124.1(17)
C212-C213-C214	119(2)

Table 25. (Continued)

C215-C214-C213	116.9(19)
C216-C215-C214	123(2)
C215-C216-C211	121(2)
C222-C221-C226	119(2)
C222-C221-P2	118.9(14)
C226-C221-P2	121.7(16)
C221-C222-C223	121(2)
C224-C223-C222	121(2)
C225-C224-C223	119(2)
C224-C225-C226	125(2)
C221-C226-C225	114(2)
C2-C4-C3	107(10)
C2-C4-C1	101(7)
C3-C4-C1	56(9)
C2-C4-C1	46(5)
C3-C4-C1	95(10)
C1-C4-C1	59(6)
C4-C3-C1	68(10)
C4-C3-C2	109(10)
C1-C3-C2	60(10)
C4-C3-C2	32(6)
C1-C3-C2	72(10)
C2-C3-C2	86(10)
C4-C2-C1	98(8)
C4-C2-C3	128(10)
C1-C2-C3	60(9)
C4-C2-C3	41(6)
C1-C2-C3	90(8)
C3-C2-C3	89(9)
C3-C1-C2	60(8)
C3-C1-C4	56(8)
C2-C1-C4	101(7)
C3-C1-C1	103(8)
C2-C1-C1	83(6)
C4-C1-C1	71(6)
C3-C1-C4	85(8)
C2-C1-C4	35(4)
C4-C1-C4	98(6)
C1-C1-C4	50(5)

Table 26. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(C_6H_5)_2CH_3)_4.C_4H_8O$

	U11	U22	U33	U23	U13	U12
I(1)	58 (1)	55(1)	30(1)	-3(1)	18(1)	6(1)
Cu(2)	63(1)	47(1)	39(1)	2(1)	31(1)	1(1)
P(2)	61(3)	42(2)	44(2)	-1(2)	33(2)	-3(2)
P(1)	54(3)	55(3)	35(2)	-2(2)	27(2)	3(2)
C(111)	68(12)	40(10)	71(11)	0(8)	53(10)	-2(9)
C(112)	130(2)	54(13)	87(15)	2(11)	78(16)	5(13)
C(113)	99(18)	76(16)	107(19)	-4(15)	75(17)	-6(14)
C(114)	110(2)	78(18)	180(3)	-30(2)	110(2)	-19(18)
C(115)	62(15)	77(19)	160(3)	-41(19)	69(19)	-18(13)
C(116)	67(13)	92(17)	64(12)	-51(12)	34(11)	-20(12)
C(121)	70(12)	87(15)	45(9)	6(9)	34(9)	0(11)
C(131)	66(11)	55(11)	33(7)	0(7)	28(8)	8(9)
C(132)	51(11)	74(14)	67(12)	-19(10)	31(10)	-3(10)
C(133)	38(9)	140(2)	50(10)	1(12)	25(8)	6(12)
C(134)	43(10)	113(18)	48(9)	-11(11)	20(8)	-21(11)
C(135)	68(12)	95(17)	23(7)	-23(8)	10(8)	-17(11)
C(136)	40(8)	101(15)	38(8)	-13(9)	22(7)	-3(10)
C(211)	56(10)	51(10)	40(8)	-7(7)	30(8)	-18(8)
C(212)	60(12)	117(19)	47(10)	35(11)	30(10)	31(13)
C(213)	77(15)	105(19)	62(12)	24(12)	34(12)	16(14)
C(214)	84(16)	97(17)	72(13)	8(12)	61(13)	-2(13)
C(215)	83(17)	160(3)	60(13)	-7(16)	48(14)	-8(17)
C(216)	85(15)	140(2)	41(9)	-1(12)	44(11)	3(15)
C(221)	99(15)	42(10)	57(10)	-5(8)	61(11)	-8(10)
C(222)	55(11)	54(11)	51(10)	3(9)	8(9)	2(10)
C(223)	108(19)	97(19)	34(9)	1(11)	19(11)	18(16)
C(224)	99(17)	89(18)	41(10)	10(11)	33(11)	26(15)
C(225)	140(2)	62(15)	72(15)	30(12)	59(17)	37(15)
C(226)	140(2)	57(14)	82(15)	-11(11)	73(17)	-5(14)
C(231)	86(15)	120(2)	82(15)	-63(15)	59(14)	-59(14)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2a*^2 U_{11} +.. + 2 h k a* b* U_{12}]$

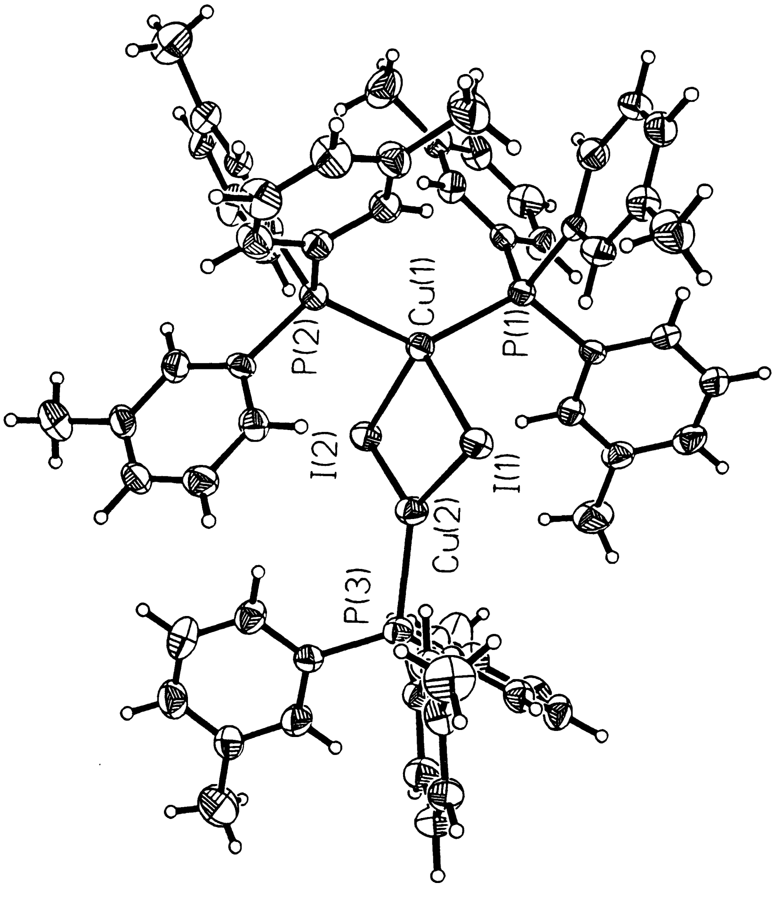


Figure 16 Projection View of $Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

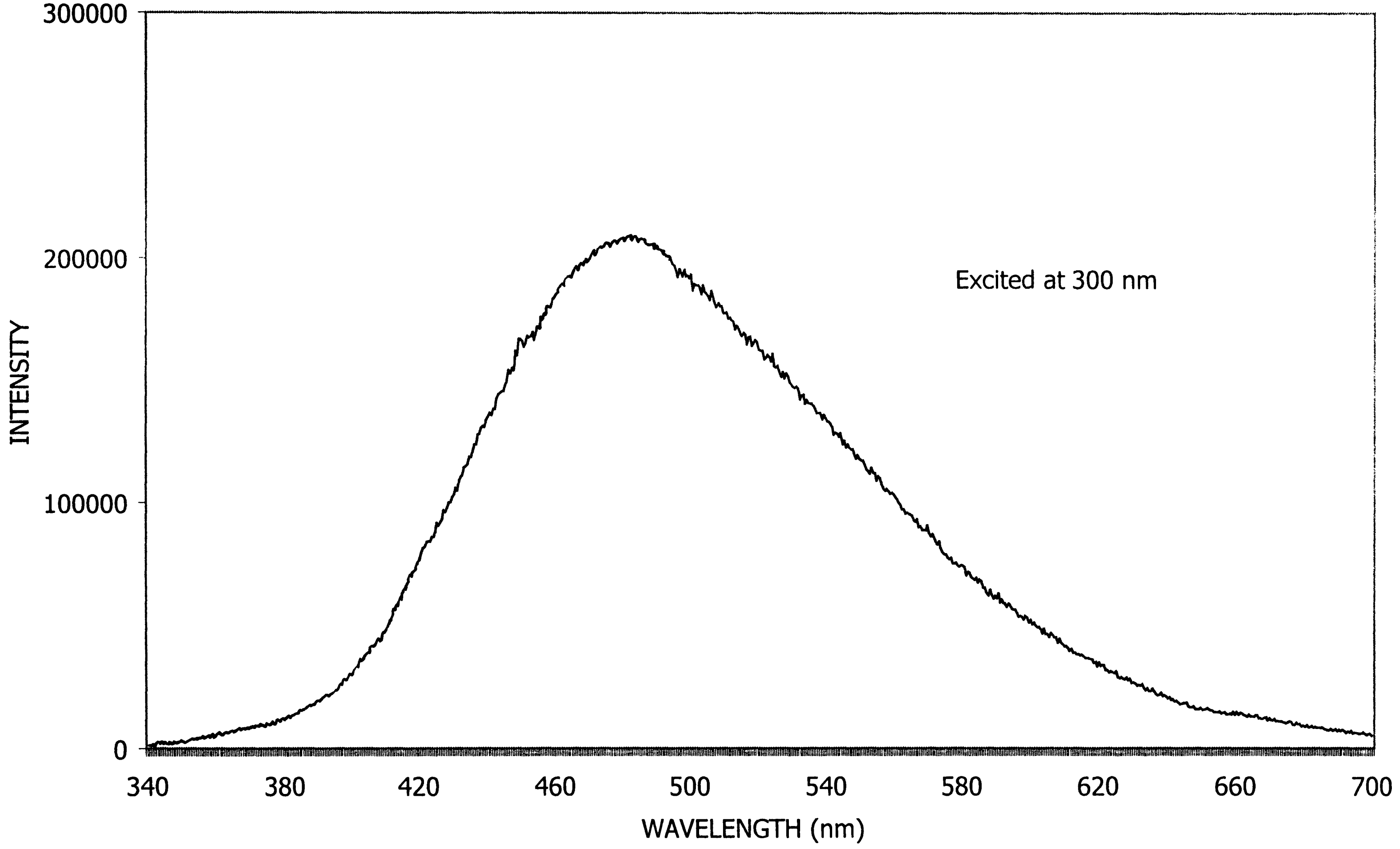


Figure 17 Emission Spectrum of $Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

Table 27. Crystal Data and Structure Refinement for
$Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

Empirical formula	$C_{63}H_{63}Cu_2I_2P_3$
Formula weight	1293.9
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 11.892(9) Å α = 86.15(4) deg. b = 13.893(12) Å β = 86.49(12) deg. c = 19.586(16) Å γ = 72.65(5) deg.
Volume	3082(4) $Å^3$
Z, Calculated density	2, 1.394 Mg/m^3
Absorption coefficient	1.805 mm^{-1}
F(000)	1300
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	2.14 to 29.98 deg.
Index ranges	$-1 \leq h \leq 16$, $-18 \leq k \leq 19$, $-27 \leq l \leq 27$
Reflections collected / unique/ observed	20424 / 18008 [R(int) = 0.0418]/ 6435(4.0>σ(F))
Goodness-of-fit	1.19
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.0641
R indices (all data)	R1 = 0.1693, wR2 = 0.0929
Extinction coefficient	-0.00012(3)
Largest diff. peak and hole	0.86 and –0.60 $eÅ^{-3}$

Table 28. Atomic Coordinates (x10^4) and Equivalent Iisotropic Displacement Parameters (Å^{2}x 10^3) for $Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

	x	y	z	U(eq)
I(1)	2755(1)	8786(1)	3424(1)	57(1)
I(2)	5430(1)	9269(1)	1869(1)	57(1)
Cu(1)	3152(1)	10197(1)	2407(1)	51(1)
Cu(2)	4771(1)	8088(1)	2783(1)	59(1)
P(2)	2048(2)	10138(2)	1486(1)	47(1)
P(1)	3180(2)	11531(2)	3041(1)	45(1)
P(3)	6108(2)	6546(2)	2964(1)	51(1)
C(111)	3597(8)	12548(6)	2523(4)	49(4)
C(112)	4451(9)	12981(7)	2719(5)	62(4)
C(113)	4690(9)	13781(8)	2316(6)	74(5)
C(114)	4072(10)	14164(8)	1728(5)	67(5)
C(115)	3206(10)	13764(7)	1520(5)	62(4)
C(116)	2993(9)	12951(7)	1928(4)	56(4)
C(117)	2532(12)	14187(9)	882(5)	103(7)
C(121)	4205(8)	11244(6)	3751(4)	45(3)
C(122)	3945(9)	11722(7)	4382(4)	59(4)
C(123)	4797(10)	11490(7)	4879(5)	67(5)
C(124)	5924(10)	10828(7)	4750(5)	71(5)
C(125)	6201(9)	10341(7)	4125(5)	66(4)
C(126)	5333(8)	10562(7)	3635(4)	54(4)
C(127)	7418(9)	9577(9)	3987(6)	94(6)
C(131)	1758(8)	12227(6)	3472(4)	46(3)
C(132)	1243(9)	13306(7)	3404(5)	62(4)
C(133)	180(9)	13776(8)	3759(5)	70(4)
C(134)	-384(9)	13203(8)	4181(5)	66(4)
C(135)	82(9)	12152(8)	4267(5)	61(4)
C(136)	1150(8)	11679(7)	3901(5)	57(4)
C(137)	-551(10)	11529(9)	4724(6)	91(6)
C(211)	443(8)	10329(7)	1670(4)	51(4)
C(212)	-237(9)	9870(7)	1311(5)	68(5)
C(213)	-1428(9)	10047(8)	1488(6)	81(5)
C(214)	-1995(9)	10713(8)	2004(6)	77(5)
C(215)	-1345(9)	11207(8)	2345(5)	64(4)
C(216)	-112(8)	10986(7)	2191(5)	58(4)
C(217)	-1971(10)	11952(9)	2885(6)	103(6)
C(221)	2526(7)	8897(6)	1087(5)	48(3)
C(222)	2475(9)	8043(7)	1511(5)	62(4)
C(223)	2815(9)	7075(7)	1252(6)	70(5)
C(224)	3254(9)	6966(8)	573(6)	67(4)
C(225)	3321(9)	7772(8)	137(5)	67(4)
C(226)	2960(9)	8745(8)	401(5)	64(4)

Table 28. (Continued)

C(227)	3819(12)	7640(9)	-600(6)	109(7)
C(231)	2106(8)	11032(6)	750(4)	50(4)
C(232)	1083(8)	11586(7)	385(5)	55(4)
C(233)	1182(10)	12233(8)	-186(5)	67(5)
C(234)	2290(11)	12302(8)	-416(5)	72(5)
C(235)	3301(11)	11765(9)	-72(5)	78(5)
C(236)	3206(9)	11160(8)	513(5)	64(4)
C(237)	81(11)	12846(10)	-573(6)	105(7)
C(311)	6711(8)	5862(7)	2175(5)	54(4)
C(312)	6010(9)	6078(8)	1602(5)	68(4)
C(313)	6398(11)	5536(10)	1013(5)	84(6)
C(314)	7469(12)	4789(9)	983(5)	79(5)
C(315)	8199(10)	4551(8)	1551(5)	72(5)
C(316)	7798(9)	5118(8)	2144(5)	71(4)
C(317)	9395(12)	3753(10)	1519(7)	141(8)
C(321)	5631(8)	5585(7)	3511(5)	54(4)
C(322)	6419(9)	4646(8)	3743(5)	70(4)
C(323)	5980(10)	3956(7)	4127(5)	70(5)
C(324)	4775(10)	4160(7)	4294(5)	66(5)
C(325)	3987(9)	5062(8)	4063(5)	63(4)
C(326)	4407(8)	5784(7)	3674(4)	53(4)
C(327)	2650(10)	5290(10)	4208(7)	103(6)
C(331)	7433(8)	6635(7)	3364(4)	51(4)
C(332)	8238(9)	7006(8)	2961(5)	71(5)
C(333)	9239(9)	7147(9)	3239(6)	72(5)
C(334)	9410(9)	6939(8)	3938(6)	75(5)
C(335)	8602(9)	6583(8)	4349(5)	69(5)
C(336)	7608(9)	6434(7)	4072(5)	61(4)
C(337)	10107(12)	7560(13)	2799(7)	147(10)
H(11A)	4874	12718	3126	80
H(11B)	5279	14069	2446	80
H(11C)	4234	14715	1459	80
H(11D)	2426	12646	1784	80
H(11E)	2784	14739	676	80
H(11F)	2674	13664	563	80
H(11G)	1705	14420	1005	80
H(12A)	3187	12204	4464	80
H(12B)	4605	11782	5318	80
H(12C)	6517	10707	5083	80
H(12D)	5525	10243	3206	80
H(12E)	7445	9323	3541	80
H(12F)	8024	9900	4008	80
H(12G)	7541	9027	4326	80
H(13A)	1649	13696	3118	80

Table 28. (Continued)

H(13B)	-156	14496	3712	80
H(13C)	-1121	13524	4414	80
H(13D)	1477	10959	3952	80
H(13E)	-1256	11962	4933	80
H(13F)	-752	11057	4455	80
H(13G)	-34	11168	5074	80
H(21A)	130	9433	950	80
H(21B)	-1883	9718	1251	80
H(21C)	-2820	10829	2117	80
H(21D)	355	11286	2442	80
H(21E)	-2793	11996	2919	80
H(21F)	-1633	11734	3322	80
H(21G)	-1883	12602	2747	80
H(22A)	2214	8128	1983	80
H(22B)	2742	6505	1536	80
H(22C)	3525	6300	403	80
H(22D)	3011	9314	108	80
H(22E)	3784	8289	-816	80
H(22F)	4624	7222	-602	80
H(22G)	3361	7328	-847	80
H(23A)	332	11497	525	80
H(23B)	2356	12710	-822	80
H(23C)	4056	11829	-232	80
H(23D)	3898	10812	759	80
H(23E)	303	13255	-940	80
H(23F)	-276	12389	-756	80
H(23G)	-472	13272	-262	80
H(31A)	5277	6609	1613	80
H(31B)	5912	5678	623	80
H(31C)	7725	4429	573	80
H(31D)	8283	4980	2534	80
H(31E)	9525	3454	1082	80
H(31F)	10008	4053	1585	80
H(31G)	9403	3242	1875	80
H(32A)	7247	4498	3627	80
H(32B)	6513	3326	4286	80
H(32C)	4481	3678	4563	80
H(32D)	3869	6417	3523	80
H(32E)	2488	4739	4476	80
H(32F)	2366	5896	4455	80
H(32G)	2262	5382	3782	80
H(33A)	8099	7182	2484	80
H(33B)	10086	7032	4137	80
H(33C)	8714	6446	4831	80

Table 28. (Continued)

H(33D)	7054	6192	4358	80
H(33E)	9858	7664	2335	80
H(33F)	10123	8191	2964	80
H(33G)	10882	7086	2813	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 29. Bond Lengths [Å] and Angles [deg] for
$Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

I(1)-Cu(1)	2.819 (3)
I(1)-Cu(2)	2.583 (3)
I(2)-Cu(1)	2.804 (3)
I(2)-Cu(2)	2.591 (3)
Cu(1)-Cu(2)	3.059 (3)
Cu(1)-P(2)	2.315 (3)
Cu(1)-P(1)	2.308 (3)
Cu(2)-P(3)	2.276 (3)
P(2)-C(211)	1.863 (10)
P(2)-C(221)	1.857 (9)
P(2)-C(231)	1.850 (9)
P(1)-C(111)	1.855 (10)
P(1)-C(121)	1.849 (9)
P(1)-C(131)	1.861 (8)
P(3)-C(311)	1.861 (9)
P(3)-C(321)	1.854 (10)
P(3)-C(331)	1.842 (10)
C(111)-C(112)	1.408 (16)
C(111)-C(116)	1.401 (12)
C(112)-C(113)	1.408 (16)
C(113)-C(114)	1.392 (15)
C(114)-C(115)	1.400 (18)
C(115)-C(116)	1.415 (14)
C(115)-C(117)	1.513 (15)
C(121)-C(122)	1.417 (12)
C(121)-C(126)	1.408 (11)
C(122)-C(123)	1.401 (15)
C(123)-C(124)	1.400 (14)
C(124)-C(125)	1.412 (15)
C(125)-C(126)	1.405 (14)
C(125)-C(127)	1.539 (13)
C(131)-C(132)	1.441 (12)
C(131)-C(136)	1.406 (14)
C(132)-C(133)	1.403 (13)
C(133)-C(134)	1.388 (16)
C(134)-C(135)	1.401 (15)
C(135)-C(136)	1.419 (13)
C(135)-C(137)	1.524 (17)
C(211)-C(212)	1.411 (16)
C(211)-C(216)	1.412 (12)
C(212)-C(213)	1.389 (15)
C(213)-C(214)	1.417 (16)
C(214)-C(215)	1.399 (18)

Table 29. (Continued)

C(215)-C(216)	1.423 (14)
C(215)-C(217)	1.526 (15)
C(221)-C(222)	1.417 (13)
C(221)-C(226)	1.414 (13)
C(222)-C(223)	1.404 (14)
C(223)-C(224)	1.399 (16)
C(224)-C(225)	1.381 (16)
C(225)-C(226)	1.415 (15)
C(225)-C(227)	1.528 (15)
C(231)-C(232)	1.434 (12)
C(231)-C(236)	1.418 (15)
C(232)-C(233)	1.409 (14)
C(233)-C(234)	1.395 (18)
C(233)-C(237)	1.544 (16)
C(234)-C(235)	1.396 (16)
C(235)-C(236)	1.395 (15)
C(311)-C(312)	1.402 (14)
C(311)-C(316)	1.395 (12)
C(312)-C(313)	1.399 (15)
C(313)-C(314)	1.382 (16)
C(314)-C(315)	1.416 (16)
C(315)-C(316)	1.423 (14)
C(315)-C(317)	1.521 (16)
C(321)-C(322)	1.424 (12)
C(321)-C(326)	1.418 (13)
C(322)-C(323)	1.382 (16)
C(323)-C(324)	1.398 (16)
C(324)-C(325)	1.388 (13)
C(325)-C(326)	1.410 (15)
C(325)-C(327)	1.537 (16)
C(331)-C(332)	1.397 (15)
C(331)-C(336)	1.411 (13)
C(332)-C(333)	1.409 (17)
C(333)-C(334)	1.394 (17)
C(333)-C(337)	1.522 (20)
C(334)-C(335)	1.397 (16)
C(335)-C(336)	1.406 (16)
Cu(1)-I(1)-Cu(2)	68.8(1)
Cu(1)-I(2)-Cu(2)	68.9(1)
I(1)-Cu(1)-I(2)	104.1(1)
I(1)-Cu(1)-Cu(2)	51.9(1)
I(2)-Cu(1)-Cu(2)	52.2(1)
I(1)-Cu(1)-P(2)	107.1(1)

Table 29. (Continued)

I(2)-Cu(1)-P(2)	100.3(1)
Cu(2)-Cu(1)-P(2)	110.1(1)
I(1)-Cu(1)-P(1)	102.4(1)
I(2)-Cu(1)-P(1)	109.5(1)
Cu(2)-Cu(1)-P(1)	119.0(1)
P(2)-Cu(1)-P(1)	130.9(1)
I(1)-Cu(2)-I(2)	117.9(1)
I(1)-Cu(2)-Cu(1)	59.2(1)
I(2)-Cu(2)-Cu(1)	58.8(1)
I(1)-Cu(2)-P(3)	127.0(1)
I(2)-Cu(2)-P(3)	115.0(1)
Cu(1)-Cu(2)-P(3)	173.7(1)
Cu(1)-P(2)-C(211)	116.5(3)
Cu(1)-P(2)-C(221)	113.0(3)
C(211)-P(2)-C(221)	102.5(4)
Cu(1)-P(2)-C(231)	116.1(3)
C(211)-P(2)-C(231)	104.3(4)
C(221)-P(2)-C(231)	102.7(4)
Cu(1)-P(1)-C(111)	113.2(3)
Cu(1)-P(1)-C(121)	116.9(3)
C(111)-P(1)-C(121)	103.3(4)
Cu(1)-P(1)-C(131)	116.5(3)
C(111)-P(1)-C(131)	102.6(4)
C(121)-P(1)-C(131)	102.3(4)
Cu(2)-P(3)-C(311)	114.9(3)
Cu(2)-P(3)-C(321)	117.9(3)
C(311)-P(3)-C(321)	102.5(4)
Cu(2)-P(3)-C(331)	112.0(3)
C(311)-P(3)-C(331)	103.4(4)
C(321)-P(3)-C(331)	104.5(4)
P(1)-C(111)-C(112)	123.0(7)
P(1)-C(111)-C(116)	119.0(8)
C(112)-C(111)-C(116)	117.9(9)
C(111)-C(112)-C(113)	120.1(9)
C(112)-C(113)-C(114)	120.5(11)
C(113)-C(114)-C(115)	121.2(10)
C(114)-C(115)-C(116)	117.3(9)
C(114)-C(115)-C(117)	120.9(10)
C(116)-C(115)-C(117)	121.8(11)
C(111)-C(116)-C(115)	123.0(10)
P(1)-C(121)-C(122)	123.6(6)
P(1)-C(121)-C(126)	117.7(6)
C(122)-C(121)-C(126)	118.6(8)
C(121)-C(122)-C(123)	119.6(8)

Table 29. (Continued)

C(122)-C(123)-C(124)	121.0(9)
C(123)-C(124)-C(125)	120.2(10)
C(124)-C(125)-C(126)	118.3(8)
C(124)-C(125)-C(127)	120.9(10)
C(126)-C(125)-C(127)	120.8(9)
C(121)-C(126)-C(125)	122.1(8)
P(1)-C(131)-C(132)	124.0(7)
P(1)-C(131)-C(136)	118.7(6)
C(132)-C(131)-C(136)	117.3(8)
C(131)-C(132)-C(133)	120.4(9)
C(132)-C(133)-C(134)	120.2(9)
C(133)-C(134)-C(135)	121.7(9)
C(134)-C(135)-C(136)	118.0(10)
C(134)-C(135)-C(137)	121.3(8)
C(136)-C(135)-C(137)	120.7(9)
C(131)-C(136)-C(135)	122.4(8)
P(2)-C(211)-C(212)	123.6(7)
P(2)-C(211)-C(216)	117.2(8)
C(212)-C(211)-C(216)	119.1(9)
C(211)-C(212)-C(213)	119.8(9)
C(212)-C(213)-C(214)	121.4(11)
C(213)-C(214)-C(215)	119.5(10)
C(214)-C(215)-C(216)	119.1(9)
C(214)-C(215)-C(217)	119.2(9)
C(216)-C(215)-C(217)	121.7(10)
C(211)-C(216)-C(215)	120.9(10)
P(2)-C(221)-C(222)	116.9(7)
P(2)-C(221)-C(226)	124.8(7)
C(222)-C(221)-C(226)	118.3(8)
C(221)-C(222)-C(223)	120.8(9)
C(222)-C(223)-C(224)	118.5(10)
C(223)-C(224)-C(225)	123.0(10)
C(224)-C(225)-C(226)	117.8(9)
C(224)-C(225)-C(227)	122.5(10)
C(226)-C(225)-C(227)	119.6(10)
C(221)-C(226)-C(225)	121.5(9)
P(2)-C(231)-C(232)	122.9(7)
P(2)-C(231)-C(236)	119.6(6)
C(232)-C(231)-C(236)	117.6(8)
C(231)-C(232)-C(233)	120.6(9)
C(232)-C(233)-C(234)	119.6(9)
C(232)-C(233)-C(237)	120.8(10)
C(234)-C(233)-C(237)	119.6(9)
C(233)-C(234)-C(235)	120.9(10)

Table 29. (Continued)

C(234)-C(235)-C(236)	119.9(11)
C(231)-C(236)-C(235)	121.4(9)
P(3)-C(311)-C(312)	117.9(6)
P(3)-C(311)-C(316)	122.8(7)
C(312)-C(311)-C(316)	119.2(9)
C(311)-C(312)-C(313)	119.8(9)
C(312)-C(313)-C(314)	121.1(10)
C(313)-C(314)-C(315)	120.6(10)
C(314)-C(315)-C(316)	117.5(9)
C(314)-C(315)-C(317)	121.2(10)
C(316)-C(315)-C(317)	121.2(10)
C(311)-C(316)-C(315)	121.7(9)
P(3)-C(321)-C(322)	123.4(8)
P(3)-C(321)-C(326)	117.5(6)
C(322)-C(321)-C(326)	119.0(9)
C(321)-C(322)-C(323)	119.6(10)
C(322)-C(323)-C(324)	121.3(9)
C(323)-C(324)-C(325)	120.2(10)
C(324)-C(325)-C(326)	119.9(10)
C(324)-C(325)-C(327)	121.6(11)
C(326)-C(325)-C(327)	118.6(9)
C(321)-C(326)-C(325)	120.1(8)
P(3)-C(331)-C(332)	118.3(7)
P(3)-C(331)-C(336)	122.4(7)
C(332)-C(331)-C(336)	119.0(10)
C(331)-C(332)-C(333)	121.6(10)
C(332)-C(333)-C(334)	119.1(11)
C(332)-C(333)-C(337)	121.3(11)
C(334)-C(333)-C(337)	119.6(11)
C(333)-C(334)-C(335)	119.9(11)
C(334)-C(335)-C(336)	121.1(10)
C(331)-C(336)-C(335)	119.3(9)

Table 30. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(m\text{-}C_7H_7)_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	58(1)	49(1)	61(1)	-12(1)	1(1)	-3(1)
I(2)	44(1)	59(1)	65(1)	-11(1)	2(1)	-4(1)
Cu(1)	47(1)	49(1)	57(1)	-12(1)	-9(1)	-9(1)
Cu(2)	50(1)	54(1)	70(1)	-11(1)	-9(1)	-2(1)
P(2)	39(1)	48(1)	53(1)	-12(1)	-4(1)	-8(1)
P(1)	45(1)	41(1)	48(1)	-11(1)	-6(1)	-3(1)
P(3)	44(1)	52(1)	57(2)	-13(1)	-6(1)	-1(1)
C(111)	56(6)	41(5)	47(5)	-10(5)	2(5)	-8(4)
C(112)	72(7)	66(7	57(6)	-33(6)	-15(5)	-4(5)
C(113)	61(7)	74(7)	96(9)	-32(6)	-6(7)	-5(7)
C(114)	82(8)	60(6)	68(7)	-37(6)	10(6)	-7(6)
C(115)	79(8)	57(6)	48(6)	-16(6)	-1(5)	2(5)
C(116)	68(7)	56(6)	51(6)	-31(5)	0(5)	-1(5)
C(117)	140(13)	99(9)	75(8)	-46(9)	-22(8)	23(7)
C(121)	47(5)	35(5)	51(5)	-7(4)	-7(4)	-6(4)
C(122)	70(7)	47(5)	50(6)	-2(5)	-13(5)	2(4)
C(123)	90(8)	53(6)	56(6)	-14(6)	-14(6)	-4(5)
C(124)	87(9)	56(6)	76(7)	-26(6)	-42(6)	5(6)
C(125)	61(7)	57(6)	78(7)	-10(5)	-25(6)	1(6)
C(126)	55(6)	54(6)	53(6)	-15(5)	-13(5)	-5(4)
C(127)	56(7)	101(9)	116(10)	-4(7)	-29(7)	0(8)
C(131)	44(5)	49(5)	40(5)	-1(4)	-12(4)	-9(4)
C(132)	66(7)	59(6)	61(6)	-20(6)	-6(5)	-3(5)
C(133)	56(7)	62(7)	77(7)	8(6)	-8(6)	-14(6)
C(134)	46(6)	82(8)	64(7)	-5(6)	-5(5)	-20(6)
C(135)	50(6)	73(7)	63(6)	-20(6)	3(5)	-7(5)
C(136)	46(6)	49(5)	74(7)	-12(5)	-1(5)	-5(5)
C(137)	68(8)	103(9)	98(9)	-19(7)	10(7)	-17(7)
C(211)	45(5)	53(5)	54(6)	-14(5)	-1(5)	-3(5)
C(212)	61(7)	60(6)	85(8)	-17(6)	-4(6)	-16(5)
C(213)	48(7)	78(8)	129(10)	-30(6)	-25(7)	-28(7)
C(214)	50(7)	86(8)	101(9)	-26(6)	-1(6)	-22(7)
C(215)	53(7)	68(7)	67(7)	-12(6)	3(5)	-15(5)
C(216)	45(6)	62(6)	68(6)	-11(5)	-13(5)	-13(5)
C(217)	57(8)	129(11)	105(9)	4(8)	7(7)	-42(8)
C(221)	38(5)	40(5)	61(6)	-2(4)	-5(4)	-9(4)
C(222)	66(7)	53(6)	71(7)	-20(5)	-16(5)	-14(5)
C(223)	68(7)	54(6)	88(8)	-15(5)	-23(6)	-5(6)
C(224)	62(7)	55(6)	81(8)	-3(5)	-17(6)	-27(6)
C(225)	57(7)	73(7)	63(7)	1(6)	-10(5)	-33(6)
C(226)	60(7)	74(7)	55(6)	-9(6)	-11(5)	-16(5)

Table 30. (Continued)

C(227)	126(12)	92(9)	93(9)	-1(8)	-3(9)	-45(7)
C(231)	54(6)	51(5)	44(5)	-12(5)	-10(5)	-11(4)
C(232)	54(6)	52(6)	58(6)	-9(5)	-13(5)	-9(5)
C(233)	68(8)	69(7)	59(7)	-12(6)	-16(6)	-4(5)
C(234)	91(9)	83(8)	42(6)	-25(7)	-18(6)	5(5)
C(235)	86(9)	111(9)	50(6)	-53(8)	15(6)	4(6)
C(236)	44(6)	79(7)	70(7)	-20(5)	-6(5)	4(6)
C(237)	115(11)	108(10)	99(9)	-43(9)	-31(9)	16(8)
C(311)	51(6)	48(5)	57(6)	-8(5)	-7(5)	-3(4)
C(312)	56(7)	83(7)	61(7)	-15(6)	-7(6)	-3(6)
C(313)	81(9)	122(10)	58(7)	-43(8)	-12(6)	-4(7)
C(314)	101(10)	83(8)	57(7)	-31(8)	10(7)	-15(6)
C(315)	86(8)	72(7)	55(7)	-17(6)	6(6)	-8(5)
C(316)	62(7)	76(7)	62(7)	0(6)	-9(6)	-6(6)
C(317)	133(14)	128(12)	117(12)	33(11)	7(10)	-40(10)
C(321)	46(6)	52(6)	62(6)	-11(5)	-5(5)	-4(5)
C(322)	58(7)	68(7)	81(7)	-15(6)	-9(6)	-1(6)
C(323)	72(8)	53(6)	84(8)	-16(6)	-7(6)	11(6)
C(324)	89(9)	53(6)	63(6)	-34(6)	-2(6)	4(5)
C(325)	60(7)	74(7)	62(6)	-30(6)	12(5)	-9(5)
C(326)	49(6)	49(5)	63(6)	-15(5)	-9(5)	0(5)
C(327)	79(9)	110(10)	118(11)	-31(8)	11(8)	5(8)
C(331)	39(5)	56(6)	53(6)	-6(5)	1(5)	-18(4)
C(332)	59(7)	93(8)	66(7)	-29(6)	-5(6)	0(6)
C(333)	51(7)	93(8)	77(8)	-29(6)	3(6)	-14(6)
C(334)	42(6)	84(8)	102(9)	-20(6)	-11(6)	-26(7)
C(335)	56(7)	91(8)	57(6)	-11(6)	-11(6)	-15(6)
C(336)	50(6)	68(7)	63(7)	-11(5)	1(5)	-13(5)
C(337)	112(12)	259(21)	110(11)	-120(14)	1(9)	-6(12)

The anisotropic displacement factor exponent takes the form:
$-2\,pi^2\,[\,h^2 a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12}\,]$

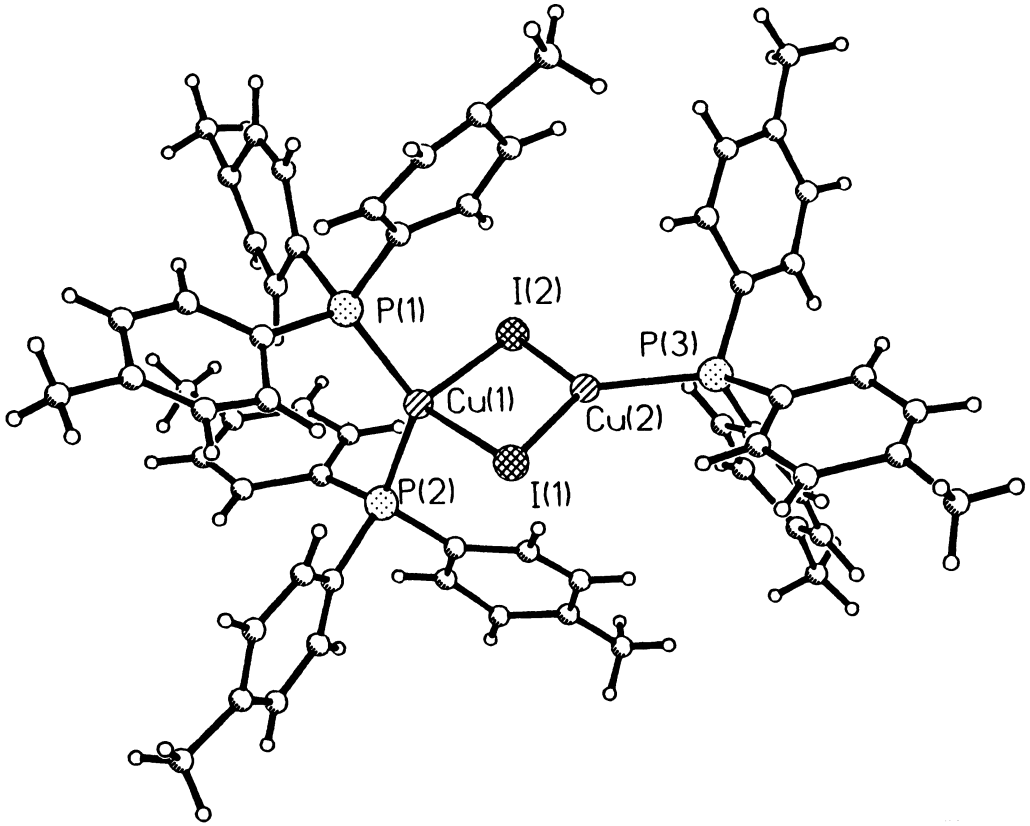


Figure 18 Projection View of $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

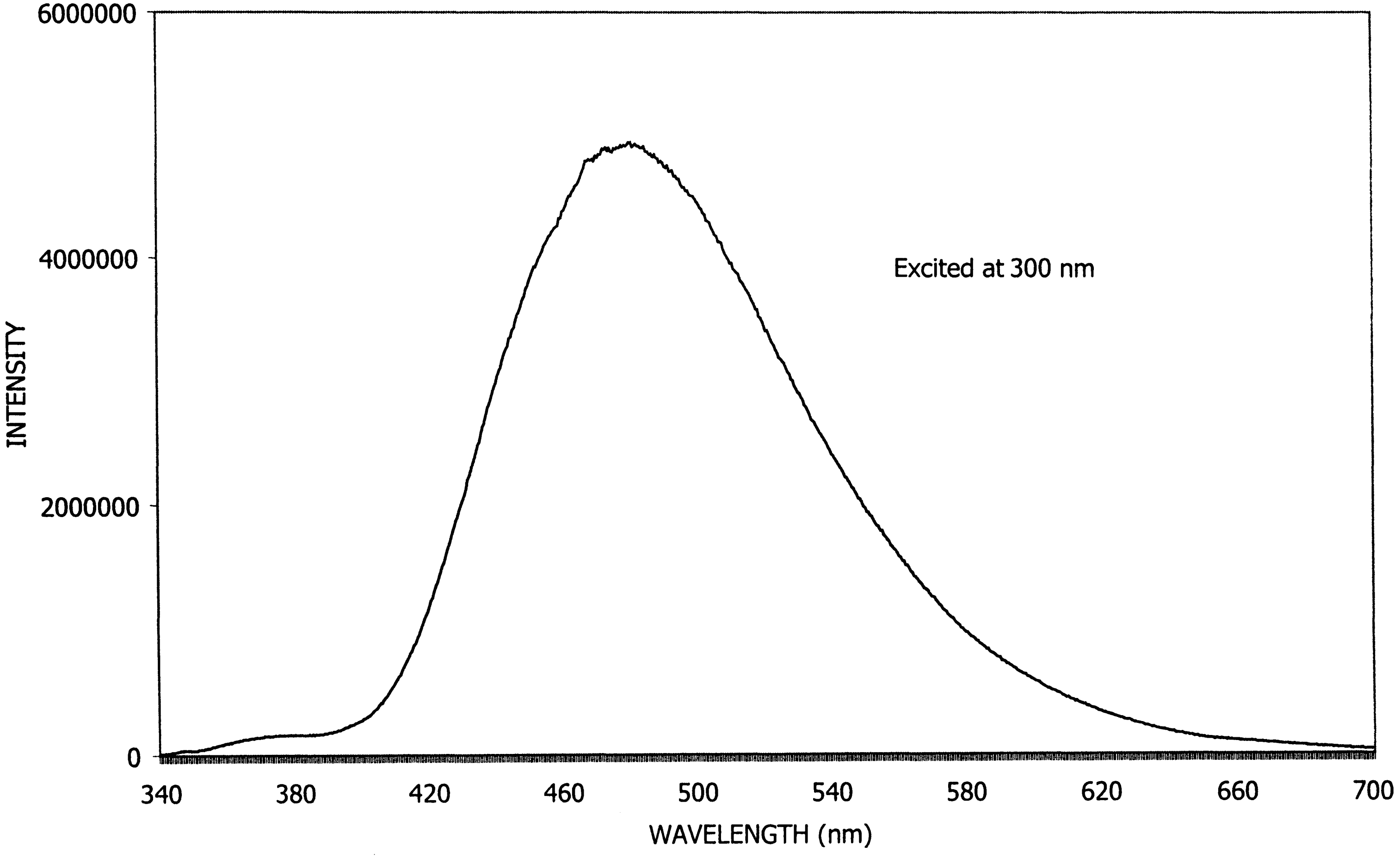


Figure 19 Emission Spectrum of $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Table 31. Crystal Data and Structure Refinement for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Empirical formula	$C_{63}H_{63}Cu_2I_2P_3$
Formula weight	1293.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 11.242(16) Å α = 94.81(2) deg.
	b = 14.056(13) Å β = 90.72(2) deg.
	c = 21.182(17) Å γ = 108.42(2) deg.
Volume	3162(6) Å^3
Z, Calculated density	2, 1.359 Mg/m^3
Absorption coefficient	1.759 mm^{-1}
F(000)	1300
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	1.89 to 30.02 deg.
Index ranges	$-1 \leq h \leq 15$, $-19 \leq k \leq 19$, $-29 \leq l \leq 29$
Reflections collected / unique	21040 / 18428 [R(int) = 0.2643]
Goodness-of-fit	0.946
Final R indices [I>2sigma(I)]	R1 = 0.2073, wR2 = 0.3030
R indices (all data)	R1 = 0.5833, wR2 = 0.4811
Extinction coefficient	-0.00149(16)
Largest diff. peak and hole	0.854 and –1.286 eÅ^{-3}

Table 32. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

	x	y	z	U(eq)
I(1)	2284(3)	3851(2)	2575(1)	86(1)
I(2)	4826(2)	1924(2)	2574(1)	61(1)
Cu(1)	2298(4)	1866(3)	2558(2)	54(1)
Cu(2)	4505(4)	3688(3)	2564(2)	66(1)
P(1)	1468(8)	1131(6)	1567(4)	46(2)
P(2)	1738(8)	1337(6)	3554(4)	51(2)
P(3)	6349(9)	4998(7)	2621(4)	60(3)
C(111)	1710(3)	-140(2)	1351(14)	48(9)
C(112)	1900(4)	-480(3)	729(17)	95(14)
C(113)	2170(4)	-1390(3)	646(18)	83(13)
C(114)	2000(5)	-2010(3)	1140(3)	130(2)
C(115)	2050(4)	-1580(4)	1750(2)	130(2)
C(116)	1660(5)	-700(3)	1848(17)	120(2)
C(117)	2480(5)	-3030(3)	990(2)	160(2)
C(121)	2150(4)	1830(2)	895(13)	73(13)
C(122)	1380(4)	2030(2)	418(14)	87(14)
C(123)	2000(4)	2600(3)	-23(12)	97(17)
C(124)	3050(6)	2890(3)	-191(19)	160(3)
C(125)	3940(4)	2770(3)	342(19)	108(16)
C(126)	3450(4)	2240(3)	875(17)	83(14)
C(127)	3920(4)	3620(3)	-633(17)	160(2)
C(131)	-250(2)	890(2)	1407(9)	44(10)
C(132)	-1010(3)	-20(3)	1097(17)	78(13)
C(133)	-2270(4)	-180(2)	940(15)	89(14)
C(134)	-2830(3)	620(3)	1100(14)	77(13)
C(135)	-2070(3)	1390(3)	1418(14)	67(12)
C(136)	-920(4)	1600(3)	1611(13)	71(12)
C(211)	240(4)	1440(2)	3832(14)	65(11)
C(212)	-610(3)	1650(3)	3413(15)	71(12)
C(213)	-1840(3)	1630(2)	3562(19)	59(10)
C(214)	-2180(4)	1490(4)	4210(2)	108(17)
C(215)	-1270(4)	1330(2)	4630(14)	67(11)
C(216)	-90(3)	1290(2)	4451(16)	56(10)
C(217)	-3550(4)	1400(3)	4370(15)	100(15)
C(221)	2880(3)	1960(3)	4204(16)	65(11)
C(222)	3670(3)	2980(2)	4188(12)	61(11)
C(223)	4490(3)	3460(3)	4627(14)	68(11)
C(224)	4660(4)	3050(3)	5203(17)	86(14)
C(225)	3900(3)	2040(3)	5304(14)	63(10)
C(226)	3040(3)	1540(2)	4745(15)	62(10)
C(227)	5610(4)	3500(3)	5759(19)	127(18)

Table 32. (Continued)

C(231)	1600(3)	0(3)	3614(11)	56(11)
C(232)	370(3)	-770(2)	3595(16)	67(11)
C(233)	390(3)	-1790(2)	3560(13)	62(10)
C(234)	1460(3)	-2070(2)	3553(15)	56(9)
C(235)	2590(3)	-1340(2)	3577(14)	56(10)
C(236)	2690(3)	-283(19)	3597(13)	49(9)
C(237)	1370(4)	-3220(2)	3516(18)	114(17)
C(311)	7160(3)	5230(3)	3403(17)	61(10)
C(312)	7460(4)	4430(3)	3636(16)	120(2)
C(313)	7940(3)	4530(2)	4240(2)	85(14)
C(314)	8160(3)	5500(3)	4640(15)	86(15)
C(315)	7790(4)	6180(3)	4383(17)	86(15)
C(316)	7320(4)	6050(3)	3816(19)	80(12)
C(317)	8800(3)	5530(2)	5354(16)	81(12)
C(321)	6230(3)	6280(2)	2464(18)	69(12)
C(322)	5220(4)	6490(3)	2561(11)	73(12)
C(323)	5010(5)	7450(3)	2514(18)	104(16)
C(324)	6220(5)	8300(3)	2446(15)	84(15)
C(325)	7220(5)	8060(2)	2420(2)	110(2)
C(326)	7390(3)	7060(3)	2403(15)	77(12)
C(327)	6040(5)	9360(3)	2500(2)	150(2)
C(331)	7510(3)	4760(2)	2116(12)	48(9)
C(332)	8810(4)	4930(3)	2240(2)	91(14)
C(333)	9560(4)	4750(3)	1760(3)	107(16)
C(334)	9200(4)	4320(3)	1140(2)	76(13)
C(335)	7940(6)	4160(3)	1050(2)	115(18)
C(336)	7100(3)	4340(3)	1472(19)	83(13)
C(337)	10090(4)	4030(3)	690(2)	150(2)
H(11A)	1815	-104	382	80
H(11C)	2471	-1578	246	80
H(11B)	2320	-1883	2090	80
H(11F)	1371	-517	2250	80
H(11G)	2439	-3244	542	80
H(11H)	3323	-2884	1153	80
H(11I)	1922	-3549	1205	80
H(12A)	484	1755	411	80
H(12B)	1469	2860	-269	80
H(12C)	4826	3080	317	80
H(12D)	3980	2139	1203	80
H(12F)	3423	3725	-976	80
H(12G)	4346	4256	-398	80
H(12H)	4528	3327	-800	80
H(13A)	-652	-537	981	80
H(13B)	-2789	-809	736	80

Table 32. (Continued)

H(13C)	-2449	1894	1550	80
H(13D)	-475	2214	1866	80
H(13E)	-4437	1007	1041	80
H(13F)	-4339	263	464	80
H(13G)	-4693	-137	1128	80
H(21A)	-320	1851	3006	80
H(21B)	-2439	1666	3246	80
H(21C)	-1483	1220	5061	80
H(21D)	495	1174	4744	80
H(21E)	-3969	1570	4021	80
H(21F)	-3964	709	4446	80
H(21G)	-3573	1829	4743	80
H(22A)	3590	3308	3819	80
H(22B)	4998	4131	4564	80
H(22C)	3953	1738	5690	80
H(22E)	2534	847	4769	80
H(22F)	6121	4175	5686	80
H(22G)	5168	3526	6140	80
H(22H)	6143	3093	5801	80
H(23A)	-392	-607	3623	80
H(23C)	-394	-2329	3527	80
H(23D)	3335	-1541	3559	80
H(23E)	3498	230	3618	80
H(23F)	2197	-3278	3519	80
H(23G)	933	-3527	3872	80
H(23H)	918	-3560	3130	80
H(31A)	7357	3822	3365	80
H(31B)	8116	3981	4415	80
H(31C)	7872	6797	4634	80
H(31D)	7047	6578	3666	80
H(31E)	8912	6175	5578	80
H(31F)	8252	5013	5583	80
H(31G)	9595	5419	5316	80
H(32A)	4528	5941	2678	80
H(32C)	4191	7532	2519	80
H(32D)	7969	8624	2425	80
H(32B)	8180	6940	2344	80
H(32G)	6833	9870	2460	80
H(32H)	5459	9393	2174	80
H(32I)	5719	9475	2908	80
H(33A)	9141	5160	2661	80
H(33B)	10440	4943	1862	80
H(33C)	7601	3894	632	80
H(33D)	6233	4176	1346	80

Table 32. (Continued)

H(33E)	9675	3753	282	80
H(33F)	10775	4630	631	80
H(33G)	10398	3551	867	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 33. Bond Lengths [Å] and Angles [deg] for
$Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

I(1)-Cu(2)	2.579(7)
I(1)-Cu(1)	2.792(5)
I(2)-Cu(2)	2.618(5)
I(2)-Cu(1)	2.817(6)
Cu(1)-P(1)	2.307(9)
Cu(1)-P(2)	2.324(10)
Cu(1)-Cu(2)	2.948(6)
Cu(2)-P(3)	2.290(10)
P(1)-C(121)	1.83(4)
P(1)-C(131)	1.88(3)
P(1)-C(111)	1.91(3)
P(2)-C(211)	1.84(4)
P(2)-C(221)	1.83(3)
P(2)-C(231)	1.85(3)
P(3)-C(331)	1.79(3)
P(3)-C(311)	1.83(4)
P(3)-C(321)	1.91(3)
C(111)-C(116)	1.36(4)
C(111)-C(112)	1.41(4)
C(112)-C(113)	1.41(4)
C(113)-C(114)	1.40(5)
C(114)-C(115)	1.36(6)
C(114)-C(117)	1.69(6)
C(115)-C(116)	1.44(6)
C(121)-C(126)	1.40(4)
C(121)-C(122)	1.42(4)
C(122)-C(123)	1.34(4)
C(123)-C(124)	1.19(6)
C(124)-C(125)	1.55(6)
C(124)-C(127)	1.56(5)
C(125)-C(126)	1.43(5)
C(131)-C(132)	1.39(4)
C(131)-C(136)	1.47(4)
C(132)-C(133)	1.39(4)
C(133)-C(134)	1.47(5)
C(134)-C(135)	1.27(4)
C(134)-C(137)	1.51(4)
C(135)-C(136)	1.29(4)
C(211)-C(216)	1.38(4)
C(211)-C(212)	1.41(4)
C(212)-C(213)	1.42(4)
C(213)-C(214)	1.45(5)
C(214)-C(215)	1.42(5)

Table 33. (Continued)

C(214)-C(217)	1.54(5)
C(215)-C(216)	1.40(4)
C(221)-C(226)	1.37(4)
C(221)-C(222)	1.43(4)
C(222)-C(223)	1.28(4)
C(223)-C(224)	1.43(4)
C(224)-C(225)	1.44(5)
C(224)-C(227)	1.54(4)
C(225)-C(226)	1.50(4)
C(231)-C(236)	1.41(4)
C(231)-C(232)	1.46(4)
C(232)-C(233)	1.43(4)
C(233)-C(234)	1.37(4)
C(234)-C(235)	1.35(4)
C(234)-C(237)	1.59(4)
C(235)-C(236)	1.45(3)
C(311)-C(316)	1.35(4)
C(311)-C(312)	1.40(5)
C(312)-C(313)	1.35(4)
C(313)-C(314)	1.49(5)
C(314)-C(315)	1.31(4)
C(314)-C(317)	1.66(4)
C(315)-C(316)	1.28(4)
C(321)-C(322)	1.27(4)
C(321)-C(326)	1.43(4)
C(322)-C(323)	1.45(5)
C(323)-C(324)	1.53(5)
C(324)-C(325)	1.28(5)
C(324)-C(327)	1.56(5)
C(325)-C(326)	1.47(4)
C(331)-C(332)	1.41(4)
C(331)-C(336)	1.45(4)
C(332)-C(333)	1.39(5)
C(333)-C(334)	1.40(5)
C(334)-C(335)	1.37(6)
C(334)-C(337)	1.51(5)
C(335)-C(336)	1.37(5)
Cu(2)-I(1)-Cu(1)	66.44(15)
Cu(2)-I(2)-Cu(1)	65.59(14)
P(1)-Cu(1)-P(2)	129.9(3)
P(1)-Cu(1)-I(1)	104.7(2)
P(2)-Cu(1)-I(1)	107.3(3)
P(1)-Cu(1)-I(2)	105.7(3)

Table 33. (Continued)

P(2)-Cu(1)-I(2)	100.4(3)
I(1)-Cu(1)-I(2)	107.25(16)
P(1)-Cu(1)-Cu(2)	115.3(3)
P(2)-Cu(1)-Cu(2)	114.7(3)
I(1)-Cu(1)-Cu(2)	53.31(14)
I(2)-Cu(1)-Cu(2)	53.96(14)
P(3)-Cu(2)-I(1)	125.7(3)
P(3)-Cu(2)-I(2)	113.4(3)
I(1)-Cu(2)-I(2)	120.69(19)
P(3)-Cu(2)-Cu(1)	173.3(3)
I(1)-Cu(2)-Cu(1)	60.25(15)
I(2)-Cu(2)-Cu(1)	60.45(15)
C(121)-P(1)-C(131)	101.5(14)
C(121)-P(1)-C(111)	102.0(14)
C(131)-P(1)-C(111)	104.4(14)
C(121)-P(1)-Cu(1)	115.9(11)
C(131)-P(1)-Cu(1)	117.4(7)
C(111)-P(1)-Cu(1)	113.6(9)
C(211)-P(2)-C(221)	104.7(15)
C(211)-P(2)-C(231)	104.1(14)
C(221)-P(2)-C(231)	101.3(14)
C(211)-P(2)-Cu(1)	116.3(11)
C(221)-P(2)-Cu(1)	115.4(13)
C(231)-P(2)-Cu(1)	113.2(8)
C(331)-P(3)-C(311)	101.7(14)
C(331)-P(3)-C(321)	107.4(15)
C(311)-P(3)-C(321)	103.6(15)
C(331)-P(3)-Cu(2)	113.3(11)
C(311)-P(3)-Cu(2)	113.0(11)
C(321)-P(3)-Cu(2)	116.4(11)
C(116)-C(111)-C(112)	122(3)
C(116)-C(111)-P(1)	115(3)
C(112)-C(111)-P(1)	123(2)
C(111)-C(112)-C(113)	117(3)
C(114)-C(113)-C(112)	120(4)
C(113)-C(114)-C(115)	119(4)
C(113)-C(114)-C(117)	114(5)
C(115)-C(114)-C(117)	121(5)
C(114)-C(115)-C(116)	118(5)
C(111)-C(116)-C(115)	118(4)
C(126)-C(121)-C(122)	119(4)
C(126)-C(121)-P(1)	119(2)
C(122)-C(121)-P(1)	122(3)

Table 33. (Continued)

C(123)-C(122)-C(121)	115(4)
C(124)-C(123)-C(122)	137(4)
C(123)-C(124)-C(125)	109(3)
C(123)-C(124)-C(127)	142(5)
C(125)-C(124)-C(127)	105(5)
C(126)-C(125)-C(124)	121(4)
C(121)-C(126)-C(125)	117(4)
C(132)-C(131)-C(136)	115(3)
C(132)-C(131)-P(1)	122(3)
C(136)-C(131)-P(1)	124(2)
C(133)-C(132)-C(131)	122(4)
C(132)-C(133)-C(134)	120(3)
C(135)-C(134)-C(133)	113(3)
C(135)-C(134)-C(137)	129(4)
C(133)-C(134)-C(137)	119(3)
C(134)-C(135)-C(136)	133(4)
C(135)-C(136)-C(131)	117(3)
C(216)-C(211)-C(212)	119(3)
C(216)-C(211)-P(2)	121(3)
C(212)-C(211)-P(2)	120(2)
C(211)-C(212)-C(213)	125(3)
C(212)-C(213)-C(214)	117(3)
C(213)-C(214)-C(215)	117(4)
C(213)-C(214)-C(217)	117(4)
C(215)-C(214)-C(217)	126(5)
C(216)-C(215)-C(214)	125(4)
C(211)-C(216)-C(215)	118(3)
C(226)-C(221)-C(222)	114(3)
C(226)-C(221)-P(2)	125(3)
C(222)-C(221)-P(2)	121(2)
C(223)-C(222)-C(221)	124(3)
C(222)-C(223)-C(224)	123(4)
C(223)-C(224)-C(225)	120(3)
C(223)-C(224)-C(227)	130(4)
C(225)-C(224)-C(227)	111(3)
C(224)-C(225)-C(226)	112(3)
C(221)-C(226)-C(225)	127(3)
C(236)-C(231)-C(232)	119(3)
C(236)-C(231)-P(2)	119(2)
C(232)-C(231)-P(2)	121(2)
C(233)-C(232)-C(231)	116(3)
C(234)-C(233)-C(232)	125(3)
C(235)-C(234)-C(233)	119(3)
C(235)-C(234)-C(237)	120(3)

Table 33. (Continued)

C(233)-C(234)-C(237)	121(3)
C(234)-C(235)-C(236)	121(3)
C(231)-C(236)-C(235)	120(3)
C(316)-C(311)-C(312)	116(3)
C(316)-C(311)-P(3)	126(3)
C(312)-C(311)-P(3)	117(3)
C(313)-C(312)-C(311)	119(4)
C(312)-C(313)-C(314)	120(3)
C(315)-C(314)-C(313)	115(3)
C(315)-C(314)-C(317)	130(4)
C(313)-C(314)-C(317)	115(3)
C(316)-C(315)-C(314)	123(4)
C(315)-C(316)-C(311)	126(4)
C(322)-C(321)-C(326)	121(3)
C(322)-C(321)-P(3)	121(3)
C(326)-C(321)-P(3)	116(3)
C(321)-C(322)-C(323)	128(4)
C(322)-C(323)-C(324)	112(4)
C(325)-C(324)-C(323)	116(4)
C(325)-C(324)-C(327)	130(4)
C(323)-C(324)-C(327)	113(4)
C(324)-C(325)-C(326)	131(4)
C(321)-C(326)-C(325)	112(3)
C(332)-C(331)-C(336)	113(3)
C(332)-C(331)-P(3)	131(3)
C(336)-C(331)-P(3)	117(3)
C(331)-C(332)-C(333)	121(4)
C(334)-C(333)-C(332)	129(4)
C(335)-C(334)-C(333)	108(4)
C(335)-C(334)-C(337)	129(4)
C(333)-C(334)-C(337)	123(4)
C(334)-C(335)-C(336)	130(5)
C(335)-C(336)-C(331)	120(4)

Table 34. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	69(2)	45(2)	141(3)	10(2)	-15(2)	15(2)
I(2)	60(2)	43(1)	79(2)	4(1)	2(1)	16(1)
Cu(1)	64(3)	41(2)	56(3)	1(2)	-5(2)	16(2)
Cu(2)	62(3)	48(3)	85(3)	1(2)	-11(3)	14(3)
P(1)	59(6)	36(5)	49(5)	-4(4)	4(4)	26(5)
P(2)	43(6)	47(5)	60(6)	-1(4)	-8(5)	11(5)
P(3)	60(7)	45(5)	73(6)	-3(5)	-8(5)	16(6)
C(111)	60(2)	50(2)	38(18)	-2(16)	-17(17)	25(19)
C(112)	130(4)	120(4)	50(2)	0(2)	-10(2)	70(3)
C(113)	110(4)	50(2)	110(3)	-20(2)	50(3)	60(3)
C(114)	140(5)	40(3)	160(5)	0(3)	-30(4)	-40(3)
C(115)	120(4)	120(5)	130(5)	10(4)	-50(4)	20(4)
C(116)	230(6)	110(4)	60(3)	30(3)	60(3)	100(4)
C(117)	280(7)	110(4)	160(4)	-40(3)	-50(4)	170(5)
C(121)	150(4)	60(2)	28(17)	-6(15)	-60(2)	60(3)
C(122)	140(4)	70(3)	40(2)	21(19)	0(2)	10(3)
C(123)	200(5)	180(4)	2(14)	11(19)	50(2)	170(4)
C(124)	380(8)	90(3)	70(3)	50(2)	200(4)	150(4)
C(125)	110(4)	90(3)	80(3)	0(3)	30(3)	-20(3)
C(126)	70(3)	70(3)	70(3)	30(2)	20(2)	-50(2)
C(127)	190(6)	130(4)	100(4)	-70(3)	-80(4)	10(4)
C(131)	16(15)	70(2)	0(11)	-11(12)	49(10)	-48(15)
C(132)	7(18)	90(3)	120(3)	-10(3)	-20(2)	0(2)
C(133)	140(4)	24(18)	80(3)	-34(18)	0(3)	0(3)
C(134)	80(3)	110(3)	40(19)	-50(2)	-50(2)	40(3)
C(135)	60(3)	90(3)	60(2)	-50(2)	-40(2)	50(2)
C(136)	120(4)	60(2)	21(17)	-27(16)	10(2)	30(3)
C(137)	40(3)	130(4)	120(3)	10(3)	-40(2)	20(3)
C(211)	100(3)	60(2)	23(18)	-10(16)	10(2)	10(2)
C(212)	10(2)	120(3)	50(2)	-20(2)	35(16)	-10(2)
C(213)	17(19)	50(2)	110(3)	0(2)	-30(2)	15(18)
C(214)	70(4)	120(4)	120(4)	-60(3)	-30(3)	20(3)
C(215)	100(3)	50(2)	50(2)	-36(16)	-40(2)	20(2)
C(216)	50(2)	60(2)	90(3)	-23(18)	10(19)	70(2)
C(217)	150(5)	130(4)	40(2)	10(2)	-10(3)	70(4)
C(221)	70(3)	70(2)	90(3)	10(2)	-20(2)	70(2)
C(222)	130(4)	40(2)	11(15)	-14(14)	-17(19)	30(2)
C(223)	100(3)	100(3)	23(17)	14(19)	-2(19)	70(3)
C(224)	90(4)	110(4)	70(3)	-60(3)	-20(2)	70(3)
C(225)	80(3)	70(3)	50(2)	9(19)	-10(2)	40(2)
C(226)	70(3)	50(2)	80(2)	-35(18)	-10(2)	40(2)

Table 34. (Continued)

C(227)	120(4)	40(2)	190(5)	-50(3)	0(4)	0(3)
C(231)	60(2)	110(3)	20(14)	71(18)	62(15)	50(2)
C(232)	20(2)	31(19)	140(3)	10(2)	-20(2)	-6(18)
C(233)	70(3)	40(2)	70(2)	43(17)	40(2)	0(2)
C(234)	20(2)	40(2)	100(3)	-9(18)	17(19)	-3(19)
C(235)	50(2)	24(16)	110(3)	29(18)	-10(2)	33(18)
C(236)	30(2)	13(14)	80(2)	-12(15)	1(18)	-12(15)
C(237)	120(4)	25(19)	160(4)	40(2)	-70(3)	-30(2)
C(311)	60(3)	35(19)	100(3)	20(2)	50(2)	20(2)
C(312)	130(4)	80(3)	60(3)	-20(2)	-70(3)	-70(3)
C(313)	80(3)	10(15)	190(4)	10(2)	0(3)	48(19)
C(314)	21(19)	130(4)	70(2)	80(3)	8(17)	-50(2)
C(315)	170(5)	60(2)	60(2)	60(2)	70(3)	60(3)
C(316)	110(4)	50(2)	90(3)	30(2)	10(3)	40(3)
C(317)	20(2)	40(2)	180(4)	60(2)	30(2)	-4(18)
C(321)	20(2)	13(15)	170(4)	-18(19)	30(2)	9(17)
C(322)	110(3)	90(3)	12(15)	39(17)	31(18)	10(3)
C(323)	120(4)	90(4)	110(3)	0(3)	-30(3)	50(4)
C(324)	170(5)	40(2)	50(2)	22(18)	20(3)	30(3)
C(325)	160(5)	11(18)	170(4)	-30(2)	-100(4)	30(3)
C(326)	50(3)	80(3)	90(3)	0(2)	30(2)	20(3)
C(327)	210(6)	30(2)	190(5)	20(3)	30(4)	20(3)
C(331)	90(3)	53(19)	30(16)	-27(14)	-1(17)	70(2)
C(332)	40(3)	110(4)	120(4)	-20(3)	-40(3)	30(3)
C(333)	80(4)	100(4)	160(5)	-20(3)	20(4)	60(3)
C(334)	40(3)	50(2)	130(4)	-10(2)	30(3)	10(2)
C(335)	180(6)	100(4)	90(3)	20(3)	80(4)	70(4)
C(336)	30(2)	100(3)	100(3)	10(3)	20(2)	10(3)
C(337)	150(5)	170(5)	180(5)	-30(4)	10(4)	150(4)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

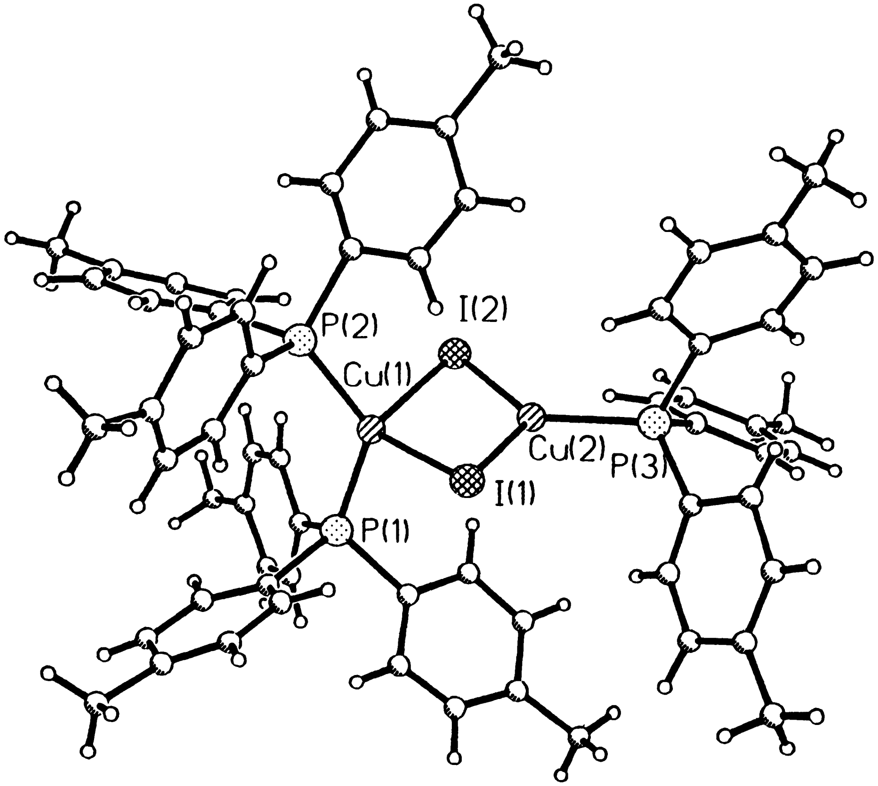


Figure 20 Projection View of $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

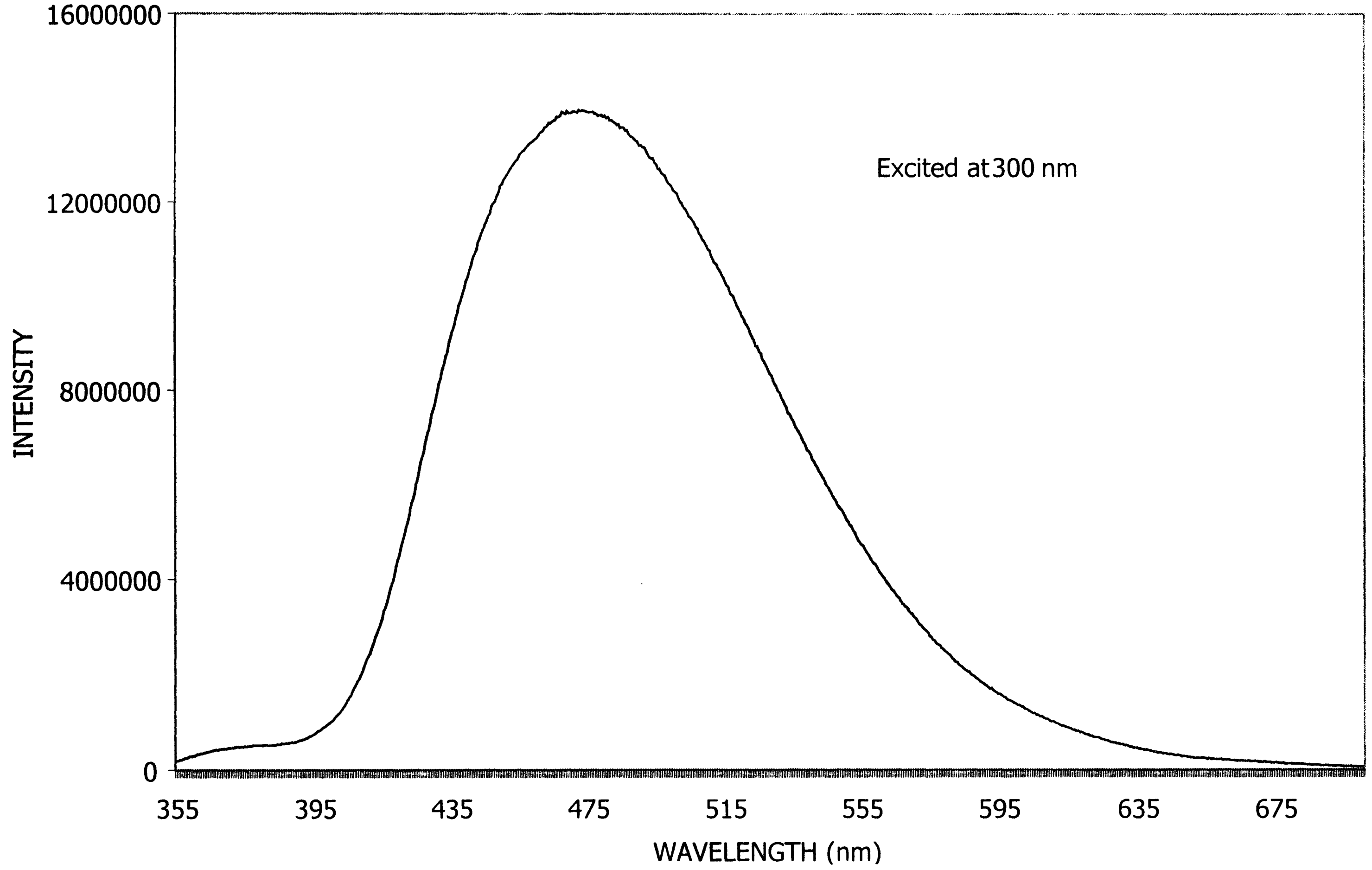


Figure 21 Emission Spectrum of $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Table 35. Crystal Data and Structure Refinement for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

Empirical formula	$C_{63}H_{63}Cu_2I_2P_3$
Formula weight	1293.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/a$
Unit cell dimensions	a = 11.300(6) Å α = 90.0 deg. b = 40.524(18) Å β = 110.47(2) deg. c = 14.283(7) Å γ = 90.0 deg.
Volume	6127(5) $Å^3$
Z, Calculated density	5, 1.753 Mg/m^3
Absorption coefficient	2.270 mm^{-1}
F(000)	3250
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	3.5 to 22.5 deg.
Index ranges	$-15 \leq h \leq 1, -57 \leq k \leq 1, -19 \leq l \leq 20$
Reflections collected / unique/	20879 / 17888 [R(int) = 0.3308]
Goodness-of-fit	0.961
Final R indices [I>2sigma(I)]	R1 = 0.2067, wR2 = 0.2606
R indices (all data)	R1 = 0.5673, wR2 = 0.4082
Extinction coefficient	0.00035(15)
Largest diff. peak and hole	0.797 and -0.910 $eÅ^{-3}$

Table 36. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

	x	y	z	U(eq)
I(1)	2341(2)	1337(1)	1411(2)	66(1)
Cu(3)	4625(3)	1354(1)	1091(2)	55(1)
Cu(4)	4294(4)	1424(1)	3024(3)	69(1)
I(2)	6466(2)	1534(1)	2896(2)	75(1)
P(1)	4940(8)	812(2)	806(6)	48(2)
P(2)	4519(7)	1807(2)	107(6)	49(2)
P(3)	3874(9)	1424(2)	4453(6)	64(3)
C(111)	4570(3)	516(9)	1630(2)	79(13)
C(112)	3700(3)	265(7)	1190(2)	56(10)
C(113)	3480(3)	69(10)	1860(2)	90(14)
C(114)	3960(4)	76(7)	2880(4)	94(15)
C(115)	4800(4)	331(11)	3290(2)	94(13)
C(116)	5080(3)	555(8)	2640(3)	78(11)
C(117)	3680(4)	-137(9)	3630(3)	141(17)
C(121)	3880(3)	676(6)	-470(2)	54(9)
C(122)	2610(4)	744(5)	-770(2)	90(13)
C(123)	1860(3)	654(7)	-1670(2)	82(13)
C(124)	2220(3)	514(7)	-2380(2)	84(13)
C(125)	3480(3)	480(9)	-2150(2)	95(14)
C(126)	4420(3)	548(7)	-1130(2)	66(10)
C(127)	1370(3)	448(10)	-3460(2)	135(17)
C(131)	6520(2)	675(7)	914(18)	42(7)
C(132)	6920(2)	351(5)	943(19)	41(8)
C(133)	8140(2)	254(6)	1052(19)	53(9)
C(134)	9050(3)	504(7)	1050(2)	62(10)
C(135)	8680(3)	828(8)	1020(2)	69(10)
C(136)	7420(3)	929(7)	940(2)	57(9)
C(137)	10340(2)	395(9)	1050(2)	110(15)
C(211)	5730(3)	1845(6)	-500(3)	55(9)
C(212)	5570(3)	1924(8)	-1450(2)	68(11)
C(213)	6480(3)	1953(11)	-1850(2)	98(17)
C(214)	7680(5)	1890(8)	-1250(3)	102(17)
C(215)	7950(2)	1792(7)	-300(3)	78(12)
C(216)	6990(3)	1790(7)	150(2)	66(10)
C(217)	8810(4)	1909(10)	-1610(3)	150(2)
C(221)	4630(3)	2225(9)	762(18)	57(11)
C(222)	5460(3)	2461(8)	800(2)	67(11)
C(223)	5520(3)	2756(8)	1390(2)	65(10)
C(224)	4700(3)	2777(8)	1920(3)	63(10)
C(225)	3900(3)	2502(8)	1880(2)	59(10)
C(226)	3900(3)	2235(7)	1320(2)	70(11)

Table 36. (Continued)

C(227)	4760(3)	3083(7)	2560(2)	76(11)
C(231)	3060(3)	1834(9)	-1010(3)	79(11)
C(232)	2470(3)	2138(8)	-1350(3)	71(11)
C(233)	1410(2)	2128(8)	-2320(3)	95(16)
C(234)	1270(4)	1820(8)	-2824(19)	120(2)
C(235)	1700(4)	1555(7)	-2510(3)	160(3)
C(236)	2670(3)	1576(8)	-1610(2)	67(11)
C(237)	20(3)	1882(8)	-3870(2)	73(10)
C(311)	2440(5)	1171(12)	4310(3)	130(2)
C(312)	1390(3)	1319(9)	4550(2)	71(10)
C(313)	260(3)	1098(12)	4330(2)	86(13)
C(314)	110(6)	786(12)	3980(3)	130(3)
C(315)	1190(4)	661(11)	3820(3)	107(16)
C(316)	2270(4)	859(12)	4010(3)	126(17)
C(317)	-960(3)	579(11)	3840(3)	137(19)
C(321)	3450(3)	1839(9)	4760(2)	74(11)
C(322)	3510(3)	1940(10)	5700(2)	79(13)
C(323)	2990(4)	2225(11)	5870(3)	96(15)
C(324)	2470(3)	2432(10)	5100(3)	72(12)
C(325)	2520(3)	2355(7)	4200(3)	70(11)
C(326)	3010(3)	2054(8)	4010(2)	62(10)
C(327)	1820(3)	2738(10)	5190(2)	107(14)
C(331)	5100(3)	1284(8)	5590(2)	67(10)
C(332)	4840(3)	1150(8)	6460(2)	78(11)
C(333)	5860(3)	1046(7)	7300(2)	71(11)
C(334)	7050(3)	1055(10)	7420(3)	102(15)
C(335)	7340(3)	1184(10)	6510(2)	100(13)
C(336)	6330(2)	1265(8)	5660(2)	77(12)
C(337)	8140(3)	948(10)	8350(2)	124(16)
H(11A)	3291	243	485	80
H(11C)	2876	-107	1628	80
H(11D)	5168	364	3996	80
H(11E)	5626	740	2897	80
H(11F)	4167	-88	4310	80
H(11G)	2795	-107	3521	80
H(11H)	3821	-362	3482	80
H(12A)	2266	840	-302	80
H(12B)	965	682	1872	80
H(12C)	3807	362	-2589	80
H(12D)	5322	534	-921	80
H(12F)	518	512	-3549	80
H(12G)	1650	561	-3931	80
H(12H)	1403	214	-3551	80
H(13A)	6295	182	864	80
H(13B)	8382	26	1133	80

Table 36. (Continued)

H(13C)	9330	989	1129	80
H(13D)	7185	1158	864	80
H(13F)	10760	599	1022	80
H(13G)	10776	285	1669	80
H(13H)	10326	257	502	80
H(21A)	4738	1988	-1886	80
H(21B)	6316	1966	-2558	80
H(21C)	8773	1706	63	80
H(21D)	7168	1768	860	80
H(21F)	8519	1987	-2286	80
H(21G)	9448	2056	-1197	80
H(21H)	9167	1692	-1582	80
H(22A)	5976	2441	401	80
H(22B)	6159	2920	1438	80
H(22C)	3389	2514	2299	80
H(22D)	3368	2052	1342	80
H(22E)	5318	3247	2468	80
H(22F)	3922	3175	2384	80
H(22G)	5045	3016	3250	80
H(23A)	2733	2333	-951	80
H(23C)	922	2324	-2569	80
H(23D)	1476	1360	-2916	80
H(23E)	3083	1370	-1379	80
H(23F)	-148	1678	-4233	80
H(23G)	-718	1949	-3729	80
H(23H)	238	2049	-4253	80
H(31A)	1463	1536	4834	80
H(31C)	-452	1198	4434	80
H(31D)	1115	448	3510	80
H(31E)	3020	760	3956	80
H(31F)	-1661	664	4004	80
H(31G)	-1235	533	3139	80
H(31H)	-660	380	4213	80
H(32A)	3949	1803	6260	80
H(32B)	2930	2270	6515	80
H(32C)	2235	2507	3654	80
H(32D)	2979	1991	3355	80
H(32E)	1544	2861	4575	80
H(32F)	1110	2684	5377	80
H(32G)	2409	2870	5705	80
H(33A)	3985	1137	6450	80
H(33B)	5658	958	7846	80
H(33C)	8194	1221	6540	80
H(33E)	6494	1292	5050	80
H(33F)	7787	867	8831	80

Table 36. (Continued)

H(33G)	8663	782	8222	80
H(33H)	8629	1142	8611	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 37. Bond Lengths [Å] and Angles [deg] for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

I(1)-Cu(4)	2.598(4)
I(1)-Cu(3)	2.775(4)
Cu(3)-P(1)	2.283(9)
Cu(3)-P(2)	2.290(9)
Cu(3)-I(2)	2.786(4)
Cu(3)-Cu(4)	2.927(5)
Cu(4)-P(3)	2.251(9)
Cu(4)-I(2)	2.563(5)
P(1)-C(131)	1.82(2)
P(1)-C(111)	1.83(4)
P(1)-C(121)	1.88(3)
P(2)-C(231)	1.85(3)
P(2)-C(211)	1.86(3)
P(2)-C(221)	1.92(3)
P(3)-C(331)	1.81(3)
P(3)-C(321)	1.84(4)
P(3)-C(311)	1.87(3)
C(111)-C(116)	1.36(4)
C(111)-C(112)	1.40(4)
C(112)-C(113)	1.33(4)
C(113)-C(114)	1.37(4)
C(114)-C(115)	1.39(4)
C(114)-C(117)	1.49(4)
C(115)-C(116)	1.41(4)
C(121)-C(122)	1.37(4)
C(121)-C(126)	1.39(4)
C(122)-C(123)	1.32(4)
C(123)-C(124)	1.34(4)
C(124)-C(125)	1.35(4)
C(124)-C(127)	1.52(4)
C(125)-C(126)	1.50(4)
C(131)-C(132)	1.38(3)
C(131)-C(136)	1.44(3)
C(132)-C(133)	1.39(3)
C(133)-C(134)	1.44(4)
C(134)-C(135)	1.38(4)
C(134)-C(137)	1.52(3)
C(135)-C(136)	1.44(4)
C(211)-C(212)	1.35(4)
C(211)-C(216)	1.42(4)
C(212)-C(213)	1.35(3)
C(213)-C(214)	1.35(5)
C(214)-C(215)	1.34(4)

Table 37. (Continued)

C(214)-C(217)	1.54(4)
C(215)-C(216)	1.45(4)
C(221)-C(222)	1.32(4)
C(221)-C(226)	1.34(4)
C(222)-C(223)	1.44(4)
C(223)-C(224)	1.40(4)
C(224)-C(225)	1.42(4)
C(224)-C(227)	1.53(4)
C(225)-C(226)	1.35(4)
C(231)-C(236)	1.33(4)
C(231)-C(232)	1.41(4)
C(232)-C(233)	1.48(4)
C(233)-C(234)	1.42(4)
C(234)-C(235)	1.20(6)
C(234)-C(237)	1.67(4)
C(235)-C(236)	1.37(5)
C(311)-C(316)	1.33(5)
C(311)-C(312)	1.47(5)
C(312)-C(313)	1.50(4)
C(313)-C(314)	1.35(5)
C(314)-C(315)	1.41(6)
C(314)-C(317)	1.43(6)
C(315)-C(316)	1.41(5)
C(321)-C(326)	1.33(4)
C(321)-C(322)	1.38(4)
C(322)-C(323)	1.36(5)
C(323)-C(324)	1.35(4)
C(324)-C(325)	1.34(4)
C(324)-C(327)	1.47(4)
C(325)-C(326)	1.40(4)
C(331)-C(336)	1.37(3)
C(331)-C(332)	1.48(3)
C(332)-C(333)	1.40(4)
C(333)-C(334)	1.30(4)
C(334)-C(337)	1.52(4)
C(334)-C(335)	1.53(4)
C(335)-C(336)	1.38(3)
Cu(4)-I(1)-Cu(3)	65.91(12)
P(1)-Cu(3)-P(2)	129.8(3)
P(1)-Cu(3)-I(1)	102.6(2)
P(2)-Cu(3)-I(1)	105.6(2)
P(1)-Cu(3)-I(2)	107.7(2)
P(2)-Cu(3)-I(2)	102.7(2)
I(1)-Cu(3)-I(2)	106.90(13)

Table 37. (Continued)

P(1)-Cu(3)-Cu(4)	109.9(2)
P(2)-Cu(3)-Cu(4)	120.3(3)
I(1)-Cu(3)-Cu(4)	54.13(11)
I(2)-Cu(3)-Cu(4)	53.26(11)
P(3)-Cu(4)-I(2)	125.1(3)
P(3)-Cu(4)-I(1)	114.9(3)
I(2)-Cu(4)-I(1)	119.88(15)
P(3)-Cu(4)-Cu(3)	172.9(3)
I(2)-Cu(4)-Cu(3)	60.55(11)
I(1)-Cu(4)-Cu(3)	59.96(11)
Cu(4)-I(2)-Cu(3)	66.19(12)
C(131)-P(1)-C(111)	100.7(15)
C(131)-P(1)-C(121)	105.5(12)
C(111)-P(1)-C(121)	102.6(14)
C(131)-P(1)-Cu(3)	119.1(10)
C(111)-P(1)-Cu(3)	115.5(12)
C(121)-P(1)-Cu(3)	111.5(8)
C(231)-P(2)-C(211)	99.9(16)
C(231)-P(2)-C(221)	104.8(15)
C(211)-P(2)-C(221)	102.6(12)
C(231)-P(2)-Cu(3)	114.6(10)
C(211)-P(2)-Cu(3)	117.5(10)
C(221)-P(2)-Cu(3)	115.4(9)
C(331)-P(3)-C(321)	104.5(14)
C(331)-P(3)-C(311)	106.5(17)
C(321)-P(3)-C(311)	104(2)
C(331)-P(3)-Cu(4)	118.4(10)
C(321)-P(3)-Cu(4)	111.7(8)
C(311)-P(3)-Cu(4)	110.7(12)
C(116)-C(111)-C(112)	122(3)
C(116)-C(111)-P(1)	120(3)
C(112)-C(111)-P(1)	118(2)
C(113)-C(112)-C(111)	113(3)
C(112)-C(113)-C(114)	130(3)
C(113)-C(114)-C(115)	115(3)
C(113)-C(114)-C(117)	130(4)
C(115)-C(114)-C(117)	115(4)
C(114)-C(115)-C(116)	119(3)
C(111)-C(116)-C(115)	121(3)
C(122)-C(121)-C(126)	122(3)
C(122)-C(121)-P(1)	119(2)
C(126)-C(121)-P(1)	119(2)
C(123)-C(122)-C(121)	119(3)
C(122)-C(123)-C(124)	127(3)
C(123)-C(124)-C(125)	115(3)

Table 37. (Continued)

C(123)-C(124)-C(127)	126(4)
C(125)-C(124)-C(127)	117(4)
C(124)-C(125)-C(126)	123(3)
C(121)-C(126)-C(125)	113(3)
C(132)-C(131)-C(136)	117(2)
C(132)-C(131)-P(1)	126(2)
C(136)-C(131)-P(1)	116(2)
C(133)-C(132)-C(131)	125(2)
C(132)-C(133)-C(134)	119(2)
C(135)-C(134)-C(133)	117(3)
C(135)-C(134)-C(137)	124(3)
C(133)-C(134)-C(137)	119(3)
C(134)-C(135)-C(136)	124(3)
C(131)-C(136)-C(135)	118(3)
C(212)-C(211)-C(216)	117(3)
C(212)-C(211)-P(2)	129(3)
C(216)-C(211)-P(2)	114(2)
C(211)-C(212)-C(213)	127(3)
C(214)-C(213)-C(212)	117(3)
C(215)-C(214)-C(213)	121(3)
C(215)-C(214)-C(217)	116(4)
C(213)-C(214)-C(217)	123(3)
C(214)-C(215)-C(216)	121(3)
C(211)-C(216)-C(215)	116(3)
C(222)-C(221)-C(226)	122(3)
C(222)-C(221)-P(2)	126(2)
C(226)-C(221)-P(2)	112(3)
C(221)-C(222)-C(223)	122(3)
C(224)-C(223)-C(222)	117(3)
C(223)-C(224)-C(225)	118(3)
C(223)-C(224)-C(227)	119(3)
C(225)-C(224)-C(227)	123(3)
C(226)-C(225)-C(224)	121(3)
C(221)-C(226)-C(225)	121(3)
C(236)-C(231)-C(232)	117(3)
C(236)-C(231)-P(2)	120(3)
C(232)-C(231)-P(2)	121(3)
C(231)-C(232)-C(233)	115(3)
C(234)-C(233)-C(232)	114(2)
C(235)-C(234)-C(233)	130(3)
C(235)-C(234)-C(237)	125(3)
C(233)-C(234)-C(237)	103(3)
C(234)-C(235)-C(236)	112(2)
C(231)-C(236)-C(235)	129(3)
C(316)-C(311)-C(312)	116(4)

Table 37. (Continued)

C(316)-C(311)-P(3)	125(5)
C(312)-C(311)-P(3)	119(3)
C(311)-C(312)-C(313)	114(3)
C(314)-C(313)-C(312)	129(4)
C(313)-C(314)-C(315)	113(5)
C(313)-C(314)-C(317)	126(6)
C(315)-C(314)-C(317)	121(4)
C(316)-C(315)-C(314)	121(5)
C(311)-C(316)-C(315)	128(5)
C(326)-C(321)-C(322)	117(3)
C(326)-C(321)-P(3)	118(2)
C(322)-C(321)-P(3)	125(3)
C(323)-C(322)-C(321)	124(3)
C(324)-C(323)-C(322)	118(4)
C(325)-C(324)-C(323)	119(4)
C(325)-C(324)-C(327)	118(4)
C(323)-C(324)-C(327)	123(4)
C(324)-C(325)-C(326)	123(3)
C(321)-C(326)-C(325)	118(3)
C(336)-C(331)-C(332)	114(2)
C(336)-C(331)-P(3)	121(2)
C(332)-C(331)-P(3)	124(2)
C(333)-C(332)-C(331)	119(3)
C(334)-C(333)-C(332)	128(3)
C(333)-C(334)-C(337)	126(4)
C(333)-C(334)-C(335)	115(3)
C(337)-C(334)-C(335)	120(3)
C(336)-C(335)-C(334)	118(3)
C(331)-C(336)-C(335)	126(3)

Table 38. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(p\text{-}C_7H_7)_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	55(1)	76(2)	78(2)	-8(1)	39(1)	-7(1)
Cu(3)	61(3)	52(2)	57(2)	0(2)	28(2)	-1(2)
Cu(4)	70(3)	87(3)	61(2)	3(2)	35(2)	-2(2)
I(2)	67(2)	108(2)	59(1)	-11(1)	33(1)	-26(2)
P(1)	57(6)	50(5)	46(5)	1(4)	28(4)	0(5)
P(2)	39(5)	57(5)	59(5)	-5(4)	29(4)	0(4)
P(3)	82(7)	66(6)	57(5)	4(5)	40(5)	2(5)
C(111)	90(3)	80(3)	31(18)	-12(19)	-20(2)	0(2)
C(112)	80(2)	70(2)	39(18)	64(17)	47(18)	27(19)
C(113)	70(3)	130(4)	50(2)	-50(2)	0(2)	-30(3)
C(114)	130(4)	0(15)	190(4)	60(2)	100(3)	11(18)
C(115)	120(4)	110(4)	60(2)	0(2)	40(2)	-10(3)
C(116)	50(2)	50(2)	130(3)	0(2)	10(2)	-21(18)
C(117)	180(5)	100(3)	150(4)	-20(3)	70(4)	0(3)
C(121)	50(2)	36(17)	70(2)	43(16)	26(18)	59(16)
C(122)	200(4)	0(13)	90(2)	-60(14)	70(3)	11(19)
C(123)	60(2)	80(3)	100(3)	-100(2)	30(2)	-30(2)
C(124)	90(3)	32(19)	70(2)	6(17)	-60(2)	-10(2)
C(125)	60(2)	160(4)	70(2)	-50(2)	30(2)	-100(3)
C(126)	31(19)	60(2)	100(3)	0(2)	15(19)	29(17)
C(127)	140(4)	180(5)	90(3)	-40(3)	50(3)	-40(4)
C(131)	18(15)	60(2)	42(17)	-13(15)	0(13)	14(15)
C(132)	24(16)	0(12)	90(2)	22(13)	4(15)	10(11)
C(133)	37(18)	17(14)	80(2)	2(14)	-8(16)	54(14)
C(134)	60(2)	27(17)	90(2)	-30(17)	10(2)	26(17)
C(135)	60(2)	60(2)	100(3)	-32(19)	40(2)	-60(2)
C(136)	37(19)	60(2)	70(2)	21(17)	14(18)	-14(17)
C(137)	40(2)	170(4)	140(4)	0(3)	50(2)	50(2)
C(211)	60(2)	16(15)	120(3)	-14(18)	70(2)	-13(16)
C(212)	50(2)	130(3)	50(2)	-10(2)	43(18)	-30(2)
C(213)	70(2)	230(5)	4(15)	10(2)	26(17)	50(3)
C(214)	240(5)	70(2)	70(3)	40(2)	160(3)	10(3)
C(215)	11(15)	50(2)	180(4)	-20(2)	40(2)	2(15)
C(216)	80(3)	70(2)	80(2)	-21(19)	60(2)	-40(2)
C(217)	220(5)	130(4)	160(4)	-40(3)	150(4)	-100(4)
C(221)	33(17)	140(3)	15(14)	26(17)	27(13)	50(2)
C(222)	50(2)	70(3)	120(3)	-20(2)	80(2)	-7(19)
C(223)	40(2)	60(2)	90(3)	0(2)	20(2)	6(19)
C(224)	31(19)	50(2)	90(3)	40(2)	1(18)	23(17)
C(225)	60(2)	80(3)	70(2)	27(19)	60(19)	0(2)
C(226)	110(3)	19(16)	90(3)	-23(17)	50(2)	-22(18)

Table 38. (Continued)

C(227)	50(2)	60(2)	110(3)	-40(2)	20(2)	-44(18)
C(231)	60(3)	70(3)	120(3)	20(2)	50(2)	-20(2)
C(232)	30(19)	50(2)	160(4)	-10(2)	60(2)	4(17)
C(233)	0(12)	120(3)	200(4)	150(3)	78(19)	87(16)
C(234)	250(5)	100(2)	32(16)	-47(17)	80(2)	-210(3)
C(235)	400(7)	47(19)	150(3)	-90(2)	240(4)	-200(3)
C(236)	80(2)	80(2)	70(2)	-70(2)	52(19)	10(2)
C(237)	60(2)	90(3)	80(2)	10(2)	40(2)	-30(2)
C(311)	160(5)	160(4)	50(2)	-30(3)	30(3)	-160(4)
C(312)	90(3)	60(2)	80(3)	0(2)	50(2)	-20(2)
C(313)	50(2)	170(4)	50(2)	30(3)	17(18)	10(3)
C(314)	150(5)	90(4)	80(3)	-50(3)	-60(4)	20(4)
C(315)	120(4)	80(3)	90(3)	-30(3)	10(3)	-50(3)
C(316)	60(3)	150(5)	160(4)	-20(3)	30(3)	-70(3)
C(317)	60(3)	180(5)	170(4)	-10(4)	40(3)	-60(3)
C(321)	70(2)	150(3)	31(17)	30(2)	52(17)	-30(2)
C(322)	50(2)	140(4)	20(17)	80(2)	-11(16)	10(2)
C(323)	70(3)	130(4)	80(3)	50(3)	30(2)	20(3)
C(324)	40(2)	100(3)	60(2)	-70(3)	1(19)	-20(2)
C(325)	70(3)	32(19)	80(3)	6(18)	-10(2)	6(19)
C(326)	100(3)	70(2)	50(2)	2(18)	70(2)	-30(2)
C(327)	90(3)	160(4)	80(3)	20(3)	40(3)	-40(3)
C(331)	38(19)	90(3)	70(2)	50(2)	27(17)	17(19)
C(332)	50(2)	140(3)	60(2)	40(2)	50(19)	20(2)
C(333)	100(3)	50(2)	50(2)	2(17)	20(2)	50(2)
C(334)	20(2)	150(4)	110(3)	50(3)	0(2)	30(3)
C(335)	30(2)	190(4)	70(2)	10(3)	-2(19)	0(3)
C(336)	4(14)	160(3)	47(18)	50(2)	-14(14)	39(19)
C(337)	80(3)	180(4)	110(3)	70(3)	30(3)	50(3)

The anisotropic displacement factor exponent takes the form:
$-2 \, pi^2 \, [\, h^2 a^{*2} U_{11} + \ldots + 2 \, h \, k \, a^* \, b^* \, U_{12} \,]$

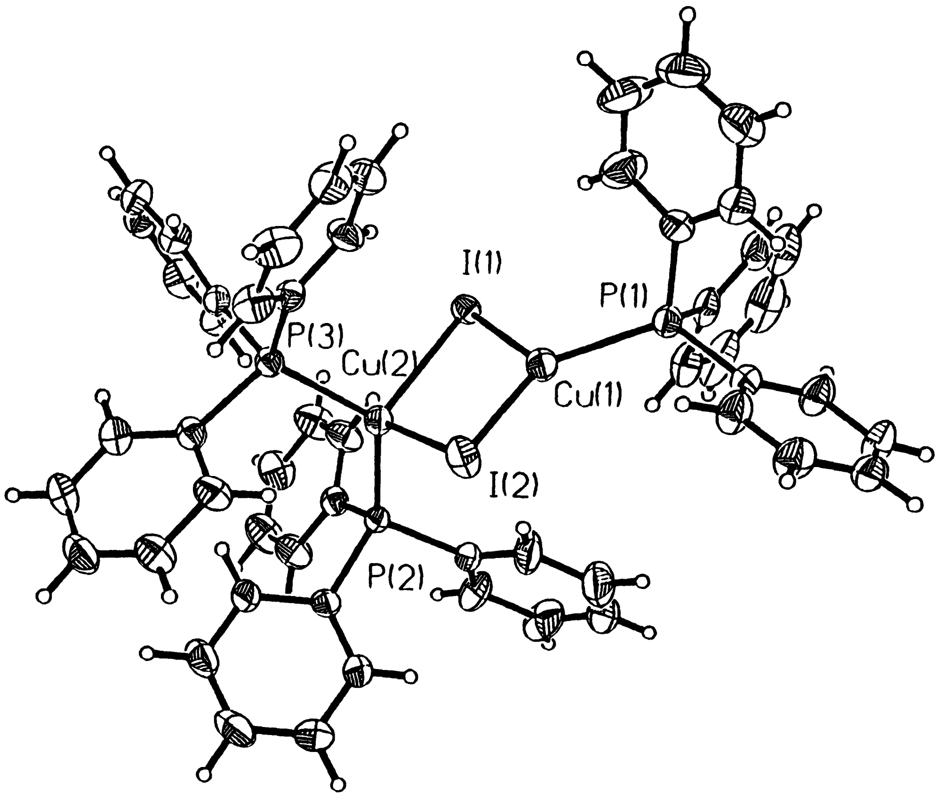


Figure 22 Projection View of $Cu_2I_2(P(C_6H_5)_3)_3$

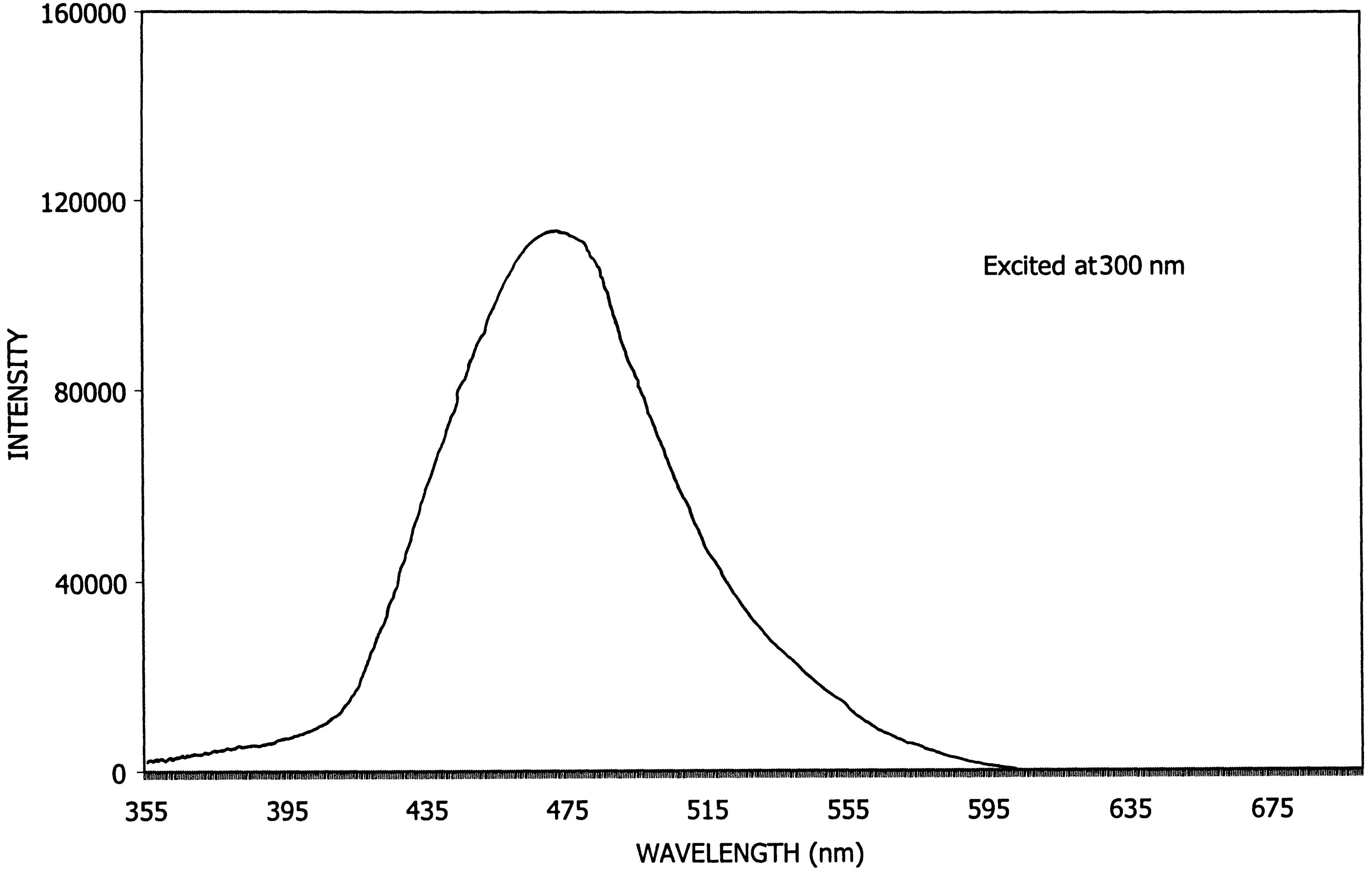


Figure 23 Emission Spectrum of $Cu_2I_2(P(C_6H_5)_3)_3$

Table 39. Crystal Data and Structure Refinement for $Cu_2I_2(P(C_6H_5)_3)_3$

Empirical formula	$C_{54}H_{45}Cu_2I_2P_3$	
Formula weight	1167.7	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	monoclinic, *P*2_1	
Unit cell dimensions	a = 10.714 (7) Å	α = 90.0 deg.
	b = 20.910 (14) Å	β = 105.92(3) deg.
	c = 11.903 (8) Å	γ = 90.0 deg.
Volume	1025(3) $Å^3$	
Z, Calculated density	2, 1.502 Mg/m^3	
Absorption coefficient	2.145 mm^{-1}	
F(000)	1156	
Crystal size	0.2 x 0.2 x 0.2 mm	
Theta range for data collection	1.8 to 30.0 deg.	
Index ranges	$-1 \leq h \leq 15$, $-29 \leq k \leq 29$, $-16 \leq l \leq 16$	
Reflections collected / unique/ observed	17220 / 15030 [R(int) = 0.418]/ 10772(4.0>σ(F))	
Goodness-of-fit	1.17	
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.0539	
R indices (all data)	R1 = 0.0694, wR2 = 0.0598	
Extinction coefficient	0.0021(5)	
Largest diff. peak and hole	1.79 and -2.20 $eÅ^{-3}$	

Table 40. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_2I_2(P(C_6H_5)_3)_3$

	x	y	z	U(eq)
I(1)	8050(1)	3882	8793(1)	48(1)
I(2)	9753(1)	2801(1)	6444(1)	70(1)
Cu(1)	8392(1)	3748(1)	6727(1)	54(1)
Cu(2)	9145(1)	2711(1)	8628(1)	47(1)
P(1)	7482(2)	4538(1)	5502(1)	52(1)
P(2)	7593(1)	1943(1)	8561(1)	43(1)
P(3)	11212(1)	2707(1)	9874(1)	42(1)
C(111)	7030(6)	4395(3)	3914(5)	52(2)
C(112)	7951(7)	4103(3)	3433(6)	70(3)
C(113)	7711(8)	4003(4)	2247(6)	77(3)
C(114)	6485(8)	4193(3)	1507(6)	69(3)
C(115)	5562(7)	4464(4)	1953(6)	75(3)
C(116)	5835(7)	4581(4)	3169(5)	67(3)
C(121)	8573(7)	5225(3)	5701(6)	60(2)
C(122)	8892(9)	5541(4)	4773(8)	89(3)
C(123)	9745(10)	6066(4)	4975(11)	108(5)
C(124)	10328(10)	6265(4)	6109(11)	105(5)
C(125)	10032(11)	5944(5)	7002(9)	121(5)
C(126)	9181(10)	5443(4)	6808(8)	97(4)
C(131)	5946(7)	4851(3)	5721(5)	64(2)
C(132)	5059(8)	4378(4)	5931(6)	78(3)
C(133)	3823(9)	4588(7)	5982(7)	116(5)
C(134)	3481(12)	5212(8)	5857(8)	126(6)
C(135)	4339(13)	5671(6)	5692(8)	126(5)
C(136)	5586(9)	5491(4)	5578(6)	81(3)
C(211)	8137(5)	1127(3)	8357(5)	50(2)
C(212)	9184(7)	872(3)	9242(7)	70(3)
C(213)	9606(7)	251(3)	9142(9)	83(3)
C(214)	9047(8)	-114(3)	8192(9)	84(4)
C(215)	8049(10)	132(4)	7323(9)	105(4)
C(216)	7581(8)	750(3)	7420(7)	81(3)
C(221)	7027(5)	1869(3)	9885(5)	50(2)
C(222)	6728(7)	1278(3)	10321(7)	71(3)
C(223)	6327(9)	1255(4)	11339(8)	88(4)
C(224)	6154(8)	1809(4)	11928(8)	85(4)
C(225)	6442(8)	2384(3)	11502(7)	83(3)
C(226)	6876(7)	2413(3)	10502(6)	68(3)
C(231)	6032(5)	2028(3)	7389(5)	54(2)
C(232)	4873(6)	1766(4)	7510(7)	78(3)
C(233)	3728(8)	1819(5)	6557(9)	102(4)
C(234)	3760(9)	2137(4)	5571(10)	105(4)

Table 40. (Continued)

C(235)	4884(11)	2370(4)	5435(9)	113(4)
C(236)	6058(8)	2326(4)	6370(7)	98(3)
C(311)	12019(5)	1919(3)	10020(5)	48(2)
C(312)	12468(7)	1594(3)	11071(6)	65(2)
C(313)	12948(8)	977(3)	11095(7)	75(3)
C(314)	13010(7)	673(3)	10087(7)	76(3)
C(315)	12590(8)	979(3)	9051(7)	76(3)
C(316)	12059(7)	1598(3)	8992(7)	67(3)
C(321)	12332(5)	3252(3)	9417(5)	47(2)
C(322)	11972(6)	3901(3)	9294(6)	65(2)
C(323)	12767(8)	4358(3)	8967(7)	76(3)
C(324)	13917(8)	4153(4)	8719(7)	78(3)
C(325)	14252(8)	3523(4)	8787(7)	80(3)
C(326)	13478(6)	3062(3)	9160(6)	66(3)
C(331)	11396(5)	2944(3)	11395(4)	46(2)
C(332)	12502(7)	3249(3)	12084(6)	63(2)
C(333)	12588(8)	3401(3)	13252(6)	76(3)
C(334)	11588(9)	3251(4)	13743(6)	77(3)
C(335)	10501(8)	2955(4)	13054(6)	73(3)
C(336)	10393(6)	2799(3)	11923(5)	59(2)
H(11A)	8767	3960	3931	80
H(11B)	8347	3811	1921	80
H(11C)	6313	4130	679	80
H(11D)	4724	4578	1456	80
H(11E)	5206	4804	3463	80
H(12A)	8454	5414	3988	80
H(12B)	9982	6267	4337	80
H(12C)	10896	6629	6238	80
H(12D)	10474	6071	7785	80
H(12E)	8957	5235	7446	80
H(13A)	5279	3932	6024	80
H(13B)	3199	4287	6112	80
H(13C)	2649	5350	5922	80
H(13D)	4106	6116	5653	80
H(13E)	6146	5800	5367	80
H(21A)	9499	1112	9952	80
H(21C)	10336	80	9722	80
H(21D)	9322	-547	8138	80
H(21E)	7727	-111	6618	80
H(21F)	6837	911	6840	80
H(22A)	6785	891	9904	80
H(22B)	6172	842	11629	80
H(22C)	5838	1792	12608	80
H(22E)	6374	2774	11908	80
H(22F)	7054	2825	10224	80

Table 40. (Continued)

H(23A)	4825	1557	8215	80
H(23B)	2930	1631	6615	80
H(23C)	2965	2181	4961	80
H(23D)	4910	2577	4722	80
H(23E)	6859	2496	6285	80
H(31A)	12432	1806	11777	80
H(31B)	13272	757	11825	80
H(31C)	13354	247	10118	80
H(31D)	12656	771	8350	80
H(31E)	11672	1800	8254	80
H(32A)	11164	4032	9424	80
H(32B)	12567	4807	8943	80
H(32C)	14431	4460	8444	80
H(32D)	15037	3395	8608	80
H(32E)	13714	2618	9224	80
H(33A)	13197	3357	11753	80
H(33B)	13359	3610	13709	80
H(33C)	11640	3359	14539	80
H(33D)	9815	2844	13393	80
H(33E)	9613	2597	11468	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 41. Bond Lengths [Å] and Angles [deg] for $Cu_2I_2(P(C_6H_5)_3)_3$

I(1)-Cu(1)	2.599 (2)
I(1)-Cu(2)	2.744 (2)
I(2)-Cu(1)	2.537 (2)
I(2)-Cu(2)	2.854 (2)
Cu(1)-P(1)	2.240 (2)
Cu(2)-P(2)	2.299 (2)
Cu(2)-P(3)	2.303 (2)
P(1)-C(111)	1.843 (6)
P(1)-C(121)	1.827 (7)
P(1)-C(131)	1.854 (8)
P(2)-C(211)	1.839 (6)
P(2)-C(221)	1.844 (7)
P(2)-C(231)	1.870 (5)
P(3)-C(311)	1.847 (6)
P(3)-C(321)	1.842 (6)
P(3)-C(331)	1.835 (6)
C(111)-C(112)	1.409 (11)
C(111)-C(116)	1.398 (9)
C(112)-C(113)	1.379 (10)
C(113)-C(114)	1.422 (10)
C(114)-C(115)	1.367 (12)
C(115)-C(116)	1.417 (10)
C(121)-C(122)	1.407 (12)
C(121)-C(126)	1.378 (10)
C(122)-C(123)	1.407 (13)
C(123)-C(124)	1.387 (16)
C(124)-C(125)	1.366 (17)
C(125)-C(126)	1.366 (15)
C(131)-C(132)	1.440 (12)
C(131)-C(136)	1.391 (11)
C(132)-C(133)	1.412 (14)
C(133)-C(134)	1.353 (22)
C(134)-C(135)	1.380 (20)
C(135)-C(136)	1.430 (17)
C(211)-C(212)	1.416 (8)
C(211)-C(216)	1.362 (9)
C(212)-C(213)	1.390 (10)
C(213)-C(214)	1.360 (12)
C(214)-C(215)	1.368 (12)
C(215)-C(216)	1.403 (11)
C(221)-C(222)	1.409 (9)
C(221)-C(226)	1.389 (9)
C(222)-C(223)	1.394 (13)

Table 41. (Continued)

C(223)-C(224)	1.393 (12)
C(224)-C(225)	1.373 (12)
C(225)-C(226)	1.392 (13)
C(231)-C(232)	1.399 (10)
C(231)-C(236)	1.371 (11)
C(232)-C(233)	1.428 (10)
C(233)-C(234)	1.358 (16)
C(234)-C(235)	1.349 (16)
C(235)-C(236)	1.436 (12)
C(311)-C(312)	1.389 (9)
C(311)-C(316)	1.406 (10)
C(312)-C(313)	1.387 (10)
C(313)-C(314)	1.375 (12)
C(314)-C(315)	1.353 (11)
C(315)-C(316)	1.408 (10)
C(321)-C(322)	1.407 (8)
C(321)-C(326)	1.402 (9)
C(322)-C(323)	1.405 (11)
C(323)-C(324)	1.411 (12)
C(324)-C(325)	1.362 (12)
C(325)-C(326)	1.421 (12)
C(331)-C(332)	1.397 (8)
C(331)-C(336)	1.418 (10)
C(332)-C(333)	1.405 (10)
C(333)-C(334)	1.389 (13)
C(334)-C(335)	1.374 (11)
C(335)-C(336)	1.360 (10)
Cu(1)-I(1)-Cu(2)	70.3(1)
Cu(1)-I(2)-Cu(2)	69.3(1)
I(1)-Cu(1)-I(2)	116.4(1)
I(1)-Cu(1)-P(1)	112.8(1)
I(2)-Cu(1)-P(1)	130.7(1)
I(1)-Cu(2)-I(2)	102.5(1)
I(1)-Cu(2)-P(2)	107.9(1)
I(2)-Cu(2)-P(2)	111.0(1)
I(1)-Cu(2)-P(3)	108.1(1)
I(2)-Cu(2)-P(3)	99.6(1)
P(2)-Cu(2)-P(3)	125.3(1)
Cu(1)-P(1)-C(111)	119.6(2)
Cu(1)-P(1)-C(121)	110.3(2)
C(111)-P(1)-C(121)	103.8(3)
Cu(1)-P(1)-C(131)	114.4(2)
C(111)-P(1)-C(131)	102.0(3)
C(121)-P(1)-C(131)	105.3(3)

Table 41. (Continued)

Cu(2)-P(2)-C(211)	113.6(2)
Cu(2)-P(2)-C(221)	115.7(2)
C(211)-P(2)-C(221)	103.0(3)
Cu(2)-P(2)-C(231)	116.7(2)
C(211)-P(2)-C(231)	103.9(2)
C(221)-P(2)-C(231)	102.0(3)
Cu(2)-P(3)-C(311)	114.0(2)
Cu(2)-P(3)-C(321)	113.4(2)
C(311)-P(3)-C(321)	104.7(3)
Cu(2)-P(3)-C(331)	117.3(2)
C(311)-P(3)-C(331)	103.1(2)
C(321)-P(3)-C(331)	102.9(3)
P(1)-C(111)-C(112)	118.1(4)
P(1)-C(111)-C(116)	122.9(6)
C(112)-C(111)-C(116)	119.0(6)
C(111)-C(112)-C(113)	121.8(6)
C(112)-C(113)-C(114)	118.3(8)
C(113)-C(114)-C(115)	121.2(6)
C(114)-C(115)-C(116)	120.0(6)
C(111)-C(116)-C(115)	119.7(7)
P(1)-C(121)-C(122)	123.5(5)
P(1)-C(121)-C(126)	120.1(6)
C(122)-C(121)-C(126)	116.3(7)
C(121)-C(122)-C(123)	121.2(8)
C(122)-C(123)-C(124)	119.9(11)
C(123)-C(124)-C(125)	118.2(9)
C(124)-C(125)-C(126)	122.1(9)
C(121)-C(126)-C(125)	122.2(9)
P(1)-C(131)-C(132)	115.8(6)
P(1)-C(131)-C(136)	123.4(6)
C(132)-C(131)-C(136)	120.5(7)
C(131)-C(132)-C(133)	117.8(9)
C(132)-C(133)-C(134)	121.5(11)
C(133)-C(134)-C(135)	121.1(12)
C(134)-C(135)-C(136)	120.4(12)
C(131)-C(136)-C(135)	118.5(9)
P(2)-C(211)-C(212)	117.7(5)
P(2)-C(211)-C(216)	124.2(5)
C(212)-C(211)-C(216)	118.1(6)
C(211)-C(212)-C(213)	119.8(6)
C(212)-C(213)-C(214)	121.1(7)
C(213)-C(214)-C(215)	119.4(7)
C(214)-C(215)-C(216)	120.5(8)
C(211)-C(216)-C(215)	121.0(7)
P(2)-C(221)-C(222)	123.3(5)

Table 41. (Continued)

P(2)-C(221)-C(226)	119.8(5)
C(222)-C(221)-C(226)	116.9(7)
C(221)-C(222)-C(223)	120.4(7)
C(222)-C(223)-C(224)	121.5(8)
C(223)-C(224)-C(225)	118.0(9)
C(224)-C(225)-C(226)	121.1(8)
C(221)-C(226)-C(225)	122.0(6)
P(2)-C(231)-C(232)	121.6(5)
P(2)-C(231)-C(236)	118.2(5)
C(232)-C(231)-C(236)	120.2(6)
C(231)-C(232)-C(233)	118.8(8)
C(232)-C(233)-C(234)	120.3(8)
C(233)-C(234)-C(235)	121.1(8)
C(234)-C(235)-C(236)	120.3(10)
C(231)-C(236)-C(235)	119.3(8)
P(3)-C(311)-C(312)	124.0(5)
P(3)-C(311)-C(316)	118.0(4)
C(312)-C(311)-C(316)	117.7(5)
C(311)-C(312)-C(313)	120.5(7)
C(312)-C(313)-C(314)	121.3(7)
C(313)-C(314)-C(315)	119.5(7)
C(314)-C(315)-C(316)	120.6(8)
C(311)-C(316)-C(315)	120.2(7)
P(3)-C(321)-C(322)	116.4(5)
P(3)-C(321)-C(326)	124.7(5)
C(322)-C(321)-C(326)	118.9(6)
C(321)-C(322)-C(323)	121.0(6)
C(322)-C(323)-C(324)	118.8(7)
C(323)-C(324)-C(325)	120.9(8)
C(324)-C(325)-C(326)	120.5(8)
C(321)-C(326)-C(325)	119.8(7)
P(3)-C(331)-C(332)	123.1(5)
P(3)-C(331)-C(336)	119.3(4)
C(332)-C(331)-C(336)	117.5(5)
C(331)-C(332)-C(333)	119.9(7)
C(332)-C(333)-C(334)	121.1(7)
C(333)-C(334)-C(335)	118.4(7)
C(334)-C(335)-C(336)	121.9(8)
C(331)-C(336)-C(335)	121.2(6)

Table 42. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(C_6H_5)_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	53(1)	44(1)	49(1)	4(1)	19(1)	1(1)
I(2)	96(1)	67(1)	54(1)	30(1)	35(1)	9(1)
Cu(1)	59(1)	52(1)	50(1)	6(1)	12(1)	2(1)
Cu(2)	44(1)	44(1)	51(1)	-4(1)	9(1)	4(1)
P(1)	61(1)	52(1)	40(1)	11(1)	9(1)	1(1)
P(2)	39(1)	39(1)	44(1)	-3(1)	0(1)	4(1)
P(3)	38(1)	42(1)	47(1)	1(1)	11(1)	3(1)
C(111)	59(4)	51(3)	44(3)	1(3)	9(3)	-2(2)
C(112)	70(4)	89(4)	51(3)	22(3)	14(3)	-8(3)
C(113)	88(5)	88(5)	59(4)	11(4)	28(4)	-15(4)
C(114)	95(6)	66(4)	47(3)	-8(4)	20(4)	-2(3)
C(115)	64(4)	105(5)	46(3)	10(4)	1(3)	-3(3)
C(116)	72(5)	87(5)	44(3)	9(4)	16(3)	-7(3)
C(121)	63(4)	50(3)	63(4)	5(3)	12(3)	-1(3)
C(122)	106(6)	78(5)	70(5)	-18(4)	0(4)	8(4)
C(123)	116(8)	75(5)	125(9)	-18(5)	19(7)	22(5)
C(124)	92(7)	67(4)	148(9)	-19(4)	20(7)	-14(5)
C(125)	122(8)	122(8)	105(7)	-46(6)	9(6)	-40(6)
C(126)	119(8)	99(6)	70(5)	-22(5)	22(5)	-24(4)
C(131)	71(4)	82(4)	35(3)	25(3)	6(3)	0(3)
C(132)	68(5)	115(6)	52(4)	20(4)	17(4)	10(4)
C(133)	65(6)	225(13)	55(4)	10(7)	11(4)	-2(5)
C(134)	103(8)	208(15)	66(5)	77(9)	24(5)	-17(7)
C(135)	142(9)	145(9)	69(5)	98(8)	-6(6)	-26(6)
C(136)	101(6)	83(5)	53(3)	36(4)	9(4)	-4(3)
C(211)	41(3)	41(3)	63(3)	-8(2)	6(3)	3(2)
C(212)	54(4)	52(3)	85(5)	-2(3)	-14(4)	7(3)
C(213)	52(4)	55(4)	127(8)	5(3)	-1(4)	17(4)
C(214)	79(5)	43(3)	127(8)	9(3)	27(5)	5(4)
C(215)	137(8)	65(4)	90(6)	22(5)	-8(6)	-31(4)
C(216)	88(5)	63(4)	70(4)	25(4)	-15(4)	-10(3)
C(221)	41(3)	51(3)	56(3)	-1(2)	11(2)	6(2)
C(222)	82(5)	55(3)	85(5)	-8(3)	35(4)	13(3)
C(223)	110(6)	68(4)	99(6)	-1(4)	53(5)	33(4)
C(224)	92(6)	89(5)	85(6)	-2(4)	43(5)	26(5)
C(225)	104(6)	64(4)	102(6)	-6(4)	66(5)	3(4)
C(226)	89(5)	48(3)	79(5)	-7(3)	41(4)	7(3)
C(231)	45(3)	47(3)	60(3)	4(2)	-6(3)	-2(2)
C(232)	42(4)	116(6)	67(4)	-2(4)	-2(3)	-5(4)
C(233)	42(4)	136(7)	111(7)	5(4)	-9(4)	-23(6)
C(234)	75(6)	87(5)	114(8)	15(4)	-38(5)	2(5)

Table 42. (Continued)

C(235)	118(8)	100(6)	95(6)	-22(6)	-15(6)	42(5)
C(236)	76(5)	94(5)	89(5)	-28(4)	-34(4)	43(4)
C(311)	39(3)	48(3)	57(3)	1(2)	13(2)	5(2)
C(312)	64(4)	64(4)	63(4)	9(3)	12(3)	9(3)
C(313)	80(5)	65(4)	81(5)	22(3)	22(4)	23(3)
C(314)	71(4)	51(3)	105(6)	18(3)	24(4)	7(4)
C(315)	83(5)	59(4)	89(5)	14(3)	30(4)	-2(4)
C(316)	77(5)	50(3)	77(4)	10(3)	28(4)	-3(3)
C(321)	40(3)	53(3)	47(3)	-2(2)	11(2)	2(2)
C(322)	54(3)	44(3)	95(5)	-5(3)	18(3)	11(3)
C(323)	80(5)	58(4)	87(5)	-20(3)	17(4)	18(3)
C(324)	70(5)	91(5)	74(5)	-31(4)	22(4)	17(4)
C(325)	62(5)	94(5)	93(6)	-21(4)	37(4)	-9(4)
C(326)	50(4)	76(4)	76(4)	-8(3)	26(3)	-3(3)
C(331)	47(3)	47(2)	42(3)	5(2)	7(2)	4(2)
C(332)	64(4)	60(3)	58(4)	-2(3)	6(3)	2(3)
C(333)	81(5)	74(4)	56(4)	1(4)	-10(4)	-1(3)
C(334)	107(6)	71(4)	49(4)	21(4)	13(4)	4(3)
C(335)	86(5)	81(4)	63(4)	19(4)	39(4)	10(3)
C(336)	60(4)	64(3)	55(3)	-1(3)	19(3)	-3(3)

The anisotropic displacement factor exponent takes the form:
$-2 \mathrm{pi}^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

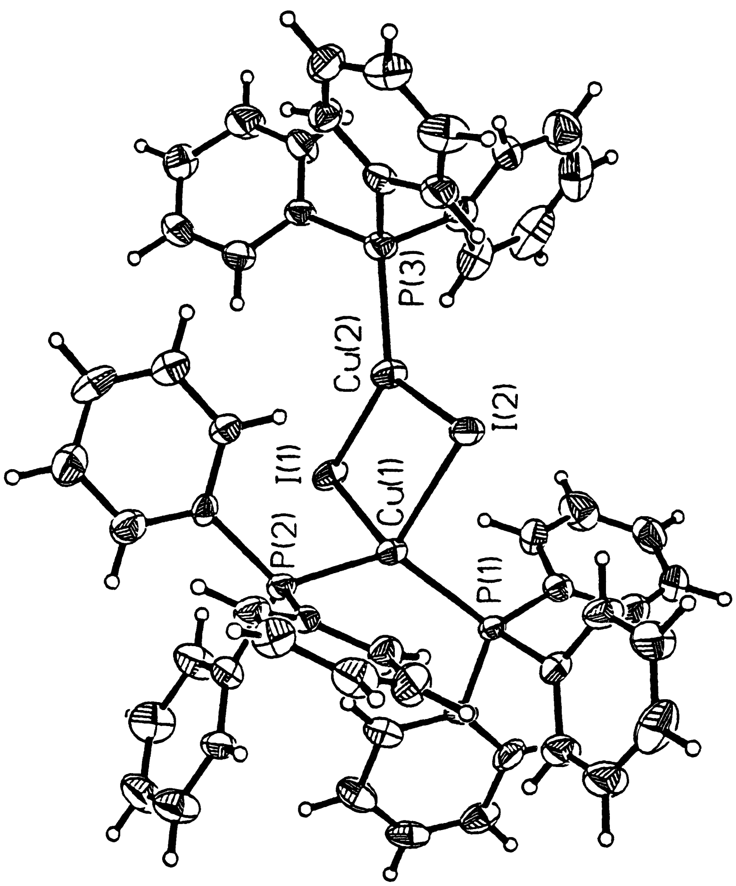


Figure 24 Projection View of $Cu_2I_2(P(C_6H_5)_3)_3$

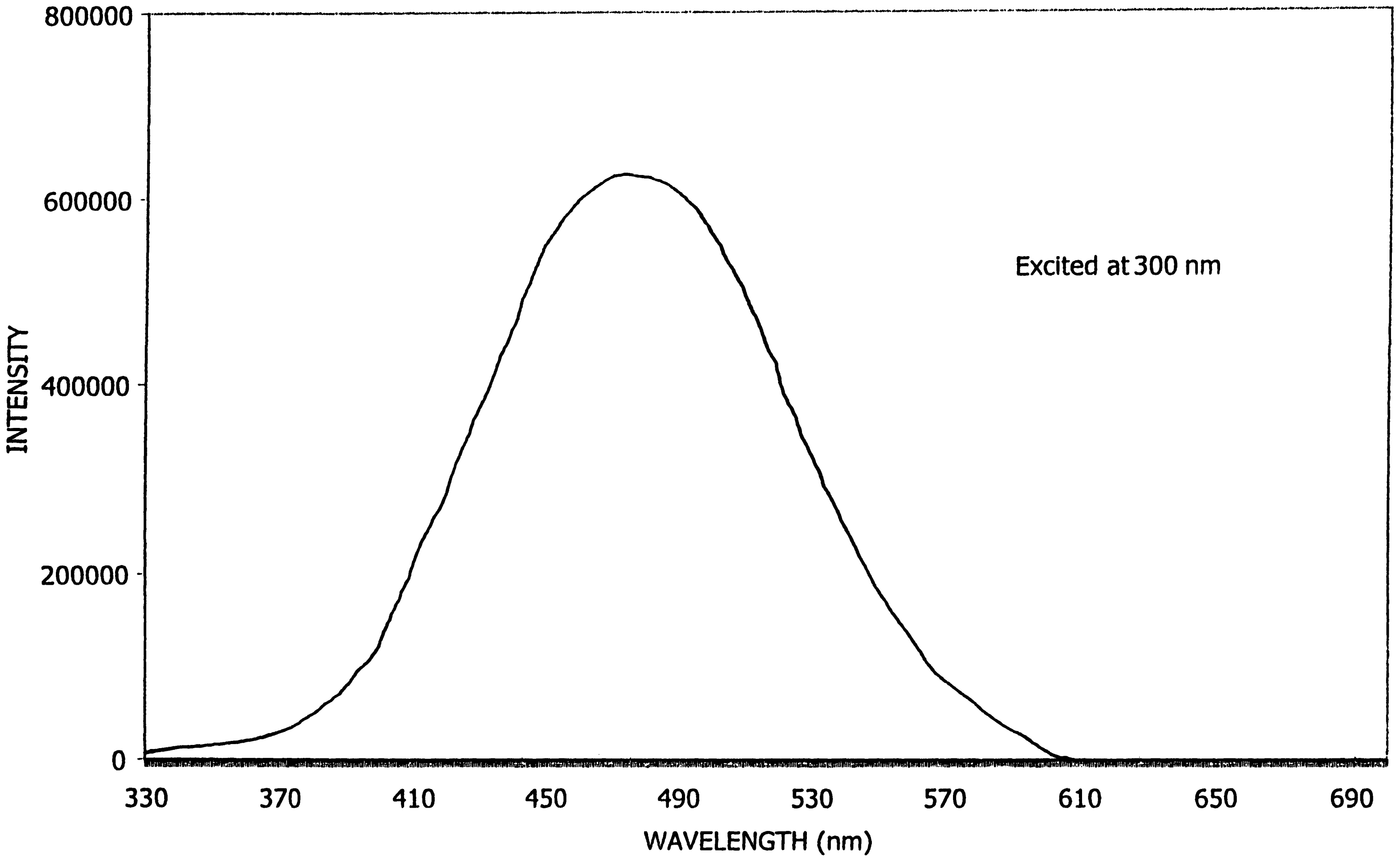


Figure 25 Emission Spectrum of $Cu_2I_2(P(C_6H_5)_3)_3$

Table 43. Crystal Data and Structure Refinement for $Cu_2I_2(P(C_6H_5)_3)_3$

Empirical formula	$C_{54}H_{45}Cu_2I_2P_3$	
Formula weight	1167.7	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	monoclinic, *P*2$_1$/*c*	
Unit cell dimensions	a = 15.921(12) Å	α = 90.0 deg.
	b = 19.763(11) Å	β = 109.69(9) deg.
	c = 18.46(2) Å	γ = 90.0 deg.
Volume	5469(8) Å^3	
Z, Calculated density	4, 1.418 Mg/m^3	
Absorption coefficient	2.026 mm^{-1}	
F(000)	2312	
Crystal size	0.2 x 0.2 x 0.2 mm	
Theta range for data collection	2.14 to 29.98 deg.	
Index ranges	$-1 \leq h \leq 22$, $-27 \leq k \leq 1$, $-26 \leq l \leq 24$	
Reflections collected / unique/ observed	18431/15924[R(int)=0.1614]/ 5546(8.0>σ(F))	
Goodness-of-fit	2.14	
Final R indices [I>2sigma(I)]	R1 = 0.0730, wR2 = 0.0955	
R indices (all data)	R1 = 0.1461, wR2 = 0.1511	
Extinction coefficient	0.00023(4)	
Largest diff. peak and hole	2.08 and –1.68 e. Å^{-3}	

Table 44. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_2I_2(P(C_6H_5)_3)_3$

	x	y	z	U(eq)
I(1)	2441(1)	-1661(1)	7500(1)	57(1)
I(2)	2638(1)	509(1)	7435(1)	55(1)
Cu(1)	3296(1)	-661(1)	6983(1)	43(1)
Cu(2)	2035(1)	-515(1)	7964(1)	57(1)
P(1)	2784(2)	-591(1)	5654(2)	41(1)
P(2)	4754(2)	-752(2)	7801(2)	42(1)
P(3)	1233(2)	-373(2)	8752(2)	54(1)
C(111)	1587(8)	-633(5)	5150(8)	48(5)
C(112)	1156(10)	-328(8)	4424(9)	74(7)
C(113)	268(11)	-400(8)	4050(9)	79(7)
C(114)	-249(10)	-762(9)	4334(10)	79(7)
C(115)	148(10)	-1083(8)	5049(12)	93(9)
C(116)	1068(8)	-994(7)	5457(8)	61(6)
C(121)	3204(8)	-1262(6)	5191(7)	47(5)
C(122)	3912(8)	-1665(6)	5662(9)	63(6)
C(123)	4234(9)	-2215(7)	5326(10)	70(7)
C(124)	3846(10)	-2345(7)	4536(10)	71(7)
C(125)	3176(11)	-1967(7)	4073(9)	71(7)
C(126)	2826(10)	-1409(7)	4391(8)	71(6)
C(131)	3141(8)	193(6)	5289(7)	49(5)
C(132)	2792(10)	814(6)	5439(9)	74(7)
C(133)	3040(14)	1396(7)	5184(12)	114(11)
C(134)	3646(13)	1385(9)	4778(11)	109(10)
C(135)	4024(11)	784(8)	4671(11)	94(9)
C(136)	3742(8)	203(7)	4871(8)	65(6)
C(211)	5441(7)	-1442(6)	7587(7)	50(5)
C(212)	5179(9)	-2101(6)	7659(10)	77(7)
C(213)	5700(11)	-2649(8)	7530(10)	89(8)
C(214)	6444(10)	-2513(8)	7323(10)	91(8)
C(215)	6662(10)	-1837(7)	7235(10)	80(8)
C(216)	6172(8)	-1316(7)	7368(7)	56(5)
C(221)	5401(7)	12(5)	7758(7)	39(4)
C(222)	6121(8)	227(6)	8377(8)	54(5)
C(223)	6579(9)	818(7)	8332(9)	67(6)
C(224)	6337(9)	1186(7)	7635(9)	66(7)
C(225)	5617(10)	959(7)	7013(10)	77(7)
C(226)	5156(8)	389(7)	7077(8)	60(6)
C(231)	4927(7)	-890(5)	8831(7)	42(4)
C(232)	4276(8)	-669(6)	9132(7)	51(5)
C(233)	4367(10)	-743(7)	9894(9)	63(6)
C(234)	5088(12)	-1049(8)	10379(9)	81(8)

Table 44. (Continued)

C(235)	5753(10)	-1291(8)	10105(9)	82(7)
C(236)	5640(9)	-1191(7)	9308(8)	67(6)
C(311)	54(8)	-272(7)	8205(8)	63(6)
C(312)	-348(11)	-777(8)	7612(9)	81(7)
C(313)	-1262(14)	-692(11)	7196(10)	110(10)
C(314)	-1756(12)	-152(14)	7313(16)	126(13)
C(315)	-1340(13)	318(11)	7881(13)	101(10)
C(316)	-469(9)	261(8)	8289(9)	74(7)
C(321)	1514(8)	375(6)	9384(8)	52(5)
C(322)	1657(8)	362(7)	10176(8)	59(6)
C(323)	1884(9)	934(9)	10617(9)	75(7)
C(324)	1922(9)	1549(8)	10274(10)	75(7)
C(325)	1802(10)	1593(7)	9530(10)	81(8)
C(326)	1595(9)	980(7)	9040(9)	68(6)
C(331)	1229(8)	-1071(6)	9412(7)	54(5)
C(332)	559(9)	-1145(7)	9729(9)	76(7)
C(333)	588(10)	-1646(8)	10252(10)	87(8)
C(334)	1311(10)	-2097(7)	10489(9)	75(7)
C(335)	1996(9)	-2012(7)	10160(9)	70(7)
C(336)	1933(8)	-1516(6)	9616(8)	58(6)
H(11A)	1508	-61	4198	80
H(11B)	-5	-177	3566	80
H(11C)	-877	-819	4066	80
H(11D)	-208	-1353	5267	80
H(11E)	1333	-1221	5940	80
H(12A)	4171	-1567	6201	80
H(12B)	4722	-2488	5635	80
H(12C)	4068	-2713	4313	80
H(12D)	2921	-2071	3535	80
H(12E)	2348	-1134	4071	80
H(13A)	2365	819	5703	80
H(13B)	2801	1820	5279	80
H(13C)	3838	1801	4615	80
H(13D)	4455	780	4411	80
H(13E)	3968	-220	4757	80
H(21A)	4663	-2195	7800	80
H(21B)	5523	-3108	7571	80
H(21C)	6790	-2883	7237	80
H(21D)	7165	-1748	7073	80
H(21E)	6364	-860	7337	80
H(22A)	6296	-26	8848	80
H(22B)	7072	976	8760	80
H(22C)	6644	1591	7582	80
H(22D)	5464	1193	6530	80

Table 44. (Continued)

H(22E)	4638	255	6657	80
H(23A)	3753	-451	8791	80
H(23B)	3905	-595	10083	80
H(23C)	5151	-1093	10913	80
H(23D)	6278	-1501	10454	80
H(23E)	6089	-1358	9113	80
H(31A)	3	-1135	7510	80
H(31B)	-1547	-1018	6805	80
H(31C)	-2384	-129	7033	80
H(31D)	-1686	693	7955	80
H(31E)	-198	598	8671	80
H(32A)	1624	-66	10410	80
H(32B)	1986	908	11159	80
H(32C)	2081	1949	10585	80
H(32D)	1827	2024	9298	80
H(32E)	1509	1003	8500	80
H(33A)	57	-843	9568	80
H(33B)	121	-1693	10470	80
H(33C)	1338	-2450	10853	80
H(33D)	2498	-2313	10321	80
H(33E)	2389	-1478	9386	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 45. Bond Lengths [Å] and Angles [deg] for $Cu_2I_2(P(C_6H_5)_3)_3$

I(1)-Cu(1)	2.746 (3)
I(1)-Cu(2)	2.579 (3)
I(2)-Cu(1)	2.779 (3)
I(2)-Cu(2)	2.569 (3)
Cu(1)-P(1)	2.314 (4)
Cu(1)-P(2)	2.311 (4)
Cu(2)-P(3)	2.254 (5)
P(1)-C(111)	1.819 (12)
P(1)-C(121)	1.824 (13)
P(1)-C(131)	1.854 (13)
P(2)-C(211)	1.871 (13)
P(2)-C(221)	1.844 (11)
P(2)-C(231)	1.848 (13)
P(3)-C(311)	1.818 (12)
P(3)-C(321)	1.841 (13)
P(3)-C(331)	1.842 (14)
C(111)-C(112)	1.418 (19)
C(111)-C(116)	1.351 (21)
C(112)-C(113)	1.356 (20)
C(113)-C(114)	1.325 (27)
C(114)-C(115)	1.408 (25)
C(115)-C(116)	1.414 (19)
C(121)-C(122)	1.413 (16)
C(121)-C(126)	1.423 (18)
C(122)-C(123)	1.429 (21)
C(123)-C(124)	1.404 (23)
C(124)-C(125)	1.345 (20)
C(125)-C(126)	1.446 (23)
C(131)-C(132)	1.413 (19)
C(131)-C(136)	1.417 (22)
C(132)-C(133)	1.352 (23)
C(133)-C(134)	1.407 (34)
C(134)-C(135)	1.375 (26)
C(135)-C(136)	1.331 (23)
C(211)-C(212)	1.387 (18)
C(211)-C(216)	1.378 (20)
C(212)-C(213)	1.432 (23)
C(213)-C(214)	1.388 (27)
C(214)-C(215)	1.404 (22)
C(215)-C(216)	1.363 (21)
C(221)-C(222)	1.384 (15)
C(221)-C(226)	1.399 (18)
C(222)-C(223)	1.393 (19)

Table 45. (Continued)

C(223)-C(224)	1.414 (22)
C(224)-C(225)	1.395 (19)
C(225)-C(226)	1.371 (21)
C(231)-C(232)	1.401 (19)
C(231)-C(236)	1.321 (16)
C(232)-C(233)	1.373 (21)
C(233)-C(234)	1.338 (20)
C(234)-C(235)	1.404 (27)
C(235)-C(236)	1.436 (23)
C(311)-C(312)	1.459 (20)
C(311)-C(316)	1.384 (22)
C(312)-C(313)	1.408 (24)
C(313)-C(314)	1.386 (35)
C(314)-C(315)	1.389 (33)
C(315)-C(316)	1.341 (22)
C(321)-C(322)	1.402 (20)
C(321)-C(326)	1.380 (19)
C(322)-C(323)	1.368 (21)
C(323)-C(324)	1.381 (24)
C(324)-C(325)	1.324 (26)
C(325)-C(326)	1.481 (21)
C(331)-C(332)	1.387 (23)
C(331)-C(336)	1.373 (17)
C(332)-C(333)	1.374 (23)
C(333)-C(334)	1.404 (21)
C(334)-C(335)	1.426 (25)
C(335)-C(336)	1.383 (20)

Cu(1)-I(1)-Cu(2)	72.1(1)
Cu(1)-I(2)-Cu(2)	71.7(1)
I(1)-Cu(1)-I(2)	102.3(1)
I(1)-Cu(1)-P(1)	111.9(1)
I(2)-Cu(1)-P(1)	103.6(1)
I(1)-Cu(1)-P(2)	102.9(1)
I(2)-Cu(1)-P(2)	105.4(1)
P(1)-Cu(1)-P(2)	127.9(2)
I(1)-Cu(2)-I(2)	113.4(1)
I(1)-Cu(2)-P(3)	125.7(1)
I(2)-Cu(2)-P(3)	120.8(1)
Cu(1)-P(1)-C(111)	118.3(5)
Cu(1)-P(1)-C(121)	113.5(4)
C(111)-P(1)-C(121)	102.3(5)
Cu(1)-P(1)-C(131)	113.2(4)
C(111)-P(1)-C(131)	104.5(5)

Table 45. (Continued)

C(121)-P(1)-C(131)	103.4(6)
Cu(1)-P(2)-C(211)	116.7(4)
Cu(1)-P(2)-C(221)	111.2(3)
C(211)-P(2)-C(221)	102.3(6)
Cu(1)-P(2)-C(231)	116.9(4)
C(211)-P(2)-C(231)	102.4(5)
C(221)-P(2)-C(231)	105.8(5)
Cu(2)-P(3)-C(311)	111.0(5)
Cu(2)-P(3)-C(321)	116.1(5)
C(311)-P(3)-C(321)	104.5(6)
Cu(2)-P(3)-C(331)	117.5(5)
C(311)-P(3)-C(331)	102.5(6)
C(321)-P(3)-C(331)	103.7(6)
P(1)-C(111)-C(112)	123.6(11)
P(1)-C(111)-C(116)	119.5(9)
C(112)-C(111)-C(116)	116.8(11)
C(111)-C(112)-C(113)	121.7(16)
C(112)-C(113)-C(114)	122.4(15)
C(113)-C(114)-C(115)	118.1(14)
C(114)-C(115)-C(116)	120.0(17)
C(111)-C(116)-C(115)	120.8(14)
P(1)-C(121)-C(122)	117.6(10)
P(1)-C(121)-C(126)	122.7(9)
C(122)-C(121)-C(126)	119.6(12)
C(121)-C(122)-C(123)	119.3(13)
C(122)-C(123)-C(124)	119.6(12)
C(123)-C(124)-C(125)	122.4(15)
C(124)-C(125)-C(126)	119.8(14)
C(121)-C(126)-C(125)	119.4(12)
P(1)-C(131)-C(132)	117.7(11)
P(1)-C(131)-C(136)	123.7(9)
C(132)-C(131)-C(136)	118.6(12)
C(131)-C(132)-C(133)	119.4(17)
C(132)-C(133)-C(134)	120.3(16)
C(133)-C(134)-C(135)	120.2(18)
C(134)-C(135)-C(136)	120.0(19)
C(131)-C(136)-C(135)	121.0(14)
P(2)-C(211)-C(212)	116.6(11)
P(2)-C(211)-C(216)	122.8(9)
C(212)-C(211)-C(216)	120.6(13)
C(211)-C(212)-C(213)	119.0(15)
C(212)-C(213)-C(214)	119.7(14)
C(213)-C(214)-C(215)	118.9(15)
C(214)-C(215)-C(216)	121.3(16)

Table 45. (Continued)

C(211)-C(216)-C(215)	120.5(13)
P(2)-C(221)-C(222)	122.4(9)
P(2)-C(221)-C(226)	118.9(8)
C(222)-C(221)-C(226)	118.7(11)
C(221)-C(222)-C(223)	120.9(12)
C(222)-C(223)-C(224)	119.8(11)
C(223)-C(224)-C(225)	118.7(13)
C(224)-C(225)-C(226)	120.6(14)
C(221)-C(226)-C(225)	121.3(11)
P(2)-C(231)-C(232)	119.3(8)
P(2)-C(231)-C(236)	123.2(12)
C(232)-C(231)-C(236)	117.5(13)
C(231)-C(232)-C(233)	122.5(11)
C(232)-C(233)-C(234)	120.3(16)
C(233)-C(234)-C(235)	119.6(16)
C(234)-C(235)-C(236)	118.3(13)
C(231)-C(236)-C(235)	121.9(15)
P(3)-C(311)-C(312)	116.9(11)
P(3)-C(311)-C(316)	124.6(10)
C(312)-C(311)-C(316)	118.4(11)
C(311)-C(312)-C(313)	116.1(16)
C(312)-C(313)-C(314)	122.9(18)
C(313)-C(314)-C(315)	118.8(17)
C(314)-C(315)-C(316)	120.4(20)
C(311)-C(316)-C(315)	123.3(15)
P(3)-C(321)-C(322)	124.4(10)
P(3)-C(321)-C(326)	116.3(11)
C(322)-C(321)-C(326)	119.2(12)
C(321)-C(322)-C(323)	121.5(13)
C(322)-C(323)-C(324)	119.9(15)
C(323)-C(324)-C(325)	121.3(15)
C(324)-C(325)-C(326)	120.3(15)
C(321)-C(326)-C(325)	117.6(14)
P(3)-C(331)-C(332)	122.1(9)
P(3)-C(331)-C(336)	118.5(11)
C(332)-C(331)-C(336)	119.3(12)
C(331)-C(332)-C(333)	121.6(13)
C(332)-C(333)-C(334)	120.4(17)
C(333)-C(334)-C(335)	117.2(14)
C(334)-C(335)-C(336)	120.9(12)
C(331)-C(336)-C(335)	120.4(14)

Table 46. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(C_6H_5)_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	79(1)	47(1)	55(1)	-13(1)	37(1)	4(1)
I(2)	73(1)	44(1)	60(1)	6(1)	40(1)	2(1)
Cu(1)	47(1)	48(1)	41(1)	-2(1)	22(1)	2(1)
Cu(2)	61(1)	64(1)	56(1)	-3(1)	32(1)	1(1)
P(1)	50(2)	41(2)	39(2)	4(1)	24(1)	4(1)
P(2)	44(2)	44(2)	44(2)	-1(1)	23(1)	4(1)
P(3)	58(2)	55(2)	59(2)	4(2)	35(2)	8(2)
C(111)	57(7)	36(6)	53(8)	3(5)	22(6)	-4(6)
C(112)	65(9)	93(11)	66(11)	-3(8)	25(8)	8(9)
C(113)	81(11)	96(12)	54(10)	26(9)	13(9)	17(9)
C(114)	58(9)	92(12)	75(12)	16(9)	6(9)	-12(10)
C(115)	70(10)	87(12)	131(17)	-2(9)	47(11)	14(12)
C(116)	58(8)	64(9)	56(9)	1(7)	11(7)	17(7)
C(121)	52(7)	44(6)	58(9)	-2(6)	36(6)	-4(6)
C(122)	56(7)	60(8)	81(10)	-1(7)	35(7)	-11(8)
C(123)	71(9)	50(8)	95(13)	8(7)	35(9)	-17(8)
C(124)	92(10)	49(8)	95(13)	-6(8)	64(10)	-23(9)
C(125)	115(12)	54(8)	62(10)	-9(9)	53(10)	-13(8)
C(126)	106(11)	74(9)	40(9)	12(8)	36(8)	7(7)
C(131)	62(7)	48(7)	39(8)	-4(6)	20(6)	3(6)
C(132)	121(12)	43(7)	87(11)	5(8)	73(10)	5(8)
C(133)	186(19)	47(9)	160(19)	45(10)	124(17)	38(10)
C(134)	139(16)	84(13)	111(16)	-25(12)	50(13)	43(12)
C(135)	111(13)	71(10)	137(17)	12(10)	90(12)	27(11)
C(136)	69(8)	56(8)	84(11)	-2(7)	47(8)	9(8)
C(211)	47(7)	44(7)	64(9)	1(5)	23(6)	0(6)
C(212)	79(9)	40(7)	136(15)	6(7)	67(10)	16(8)
C(213)	106(12)	55(9)	117(15)	-15(9)	54(11)	-6(9)
C(214)	79(10)	71(11)	136(16)	25(8)	55(11)	11(11)
C(215)	90(10)	57(9)	114(14)	5(8)	64(10)	-6(9)
C(216)	56(7)	61(8)	63(9)	6(6)	36(7)	2(7)
C(221)	39(6)	41(6)	43(7)	0(5)	20(6)	6(6)
C(222)	61(8)	56(8)	55(9)	-4(6)	33(7)	5(7)
C(223)	64(8)	73(9)	67(10)	-18(7)	25(8)	-10(8)
C(224)	65(9)	50(8)	93(12)	-9(7)	39(9)	-1(8)
C(225)	79(10)	68(9)	96(13)	-1(8)	46(10)	40(9)
C(226)	51(7)	70(9)	56(9)	-6(6)	14(7)	13(7)
C(231)	42(6)	41(6)	40(7)	-2(5)	12(6)	14(6)
C(232)	56(7)	57(8)	44(8)	-2(6)	22(6)	3(6)
C(233)	68(9)	71(9)	56(10)	-11(8)	27(8)	-5(8)
C(234)	108(12)	98(12)	52(10)	-29(10)	46(10)	-2(9)

Table 46. (Continued)

C(235)	87(10)	91(12)	66(11)	5(9)	24(9)	18(9)
C(236)	70(9)	78(10)	60(10)	-4(8)	30(8)	8(8)
C(311)	58(8)	78(9)	60(9)	-6(7)	30(7)	18(8)
C(312)	92(11)	75(10)	65(11)	-22(9)	12(9)	5(9)
C(313)	104(14)	133(18)	72(13)	-77(13)	3(11)	10(12)
C(314)	60(11)	162(23)	161(24)	-1(14)	43(14)	103(20)
C(315)	83(14)	105(15)	119(18)	10(11)	41(12)	27(13)
C(316)	58(9)	97(11)	66(10)	26(8)	21(8)	15(9)
C(321)	53(7)	41(6)	73(10)	5(5)	36(7)	6(6)
C(322)	72(8)	59(8)	46(8)	0(7)	18(7)	-6(7)
C(323)	65(9)	111(13)	50(10)	2(9)	20(8)	3(10)
C(324)	74(9)	83(11)	75(12)	-12(8)	35(9)	-20(10)
C(325)	95(11)	60(9)	110(14)	-18(8)	63(11)	-12(10)
C(326)	82(9)	64(9)	77(11)	15(7)	50(8)	18(8)
C(331)	62(7)	52(7)	64(9)	6(6)	42(7)	8(7)
C(332)	76(9)	71(9)	106(13)	29(7)	63(9)	45(9)
C(333)	90(10)	91(11)	104(13)	7(9)	65(10)	21(11)
C(334)	115(12)	43(7)	75(11)	12(8)	43(10)	17(7)
C(335)	77(9)	57(9)	80(11)	22(7)	32(9)	4(8)
C(336)	62(8)	56(8)	64(9)	4(6)	32(7)	-1(7)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

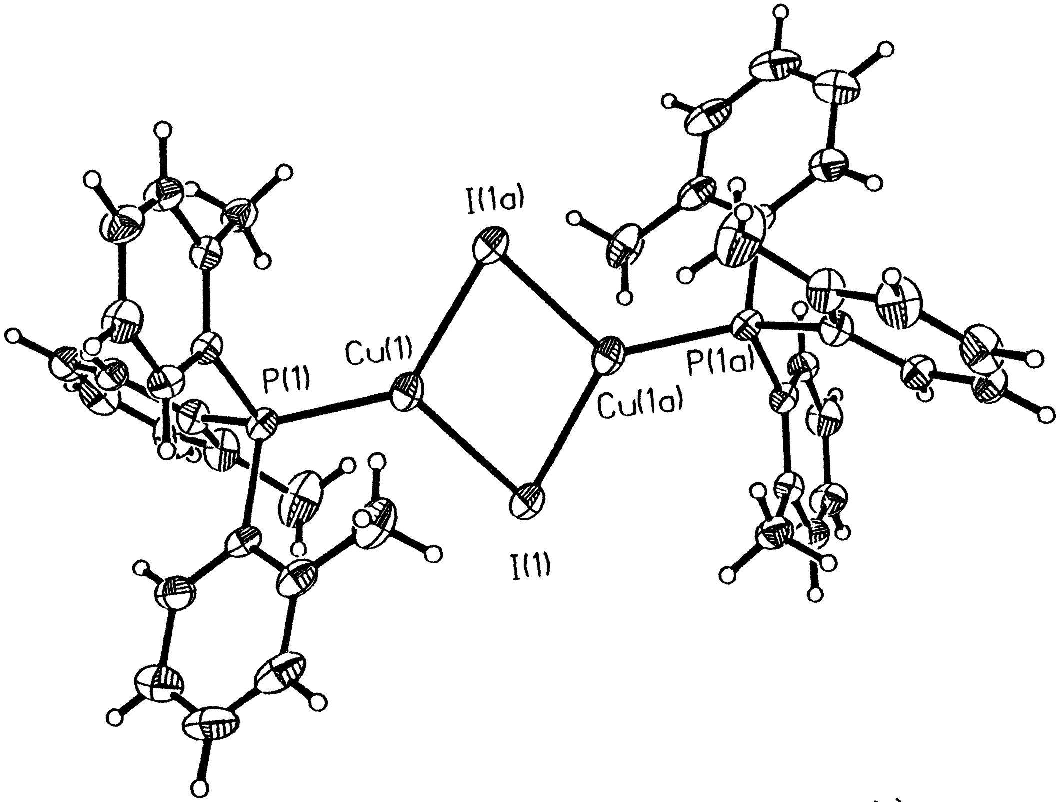


Figure 26 Projection View of $Cu_2I_2(P(o\text{-}C_7H_7)_3)_2$

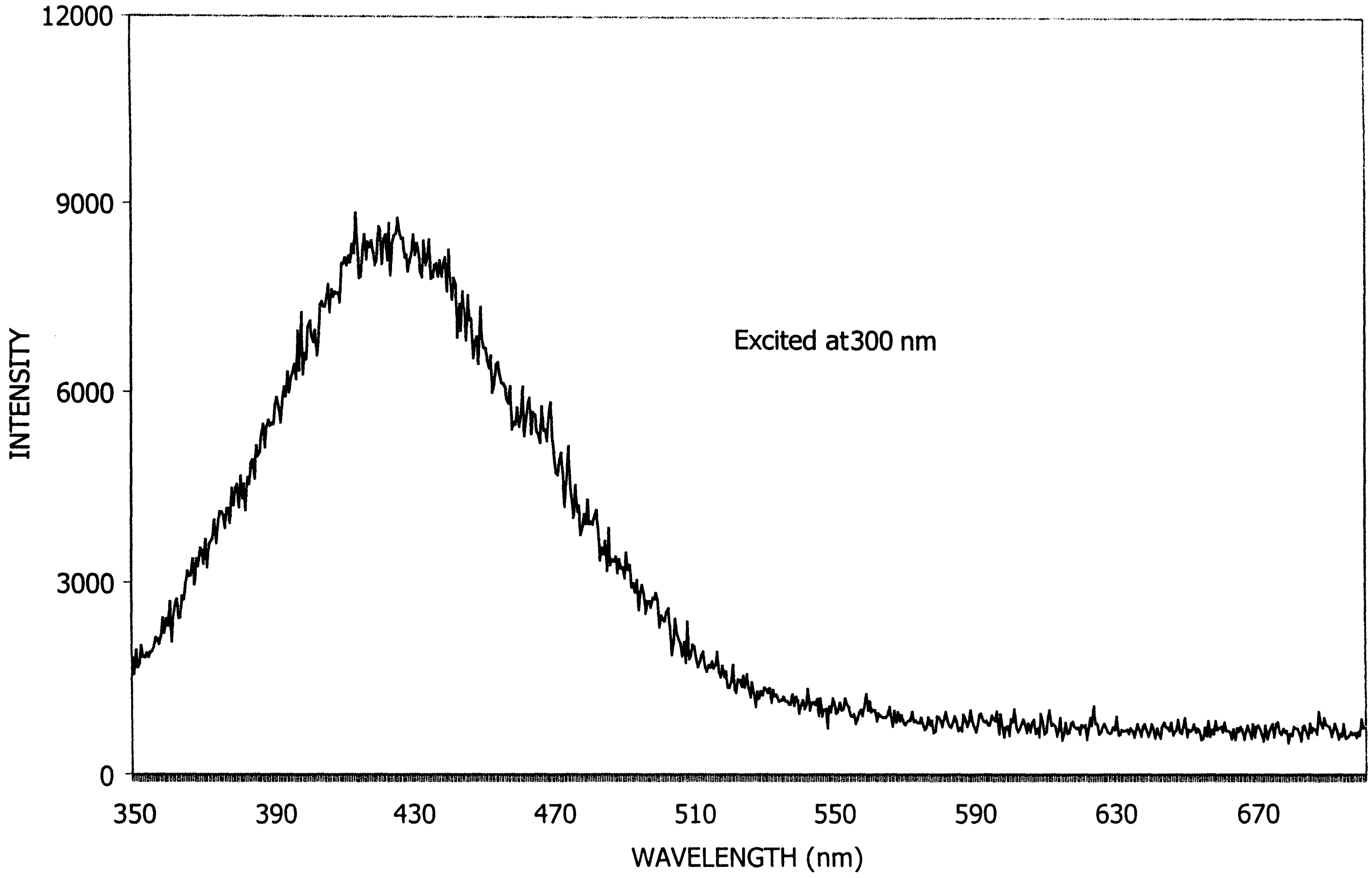


Figure 27 Emission Spectrum of $Cu_2I_2(P(o\text{-}C_7H_7)_3)_2$

Table 47. Crystal Data and Structure Refinement for $Cu_2I_2(P(C_7H_7)_3)_2$

Empirical formula	$C_{21}H_{21}CuIP$	
Formula weight	494.8	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell dimensions	a = 9.363(2) Å	α = 102.180(10) deg.
	b = 10.130(2) Å	β = 99.01(2) deg.
	c = 11.689(3) Å	γ = 101.79(2) deg.
Volume	1037.6(4) $Å^3$	
Z, Calculated density	2, 1.584 Mg/m^3	
Absorption coefficient	2.616 mm^{-1}	
F(000)	488	
Crystal size	0.1 x 0.1 x 0.1 mm	
Theta range for data collection	2.14 to 29.98 deg.	
Index ranges	$-13 \leq h \leq 1$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$	
Reflections collected / unique/ observed	7003 / 5983 [R(int) = 0.0416]/ 3578(4.0>σ(F))	
Goodness-of-fit	1.20	
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.0641	
R indices (all data)	R1 = 0.0908, wR2 = 0.0694	
Extinction coefficient	-0.00149(16)	
Largest diff. peak and hole	1.42 and –0.59 $eÅ^{-3}$	

Table 48. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $Cu_2I_2(P(C_7H_7)_3)_2$

	x	y	z	U(eq)
I(1)	777(1)	6053(1)	8802(1)	58(1)
Cu(1)	1225(1)	6039(1)	11054(1)	48(1)
P(1)	2856(2)	7662(2)	12566(1)	37(1)
C(111)	3065(6)	9441(6)	12352(4)	41(2)
C(121)	4771(6)	7452(6)	12899(5)	43(2)
C(131)	2233(6)	7759(5)	13994(4)	37(2)
C(112)	1816(7)	9897(7)	11927(5)	51(2)
C(132)	1917(6)	8975(6)	14582(5)	42(2)
C(116)	4493(8)	10330(7)	12597(6)	56(3)
C(126)	5474(7)	7629(6)	14101(5)	48(2)
C(133)	1371(7)	9056(7)	15638(5)	55(2)
C(114)	3448(11)	12125(8)	12010(7)	77(4)
C(122)	5534(7)	7074(7)	11985(6)	56(2)
C(125)	6882(7)	7368(7)	14370(6)	59(3)
C(117)	247(8)	8998(8)	11659(6)	67(3)
C(124)	7602(8)	6940(7)	13448(8)	70(3)
C(115)	4676(10)	11669(8)	12418(7)	74(3)
C(123)	6911(8)	6811(8)	12291(7)	69(3)
C(127)	4899(10)	6962(12)	10693(6)	93(4)
C(113)	2041(10)	11254(8)	11763(6)	69(3)
C(136)	2015(6)	6574(6)	14476(5)	43(2)
C(137)	2421(7)	5236(6)	13960(5)	51(2)
C(135)	1461(7)	6714(7)	15540(5)	53(2)
C(134)	1143(7)	7918(7)	16106(5)	57(3)
H(13A)	2079	9771	14252	80
H(11A)	5347	10012	12881	80
H(12A)	4985	7931	14736	80
H(13B)	1151	9901	16030	80
H(11B)	3573	13048	11893	80
H(12B)	7350	7484	15189	80
H(11C)	270	8107	11810	80
H(11D)	-322	9445	12164	80
H(11E)	-206	8874	10835	80
H(12C)	8554	6730	13626	80
H(11F)	5655	12279	12587	80
H(12D)	7417	6531	11662	80
H(12E)	5574	6703	10199	80
H(12F)	3967	6270	10444	80
H(12G)	4733	7847	10618	80
H(11G)	1195	11581	11477	80
H(13C)	2781	5305	13244	80

Table 48. (Continued)

H(13D)	3185	5082	14531	80
H(13E)	1555	4473	13773	80
H(13F)	1300	5925	15880	80
H(13G)	765	7961	16827	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 49. Bond Lengths [Å] and Angles [deg] for $Cu_2I_2(P(C_7H_7)_3)_2$

I(1)-Cu(1)	2.604 (1)
I(1)-Cu(1A)	2.581 (1)
Cu(1)-P(1)	2.250 (1)
Cu(1)-I(1A)	2.581 (1)
P(1)-C(111)	1.847 (6)
P(1)-C(121)	1.839 (6)
P(1)-C(131)	1.842 (6)
C(111)-C(112)	1.401 (9)
C(111)-C(116)	1.400 (8)
C(121)-C(126)	1.413 (8)
C(121)-C(122)	1.406 (9)
C(131)-C(132)	1.391 (8)
C(131)-C(136)	1.422 (8)
C(112)-C(117)	1.508 (9)
C(112)-C(113)	1.405 (11)
C(132)-C(133)	1.401 (9)
C(116)-C(115)	1.396 (11)
C(126)-C(125)	1.398 (10)
C(133)-C(134)	1.370 (11)
C(114)-C(115)	1.379 (14)
C(114)-C(113)	1.376 (12)
C(122)-C(123)	1.377 (10)
C(122)-C(127)	1.506 (10)
C(125)-C(124)	1.398 (12)
C(124)-C(123)	1.371 (12)
C(136)-C(137)	1.511 (9)
C(136)-C(135)	1.412 (9)
C(135)-C(134)	1.372 (10)
Cu(1)-I(1)-Cu(1A)	74.4(1)
I(1)-Cu(1)-P(1)	126.5(1)
I(1)-Cu(1)-I(1A)	105.6(1)
P(1)-Cu(1)-I(1A)	127.7(1)
Cu(1)-P(1)-C(111)	112.8(2)
Cu(1)-P(1)-C(121)	117.3(2)
C(111)-P(1)-C(121)	105.1(3)
Cu(1)-P(1)-C(131)	111.7(2)
C(111)-P(1)-C(131)	104.4(3)
C(121)-P(1)-C(131)	104.5(3)
P(1)-C(111)-C(112)	120.8(4)
P(1)-C(111)-C(116)	119.4(5)
C(112)-C(111)-C(116)	119.9(6)
P(1)-C(121)-C(126)	119.2(5)

Table 49. (Continued)

P(1)-C(121)-C(122)	121.7(4)
C(126)-C(121)-C(122)	119.1(6)
P(1)-C(131)-C(132)	120.1(4)
P(1)-C(131)-C(136)	120.2(4)
C(132)-C(131)-C(136)	119.6(5)
C(111)-C(112)-C(117)	122.6(6)
C(111)-C(112)-C(113)	118.4(6)
C(117)-C(112)-C(113)	119.0(7)
C(131)-C(132)-C(133)	121.4(6)
C(111)-C(116)-C(115)	120.2(7)
C(121)-C(126)-C(125)	120.2(6)
C(132)-C(133)-C(134)	119.6(6)
C(115)-C(114)-C(113)	120.0(8)
C(121)-C(122)-C(123)	118.5(6)
C(121)-C(122)-C(127)	122.0(7)
C(123)-C(122)-C(127)	119.4(7)
C(126)-C(125)-C(124)	119.9(7)
C(125)-C(124)-C(123)	118.7(7)
C(116)-C(115)-C(114)	120.0(7)
C(122)-C(123)-C(124)	123.4(7)
C(112)-C(113)-C(114)	121.4(8)
C(131)-C(136)-C(137)	124.0(5)
C(131)-C(136)-C(135)	116.6(5)
C(137)-C(136)-C(135)	119.3(6)
C(136)-C(135)-C(134)	123.1(7)
C(133)-C(134)-C(135)	119.7(6)

Table 50. Anisotropic Displacement Parameters ($A^2 \times 10^3$) for $Cu_2I_2(P(C_7H_7)_3)_2$

	U11	U22	U33	U23	U13	U12
I(1)	66(1)	67(1)	38(1)	11(1)	6(1)	17(1)
Cu(1)	53(1)	55(1)	38(1)	20(1)	7(1)	7(1)
P(1)	40(1)	44(1)	33(1)	18(1)	10(1)	11(1)
C(111)	50(3)	48(3)	34(2)	21(3)	14(2)	18(2)
C(121)	43(3)	46(3)	42(3)	16(2)	9(2)	9(2)
C(131)	37(3)	45(3)	32(2)	12(2)	6(2)	11(2)
C(112)	67(4)	63(4)	37(3)	35(3)	21(3)	17(3)
C(132)	43(3)	46(3)	43(3)	14(2)	12(2)	15(2)
C(116)	63(4)	54(4)	57(4)	14(3)	15(3)	22(3)
C(126)	48(3)	49(3)	50(3)	15(3)	5(3)	17(3)
C(133)	63(4)	62(4)	41(3)	21(3)	21(3)	4(3)
C(114)	121(7)	58(4)	75(5)	36(5)	43(5)	37(4)
C(122)	48(4)	67(4)	53(3)	24(3)	14(3)	5(3)
C(125)	49(4)	53(4)	75(4)	16(3)	-6(3)	28(3)
C(117)	60(4)	95(5)	58(4)	47(4)	8(3)	20(4)
C(124)	45(4)	60(4)	108(6)	27(3)	11(4)	17(4)
C(115)	83(5)	63(5)	83(5)	12(4)	27(4)	31(4)
C(123)	49(4)	81(5)	79(5)	31(4)	23(4)	5(4)
C(127)	79(5)	164(9)	50(4)	56(6)	30(4)	16(5)
C(113)	100(6)	81(5)	55(4)	58(5)	30(4)	34(4)
C(136)	44(3)	43(3)	38(3)	9(2)	4(2)	10(2)
C(137)	65(4)	44(3)	48(3)	20(3)	9(3)	16(3)
C(135)	56(4)	61(4)	46(3)	9(3)	14(3)	22(3)
C(134)	63(4)	72(4)	44(3)	17(3)	25(3)	20(3)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

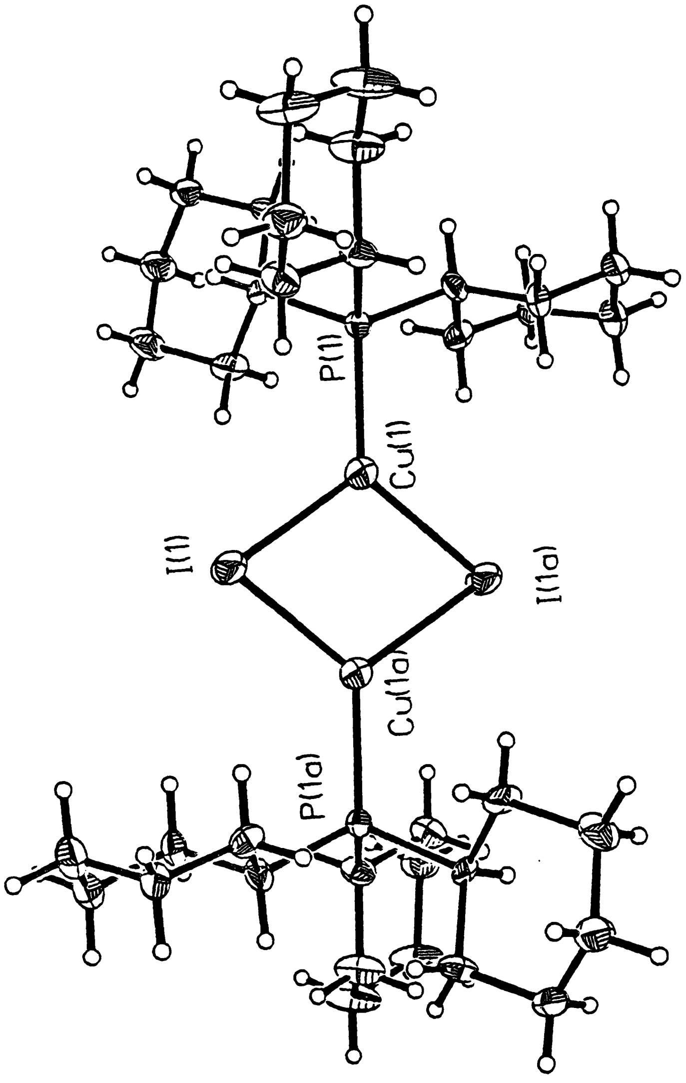


Figure 28 Projection View of $Cu_2I_2(P(C_6H_{11})_3)_2$

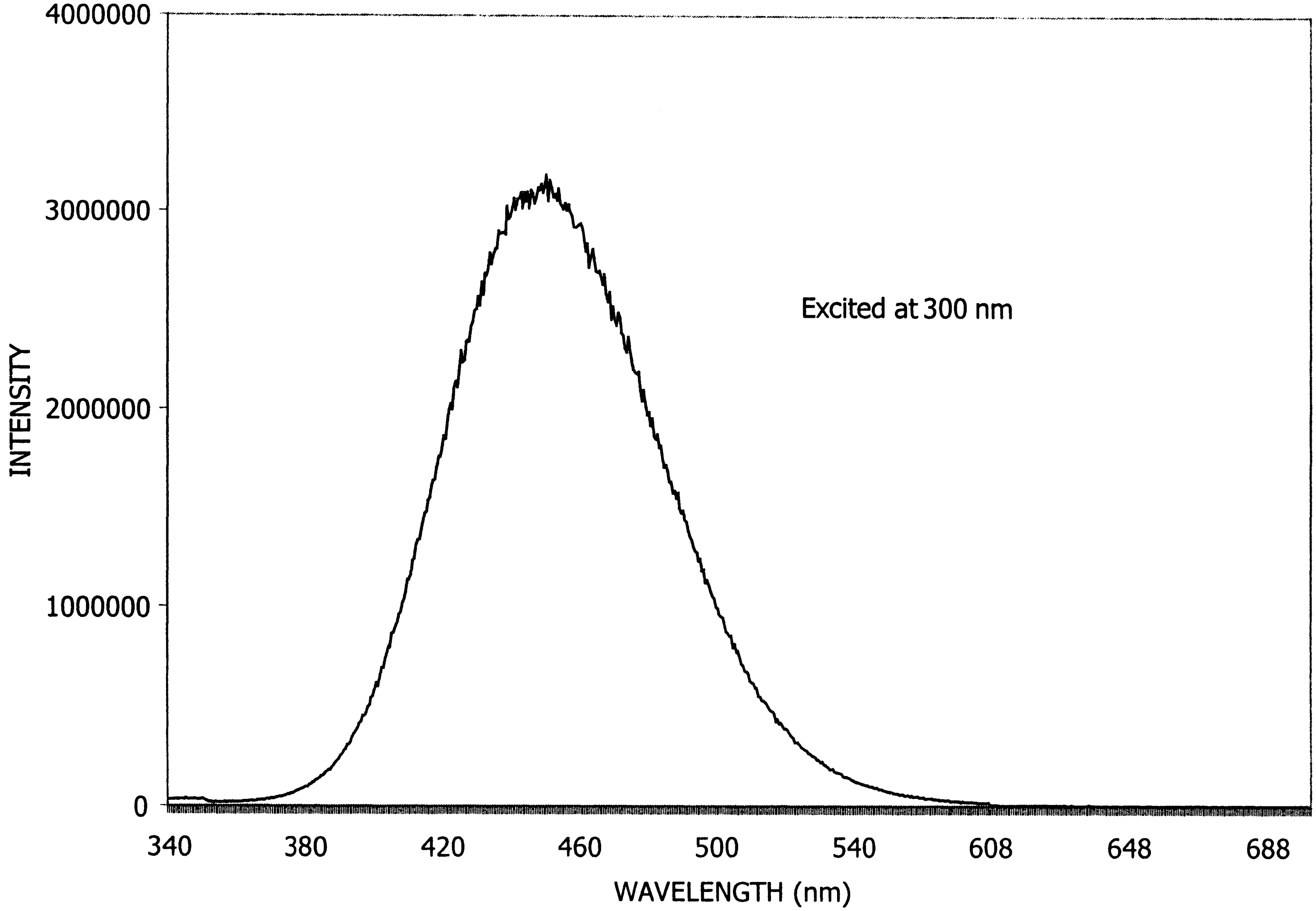


Figure 29 Emission Spectrum of $Cu_2I_2(P(C_6H_{11})_3)_2$

Table 51. Crystal Data and Structure Refinement for
$Cu_2I_2(P(C_6H_{11})_3)_2$

Empirical formula	$C_{36}H_{66}Cu_2I_2P_2$
Formula weight	941.7
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.980(10) Å α = 96.500(10) deg.
	b = 9.923(10) Å β = 94.050(0) deg.
	c = 13.061(7) Å γ = 116.520(10) deg.
Volume	1025(3) $Å^3$
Z, Calculated density	1, 1.526 Mg/m^3
Absorption coefficient	2.643 mm^{-1}
F(000)	476
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	3.5 to 22.5 deg.
Index ranges	$-12 \le h \le 1, -12 \le k \le 13, -18 \le l \le 18$
Reflections collected / unique/ observed	7000 / 5950 [R(int) = 0.1228]/ 2806(5.0>σ(F))
Goodness-of-fit	2.30
Final R indices [I>2sigma(I)]	R1 = 0.1019, wR2 = 0.1210
R indices (all data)	R1 = 0.1786, wR2 = 0.1661
Extinction coefficient	-0.0007(6)
Largest diff. peak and hole	2.49 and –1.13 $eÅ^{-3}$

Table 52. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for $Cu_2I_2(P(C_6H_{11})_3)_2$

	x	y	z	U(eq)
I(1)	1492(1)	9346(2)	4084(1)	73(1)
Cu(1)	1519(2)	10930(2)	5837(1)	48(1)
P(1)	3742(4)	12160(4)	7092(3)	31(1)
C(11)	5479(16)	13839(16)	6738(11)	45(6)
C(12)	7063(19)	14759(21)	7550(12)	67(8)
C(13)	8390(20)	16224(21)	7213(13)	78(8)
C(14)	8892(19)	15850(24)	6173(13)	77(9)
C(15)	7351(18)	14891(21)	5332(12)	59(8)
C(16)	6031(18)	13462(17)	5673(11)	50(7)
C(21)	4646(13)	10829(13)	7472(9)	26(5)
C(22)	3333(17)	9207(16)	7192(12)	46(6)
C(23)	4107(20)	8101(17)	7365(14)	60(7)
C(24)	5016(20)	8464(18)	8490(14)	59(8)
C(25)	6342(16)	10159(16)	8720(12)	48(6)
C(26)	5608(17)	11253(15)	8558(10)	42(6)
C(31)	3185(15)	12901(14)	8337(11)	39(5)
C(32)	2653(17)	14151(15)	8109(11)	40(6)
C(33)	2194(18)	14770(16)	9134(12)	48(6)
C(34)	786(19)	13481(18)	9533(12)	50(7)
C(35)	1250(18)	12208(17)	9726(11)	46(7)
C(36)	1771(15)	11623(16)	8746(11)	40(6)
H(11A)	5043	14542	6623	80
H(12A)	7583	14110	7631	80
H(12B)	6737	14981	8207	80
H(13A)	9350	16748	7739	80
H(13B)	7885	16883	7121	80
H(14A)	9439	15229	6284	80
H(14B)	9676	16753	5939	80
H(15A)	7707	14623	4698	80
H(15B)	6838	15531	5197	80
H(16A)	5081	12937	5140	80
H(16B)	6521	12795	5775	80
H(21A)	5479	10934	7023	80
H(22A)	2802	8993	6488	80
H(22B)	2491	9028	7645	80
H(23A)	4925	8257	6896	80
H(23B)	3267	7053	7211	80
H(24A)	5501	7792	8587	80
H(24B)	4191	8296	8955	80
H(25A)	7189	10330	8271	80
H(25B)	6863	10373	9427	80

Table 52. (Continued)

H(26A)	4813	11123	9039	80
H(26B)	6454	12300	8692	80
H(31A)	4146	13333	8864	80
H(32A)	1740	13757	7551	80
H(32B)	3598	14977	7907	80
H(33A)	1853	15529	8995	80
H(33B)	3148	15243	9667	80
H(34A)	-194	13053	9021	80
H(34B)	520	13887	10157	80
H(35A)	315	11396	9948	80
H(35B)	2185	12608	10270	80
H(36A)	2105	10857	8876	80
H(36B)	809	11163	8219	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 53. Bond Lengths [Å] and Angles [deg] for
$Cu_2I_2(P(C_6H_{11})_3)_2$

I(1)-Cu(1)	2.618 (4)
I(1)-Cu(1A)	2.604 (4)
Cu(1)-P(1)	2.252 (4)
Cu(1)-I(1A)	2.604 (4)
P(1)-C(11)	1.838 (13)
P(1)-C(21)	1.923 (15)
P(1)-C(31)	1.899 (15)
C(11)-C(12)	1.546 (18)
C(11)-C(16)	1.570 (22)
C(12)-C(13)	1.549 (23)
C(13)-C(14)	1.519 (26)
C(14)-C(15)	1.550 (20)
C(15)-C(16)	1.527 (21)
C(21)-C(22)	1.492 (15)
C(21)-C(26)	1.516 (17)
C(22)-C(23)	1.566 (28)
C(23)-C(24)	1.550 (24)
C(24)-C(25)	1.544 (19)
C(25)-C(26)	1.527 (26)
C(31)-C(32)	1.565 (24)
C(31)-C(36)	1.522 (17)
C(32)-C(33)	1.567 (22)
C(33)-C(34)	1.519 (20)
C(34)-C(35)	1.536 (28)
C(35)-C(36)	1.534 (22)

Cu(1)-I(1)-Cu(1A)	71.8(1)
I(1)-Cu(1)-P(1)	124.9(2)
I(1)-Cu(1)-I(1A)	108.2(1)
P(1)-Cu(1)-I(1A)	126.8(1)
Cu(1)-P(1)-C(11)	114.1(5)
Cu(1)-P(1)-C(21)	111.3(3)
C(11)-P(1)-C(21)	107.1(7)
Cu(1)-P(1)-C(31)	112.7(4)
C(11)-P(1)-C(31)	105.1(6)
C(21)-P(1)-C(31)	106.0(6)
P(1)-C(11)-C(12)	117.9(11)
P(1)-C(11)-C(16)	112.4(9)
C(12)-C(11)-C(16)	108.9(12)
C(11)-C(12)-C(13)	114.0(14)
C(12)-C(13)-C(14)	110.7(15)
C(13)-C(14)-C(15)	112.3(13)
C(14)-C(15)-C(16)	113.4(14)

Table 53. (Continued)

C(11)-C(16)-C(15)	112.0(12)
P(1)-C(21)-C(22)	109.9(10)
P(1)-C(21)-C(26)	116.1(10)
C(22)-C(21)-C(26)	115.0(11)
C(21)-C(22)-C(23)	110.5(12)
C(22)-C(23)-C(24)	111.3(14)
C(23)-C(24)-C(25)	109.1(14)
C(24)-C(25)-C(26)	113.2(12)
C(21)-C(26)-C(25)	110.0(12)
P(1)-C(31)-C(32)	108.5(10)
P(1)-C(31)-C(36)	111.5(9)
C(32)-C(31)-C(36)	110.1(12)
C(31)-C(32)-C(33)	108.8(12)
C(32)-C(33)-C(34)	110.6(11)
C(33)-C(34)-C(35)	111.8(15)
C(34)-C(35)-C(36)	110.9(13)
C(31)-C(36)-C(35)	112.3(11)

Table 54. Anisotropic Displacement Parameters (A^2 x 10^3) for $Cu_2I_2(P(C_6H_{11})_3)_2$

	U11	U22	U33	U23	U13	U12
I(1)	47(1)	120(1)	53(1)	49(1)	-4(1)	-24(1)
Cu(1)	46(1)	57(1)	46(1)	28(1)	-1(1)	1(1)
P(1)	33(2)	28(2)	34(2)	16(1)	1(1)	3(1)
C(11)	36(7)	38(8)	44(8)	5(6)	2(6)	0(6)
C(12)	49(9)	80(13)	41(9)	1(8)	-2(7)	12(9)
C(13)	53(9)	70(13)	50(10)	-26(8)	-8(7)	20(9)
C(14)	38(8)	97(15)	56(11)	-3(9)	-7(7)	18(10)
C(15)	50(9)	77(12)	41(9)	24(8)	0(7)	2(8)
C(16)	51(8)	48(9)	40(8)	15(7)	5(6)	1(7)
C(21)	29(6)	24(6)	33(6)	16(5)	1(5)	13(5)
C(22)	53(8)	37(8)	48(8)	22(7)	-21(6)	15(7)
C(23)	67(10)	29(9)	70(11)	14(7)	-8(8)	-4(8)
C(24)	63(9)	46(10)	64(11)	27(8)	-18(8)	0(8)
C(25)	43(7)	48(9)	49(9)	20(7)	-10(6)	1(7)
C(26)	51(8)	30(7)	29(7)	7(6)	-11(6)	6(6)
C(31)	39(7)	22(7)	49(8)	11(6)	6(6)	-3(6)
C(32)	51(8)	33(8)	44(8)	27(6)	10(6)	5(6)
C(33)	47(7)	43(9)	52(9)	23(7)	7(6)	-5(7)
C(34)	64(9)	54(10)	44(9)	36(8)	17(7)	7(7)
C(35)	51(8)	55(10)	44(8)	36(7)	5(6)	2(7)
C(36)	39(7)	42(8)	43(8)	23(6)	2(6)	17(6)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

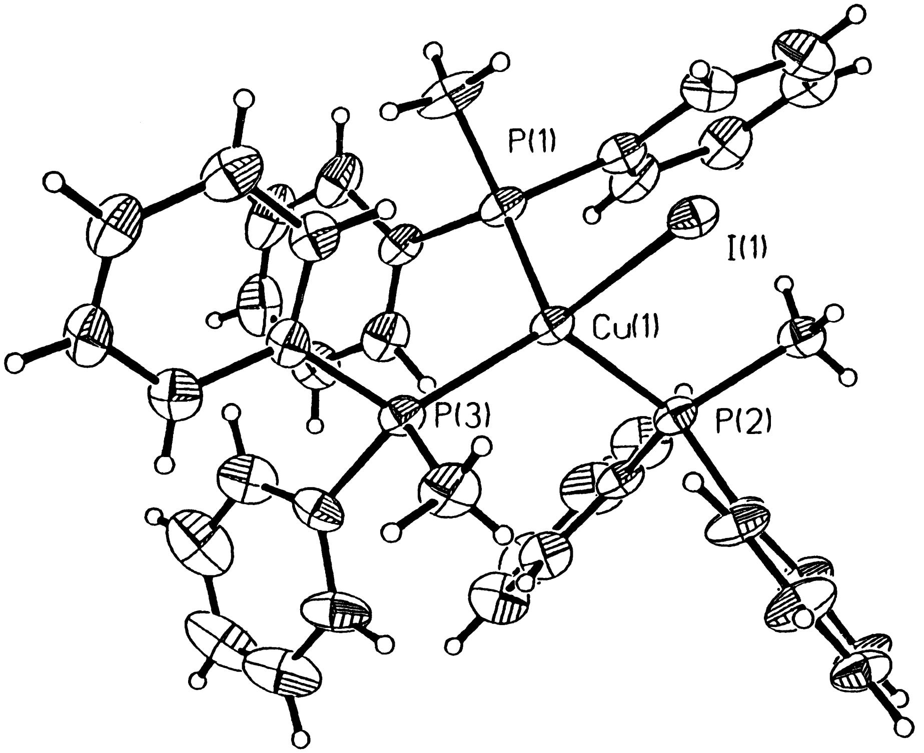


Figure 30 Projection View of $CuI(P(C_6H_5)_2CH_3)_3$

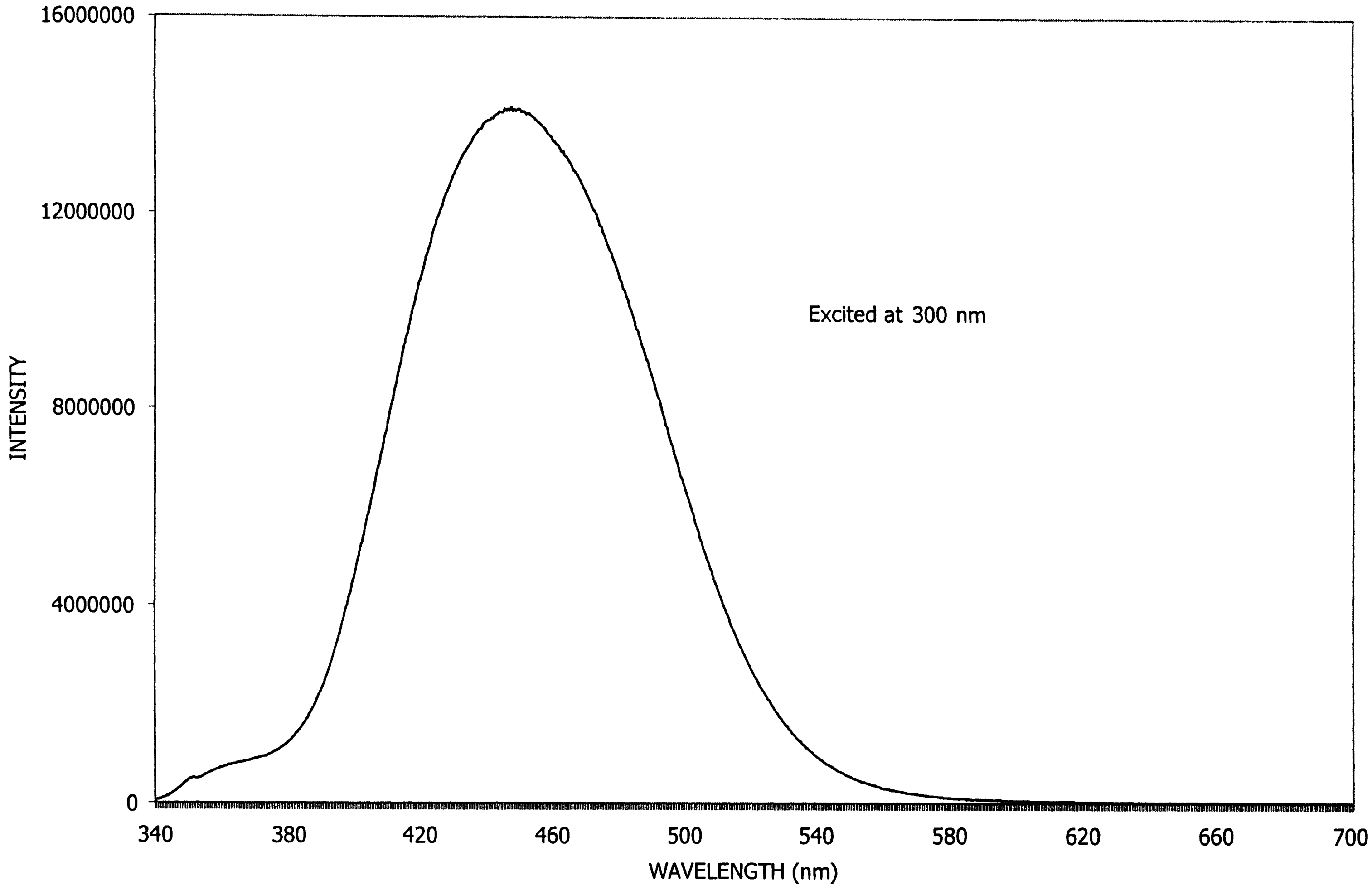


Figure 31 Emission Spectrum of $CuI(P(C_6H_5)_2CH_3)_3$

Table 55. Crystal Data and Structure Refinement for $CuI(P(C_6H_5)_2CH_3)_3$

Empirical formula	$C_{13}H_{13}Cu_{0.3333}I_{0.3333}P$
Formula weight	263.7
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *Pna*2_1
Unit cell dimensions	a = 17.575 Å α = 90.0 deg.
	b = 10.578 Å β = 90.0 deg.
	c = 20.341 Å γ = 90.0 deg.
Volume	3782(4) $Å^3$
Z, Calculated density	12, 1.584 Mg/m^3
Absorption coefficient	2.616 mm^{-1}
F(000)	1600
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	3.5 to 22.5 deg.
Index ranges	$-1 \leq h \leq 28$, $-1 \leq k \leq 14$, $-1 \leq l \leq 24$
Reflections collected / unique/ observed	6945 / 6032 [R(int) = 0.0327]/ 3797(4.0>σ(F))
Goodness-of-fit	1.25
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.0597
R indices (all data)	R1 = 0.0901, wR2 = 0.0704
Extinction coefficient	-0.00033(3)
Largest diff. peak and hole	1.37 and –0.57 $eÅ^{-3}$

Table 56. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters (Å^2x 10^3) for $CuI(P(C_6H_5)_2CH_3)_3$

	x	y	z	U(eq)
I(1)	3146(1)	6161(1)	1930	52(1)
Cu(1)	3809(1)	7069(1)	3136(1)	43(1)
P(1)	4732(1)	5818(2)	3214(2)	50(1)
P(2)	4099(1)	9054(2)	2731(2)	46(1)
P(3)	3057(1)	6917(3)	4125(2)	48(1)
C(1)	4588(5)	4122(9)	3147(10)	79(5)
C(2)	4512(5)	9022(9)	1805(7)	60(4)
C(3)	2234(5)	7534(14)	3900(8)	81(5)
C(111)	5283(5)	6110(10)	2410(7)	53(4)
C(112)	5090(6)	5722(12)	1675(7)	64(4)
C(113)	5458(6)	6015(15)	1051(9)	85(6)
C(114)	6050(6)	6680(14)	1136(9)	76(5)
C(115)	6242(5)	7062(12)	1850(9)	77(5)
C(116)	5878(5)	6791(12)	2484(8)	68(4)
C(121)	5258(5)	5965(10)	4057(7)	52(3)
C(122)	5252(5)	7066(13)	4471(7)	71(5)
C(123)	5652(6)	7236(15)	5118(8)	79(5)
C(124)	6029(7)	6264(17)	5362(9)	92(6)
C(125)	6051(6)	5168(18)	4970(10)	100(7)
C(126)	5679(6)	4972(13)	4317(8)	81(5)
C(211)	3443(5)	10228(8)	2541(6)	52(3)
C(212)	3596(6)	11484(9)	2393(7)	70(4)
C(213)	3085(6)	12338(10)	2234(8)	81(5)
C(214)	2460(6)	11963(10)	2197(7)	76(4)
C(215)	2306(6)	10710(10)	2315(9)	86(5)
C(216)	2799(5)	9821(9)	2507(8)	69(4)
C(221)	4665(4)	9950(9)	3363(6)	54(3)
C(222)	5329(5)	10039(13)	3224(9)	89(5)
C(223)	5732(8)	10655(16)	3765(10)	108(7)
C(224)	5501(9)	11120(13)	4403(10)	100(7)
C(225)	4843(8)	10988(13)	4581(9)	95(6)
C(226)	4438(6)	10390(11)	4045(7)	71(4)
C(311)	3289(5)	7760(12)	4985(6)	64(4)
C(312)	3038(6)	8960(12)	5157(9)	90(6)
C(313)	3281(8)	9605(16)	5778(11)	113(7)
C(314)	3758(9)	9207(20)	6189(10)	120(8)
C(315)	4039(7)	7983(22)	6058(9)	119(8)
C(316)	3786(6)	7279(14)	5447(8)	81(5)
C(321)	2822(4)	5338(10)	4481(5)	49(3)
C(322)	2516(6)	5172(12)	5194(7)	68(4)
C(323)	2301(6)	3967(12)	5414(8)	74(4)

Table 56. (Continued)

C(324)	2396(6)	2944(12)	4944(7)	75(5)
C(325)	2714(6)	3103(11)	4234(8)	81(5)
C(326)	2907(5)	4301(10)	4020(7)	60(4)
H(1A)	5068	3696	3194	80
H(1B)	4249	3848	3489	80
H(1C)	4372	3924	2727	80
H(2A)	4621	9868	1663	80
H(2B)	4970	8529	1798	80
H(2C)	4144	8649	1516	80
H(3A)	1887	7517	4264	80
H(3B)	2308	8392	3759	80
H(3C)	2027	7048	3543	80
H(11A)	4636	5224	1631	80
H(11B)	5280	5737	628	80
H(11C)	6370	6929	777	80
H(11D)	6689	7580	1887	80
H(11E)	6051	7103	2902	80
H(12A)	4965	7776	4313	80
H(12B)	5643	8034	5343	80
H(12C)	6273	6311	5783	80
H(12D)	6327	4462	5147	80
H(12E)	5724	4186	4084	80
H(21A)	4118	11749	2413	80
H(21E)	3214	13207	2158	80
H(21B)	2059	12527	2069	80
H(21C)	1785	10454	2263	80
H(21D)	2662	8963	2606	80
H(22A)	5557	9749	2823	80
H(22B)	6264	10770	3674	80
H(22C)	5862	11528	4686	80
H(22D)	4634	11227	4999	80
H(22E)	3911	10246	4142	80
H(31A)	2673	9364	4876	80
H(31B)	3068	10430	5848	80
H(31C)	3916	9703	6560	80
H(31D)	4381	7579	6359	80
H(31E)	3992	6453	5368	80
H(32A)	2460	5894	5476	80
H(32B)	2126	3817	5854	80
H(32C)	2236	2119	5083	80
H(32D)	2772	2381	3953	80
H(32F)	3088	4450	3582	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 57. Bond Lengths [Å] and Angles [deg] for
$CuI(P(C_6H_5)_2CH_3)_3$

I(1)-Cu(1)	2.881 (3)
Cu(1)-P(1)	2.099 (3)
Cu(1)-P(2)	2.312 (3)
Cu(1)-P(3)	2.412 (4)
P(1)-C(1)	1.818 (10)
P(1)-C(111)	1.925 (13)
P(1)-C(121)	1.954 (13)
P(2)-C(2)	2.018 (14)
P(2)-C(211)	1.738 (9)
P(2)-C(221)	1.882 (11)
P(3)-C(3)	1.652 (11)
P(3)-C(311)	2.006 (13)
P(3)-C(321)	1.867 (11)
C(111)-C(112)	1.587 (19)
C(111)-C(116)	1.279 (14)
C(112)-C(113)	1.459 (21)
C(113)-C(114)	1.267 (17)
C(114)-C(115)	1.544 (24)
C(115)-C(116)	1.469 (22)
C(121)-C(122)	1.437 (18)
C(121)-C(126)	1.390 (17)
C(122)-C(123)	1.504 (21)
C(123)-C(124)	1.321 (22)
C(124)-C(125)	1.407 (26)
C(125)-C(126)	1.495 (24)
C(211)-C(212)	1.389 (13)
C(211)-C(216)	1.214 (13)
C(212)-C(213)	1.314 (15)
C(213)-C(214)	1.169 (16)
C(214)-C(215)	1.374 (16)
C(215)-C(216)	1.337 (15)
C(221)-C(222)	1.205 (13)
C(221)-C(226)	1.516 (18)
C(222)-C(223)	1.461 (25)
C(223)-C(224)	1.445 (29)
C(224)-C(225)	1.220 (22)
C(225)-C(226)	1.448 (21)
C(311)-C(312)	1.388 (18)
C(311)-C(316)	1.381 (18)
C(312)-C(313)	1.496 (27)
C(313)-C(314)	1.256 (26)
C(314)-C(315)	1.411 (30)
C(315)-C(316)	1.514 (25)

Table 57. (Continued)

C(321)-C(322)	1.557 (17)
C(321)-C(326)	1.451 (16)
C(322)-C(323)	1.404 (18)
C(323)-C(324)	1.454 (20)
C(324)-C(325)	1.557 (22)
C(325)-C(326)	1.382 (16)
I(1)-Cu(1)-P(1)	99.6(1)
I(1)-Cu(1)-P(2)	95.1(1)
P(1)-Cu(1)-P(2)	115.4(1)
I(1)-Cu(1)-P(3)	117.8(1)
P(1)-Cu(1)-P(3)	108.6(1)
P(2)-Cu(1)-P(3)	118.6(1)
Cu(1)-P(1)-C(1)	120.6(3)
Cu(1)-P(1)-C(111)	102.9(3)
C(1)-P(1)-C(111)	99.5(7)
Cu(1)-P(1)-C(121)	112.4(3)
C(1)-P(1)-C(121)	102.1(7)
C(111)-P(1)-C(121)	119.6(4)
Cu(1)-P(2)-C(2)	113.4(3)
Cu(1)-P(2)-C(211)	125.6(3)
C(2)-P(2)-C(211)	92.4(5)
Cu(1)-P(2)-C(221)	109.3(4)
C(2)-P(2)-C(221)	117.1(4)
C(211)-P(2)-C(221)	98.2(5)
Cu(1)-P(3)-C(3)	102.9(6)
Cu(1)-P(3)-C(311)	125.9(3)
C(3)-P(3)-C(311)	104.2(6)
Cu(1)-P(3)-C(321)	120.3(3)
C(3)-P(3)-C(321)	105.5(5)
C(311)-P(3)-C(321)	96.0(5)
P(1)-C(111)-C(112)	130.6(7)
P(1)-C(111)-C(116)	113.7(11)
C(112)-C(111)-C(116)	115.6(12)
C(111)-C(112)-C(113)	132.1(10)
C(112)-C(113)-C(114)	111.2(15)
C(113)-C(114)-C(115)	117.1(14)
C(114)-C(115)-C(116)	132.8(9)
C(111)-C(116)-C(115)	111.2(13)
P(1)-C(121)-C(122)	125.1(8)
P(1)-C(121)-C(126)	121.7(10)
C(122)-C(121)-C(126)	113.1(12)
C(121)-C(122)-C(123)	127.4(11)
C(122)-C(123)-C(124)	118.0(14)

Table 57. (Continued)

C(123)-C(124)-C(125)	116.3(16)
C(124)-C(125)-C(126)	127.3(15)
C(121)-C(126)-C(125)	117.8(13)
P(2)-C(211)-C(212)	127.2(8)
P(2)-C(211)-C(216)	112.2(8)
C(212)-C(211)-C(216)	120.5(10)
C(211)-C(212)-C(213)	125.4(10)
C(212)-C(213)-C(214)	115.1(11)
C(213)-C(214)-C(215)	120.1(11)
C(214)-C(215)-C(216)	127.0(10)
C(211)-C(216)-C(215)	111.8(10)
P(2)-C(221)-C(222)	113.0(11)
P(2)-C(221)-C(226)	129.8(7)
C(222)-C(221)-C(226)	116.5(12)
C(221)-C(222)-C(223)	109.1(15)
C(222)-C(223)-C(224)	133.7(13)
C(223)-C(224)-C(225)	119.7(16)
C(224)-C(225)-C(226)	107.0(16)
C(221)-C(226)-C(225)	133.9(11)
P(3)-C(311)-C(312)	124.2(10)
P(3)-C(311)-C(316)	124.0(10)
C(312)-C(311)-C(316)	111.5(13)
C(311)-C(312)-C(313)	122.7(13)
C(312)-C(313)-C(314)	126.7(17)
C(313)-C(314)-C(315)	114.5(18)
C(314)-C(315)-C(316)	120.3(15)
C(311)-C(316)-C(315)	124.2(14)
P(3)-C(321)-C(322)	122.6(8)
P(3)-C(321)-C(326)	113.7(8)
C(322)-C(321)-C(326)	123.5(9)
C(321)-C(322)-C(323)	119.5(11)
C(322)-C(323)-C(324)	115.8(13)
C(323)-C(324)-C(325)	124.8(11)
C(324)-C(325)-C(326)	118.6(12)
C(321)-C(326)-C(325)	117.7(12)

Table 58. Anisotropic Displacement Parameters (A^2 x 10^3) for $CuI(P(C_6H_5)_2CH_3)_3$

	U11	U22	U33	U23	U13	U12
I(1)	42(1)	46(1)	69(1)	4(1)	-12(1)	-4(1)
Cu(1)	25(1)	40(1)	64(1)	-1(1)	2(1)	4(1)
P(1)	27(1)	42(1)	79(2)	3(1)	-2(1)	3(2)
P(2)	36(1)	37(1)	65(2)	-3(1)	1(1)	4(1)
P(3)	29(1)	51(1)	66(2)	4(1)	6(1)	2(1)
C(1)	37(4)	40(5)	160(14)	-2(4)	-10(8)	8(8)
C(2)	47(5)	57(6)	75(11)	-1(4)	16(6)	4(7)
C(3)	27(4)	101(9)	114(12)	13(5)	10(6)	12(9)
C(111)	22(3)	53(6)	84(9)	2(4)	-7(5	0(7)
C(112)	32(4)	74(8)	87(9)	-3(5)	-6(5)	-14(7)
C(113)	43(5)	116(11)	95(11)	9(6)	16(7)	-26(10)
C(114)	29(5)	89(9)	108(12)	8(5)	14(6)	4(9)
C(115)	25(3)	88(8)	118(12)	-5(4)	13(6)	20(10)
C(116)	26(4)	71(7)	105(10)	1(4)	-13(6)	15(8)
C(121)	23(3)	53(6)	79(8)	4(4)	-3(4)	12(6)
C(122)	36(4)	86(8)	92(10)	7(5)	-10(6)	16(9)
C(123)	58(6)	94(10)	85(10)	0(7)	1(7)	-2(9)
C(124)	48(6)	142(14)	85(11)	-6(8)	-24(7)	33(11)
C(125)	53(6)	115(13)	131(15)	15(7)	-39(8)	58(12)
C(126)	49(5)	79(8)	114(12)	8(6)	-5(7)	34(9)
C(211)	48(5)	32(4)	76(7)	-3(4)	-3(5)	2(5)
C(212)	60(6)	42(5)	107(10)	-5(4)	3(7)	7(6)
C(213)	70(6)	38(5)	134(12)	15(5)	-14(8)	14(6)
C(214)	59(6)	61(6)	107(10)	23(5)	-23(7)	-13(7)
C(215)	44(5)	60(6)	155(14)	6(5)	-33(7)	0(8)
C(216)	44(5)	36(5)	128(11)	-1(4)	-7(7)	-7(7)
C(221)	28(3)	43(4)	92(9)	0(3)	-3(4)	6(5)
C(222)	37(4)	99(9)	131(12)	-18(5)	-4(7)	-13(10)
C(223)	53(7)	113(12)	159(17)	-9(7)	-24(9)	-25(12)
C(224)	83(9)	82(9)	136(15)	-21(8)	-50(10)	-8(11)
C(225)	77(8)	96(10)	111(12)	-22(8)	-12(8)	-30(9)
C(226)	49(5)	69(7)	96(10)	-7(5)	-5(7)	-3(7)
C(311)	42(5)	77(7)	72(8)	-18(5)	20(5)	-19(6)
C(312)	51(6)	74(8)	144(14)	-5(6)	26(8)	-42(9)
C(313)	63(7)	107(11)	169(18)	-36(8)	31(10)	-71(13)
C(314)	62(8)	172(17)	124(15)	-58(10)	28(9)	-87(13)
C(315)	49(6)	201(21)	107(12)	-5(10)	-9(8)	-26(15)
C(316)	42(5)	98(9)	101(10)	-4(6)	-10(6)	-19(9)
C(321)	24(3)	61(6)	62(6)	-8(4)	7(4)	8(5)
C(322)	46(5)	77(8)	82(9)	-6(5)	5(5)	-2(7)
C(323)	41(5)	90(8)	92(9)	-18(6)	16(6)	25(8)

Table 58. (Continued)

C(324)	53(6)	69(7)	104(10)	-26(6)	-10(7)	19(8)
C(325)	58(6)	62(7)	123(12)	-13(5)	0(7)	5(8)
C(326)	45(5)	59(6)	77(8)	-14(5)	1(5)	0(6)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

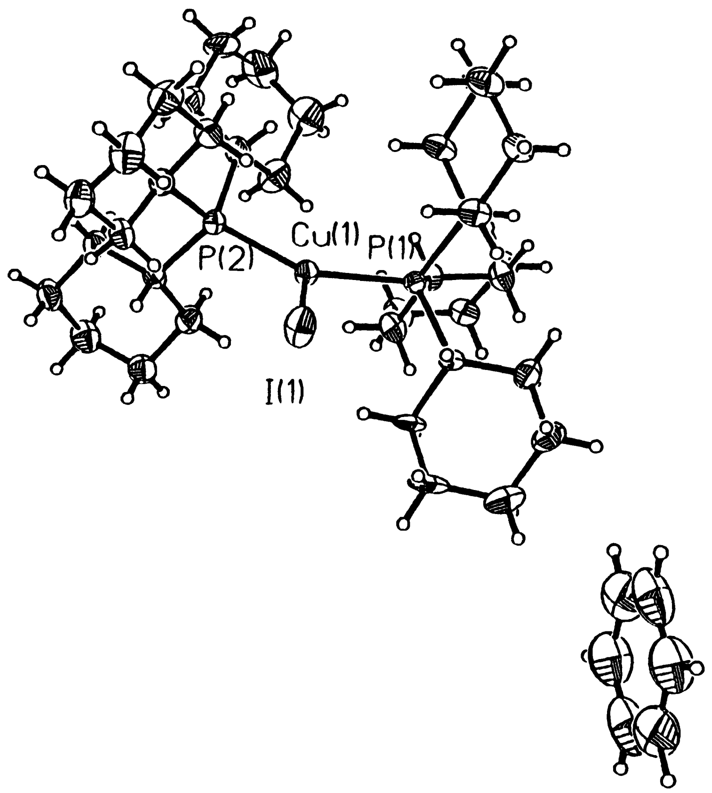


Figure 32 Projection View of $CuI(P(C_6H_{11})_3)_2.C_6H_6$

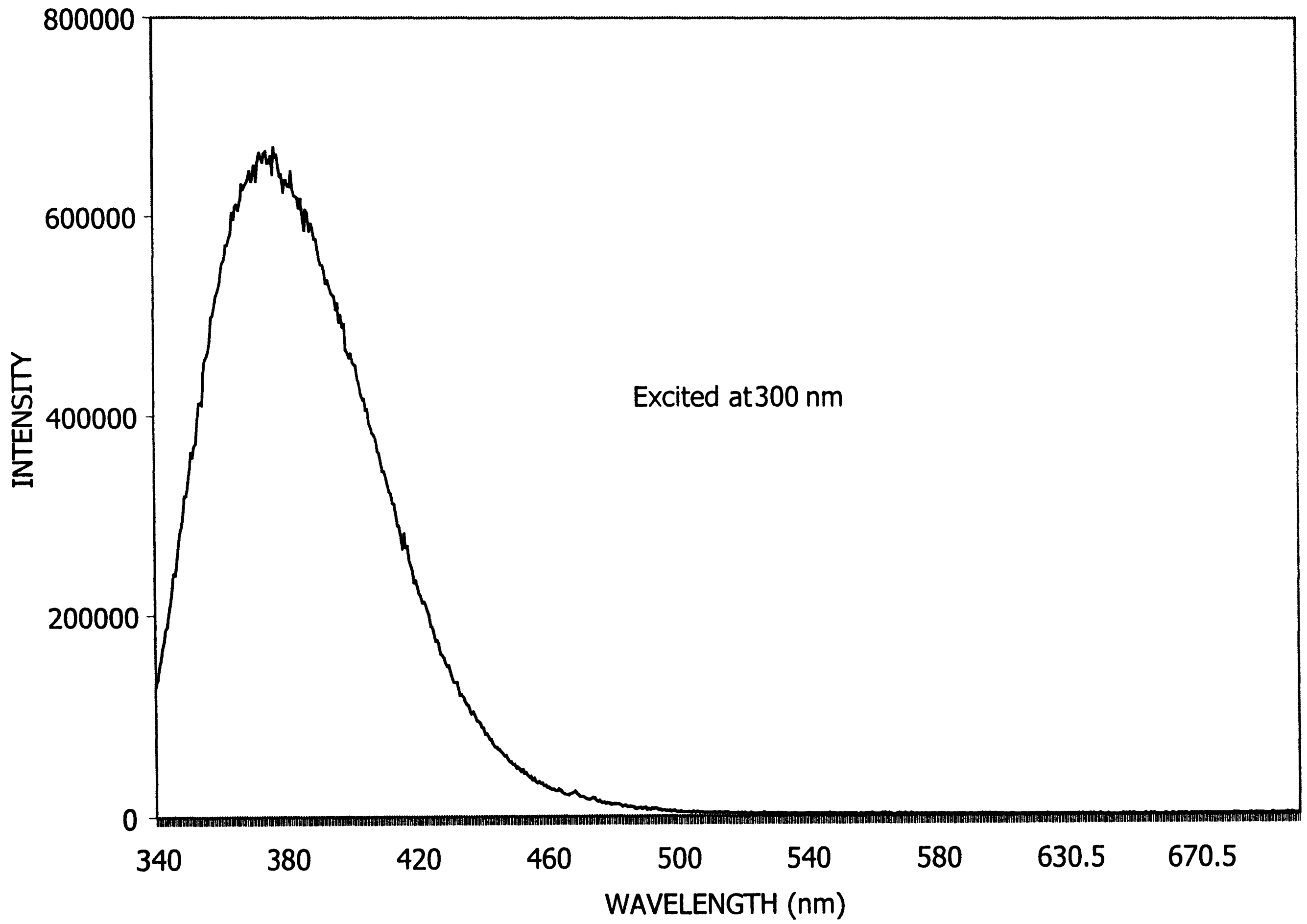


Figure 33 Emission Spectrum of $CuI(P(C_6H_{11})_3)_2.C_6H_6$

Table 59. Crystal Data and Structure Refinement for $CuI(P(C_6H_{11})_3)_2.C_6H_6$

Empirical formula	$C_{39}H_{69}CuIP_2$	
Formula weight	790.3	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell dimensions	a = 9.534(6) Å	α = 92.44(2) deg.
	b = 9.644(5) Å	β = 98.07(3) deg.
	c = 25.519(13) Å	γ = 116.42(4) deg.
Volume	2067(2) $Å^3$	
Z, Calculated density	2, 1.270 Mg/m^3	
Absorption coefficient	1.376 mm^{-1}	
F(000)	830	
Crystal size	0.2 x 0.2 x 0.2 mm	
Theta range for data collection	1.75 to 22.5 deg.	
Index ranges	$-1 \le h \le 13, -11 \le k \le 7, -35 \le l \le 35$	
Reflections collected / unique/ observed	7593 / 7429 [R(int) = 0.2079]/ 4737(4.0>σ(F))	
Goodness-of-fit	1.54	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.0669	
R indices (all data)	R1 = 0.0915, wR2 = 0.1783	
Extinction coefficient	-0.00048(10)	
Largest diff. peak and hole	1.17 and –0.48 $eÅ^{-3}$	

Table 60. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $CuI(P(C_6H_{11})_3)_2.C_6H_6$

	x	y	z	U(eq)
I(1)	4391(1)	5541(1)	2818(1)	74(1)
Cu(1)	2440(1)	6800(1)	2728(1)	43(1)
P(1)	1985(1)	7088(2)	1842(1)	36(1)
P(2)	1915(1)	7608(2)	3496(1)	41(1)
C(111)	2076(5)	5478(8)	1445(2)	39(3)
C(112)	2069(8)	5495(11)	842(2)	64(5)
C(113)	2459(9)	4172(12)	631(3)	76(5)
C(114)	1326(8)	2566(12)	767(3)	79(5)
C(115)	1302(8)	2580(10)	1358(3)	74(5)
C(116)	877(7)	3841(9)	1561(3)	55(4)
C(121)	181(5)	7336(9)	1567(2)	49(3)
C(122)	-6(6)	7712(9)	985(2)	56(4)
C(123)	-1438(6)	8040(10)	843(3)	62(4)
C(124)	-2977(6)	6700(10)	947(3)	58(4)
C(125)	-2816(7)	6323(10)	1513(3)	68(4)
C(126)	-1390(6)	5963(9)	1654(3)	57(4)
C(131)	3662(5)	8935(8)	1694(2)	40(3)
C(132)	3780(6)	10342(10)	2030(3)	59(4)
C(133)	5183(7)	11904(11)	1949(3)	67(5)
C(134)	6762(7)	11775(10)	2056(3)	74(4)
C(135)	6677(6)	10430(10)	1707(3)	56(4)
C(136)	5267(5)	8853(9)	1800(3)	53(3)
C(211)	198(5)	6049(8)	3750(2)	44(3)
C(212)	-1299(6)	5177(10)	3311(2)	59(4)
C(213)	-2580(6)	3789(10)	3517(3)	65(4)
C(214)	-3011(6)	4275(10)	4019(3)	71(4)
C(215)	-1539(7)	5130(11)	4456(3)	69(4)
C(216)	-230(6)	6576(9)	4260(2)	56(4)
C(221)	1669(7)	9439(10)	3435(2)	57(4)
C(222)	188(9)	9128(12)	3009(3)	77(6)
C(223)	311(12)	10767(15)	2878(3)	98(7)
C(224)	426(12)	11718(15)	3352(4)	102(8)
C(225)	1789(12)	11980(14)	3788(4)	90(7)
C(226)	1747(10)	10405(13)	3927(3)	80(6)
C(231)	3640(5)	8252(9)	4064(2)	46(3)
C(232)	5190(6)	9468(9)	3890(2)	55(4)
C(233)	6654(6)	9967(10)	4336(3)	70(4)
C(234)	6849(7)	8568(12)	4513(3)	74(5)
C(235)	5374(7)	7429(10)	4701(2)	69(5)
C(236)	3856(6)	6849(9)	4262(2)	55(4)
C(3)	6480(16)	203(27)	-30(5)	127(11)

Table 60. (Continued)

C(2)	6312(16)	1463(23)	145(5)	132(12)
C(1)	4803(21)	1263(24)	161(4)	134(14)
H(11A)	3103	5564	1586	80
H(11B)	2841	6486	767	80
H(11C)	1039	5328	667	80
H(11D)	3532	4401	780	80
H(11E)	2381	4165	252	80
H(11F)	1650	1815	646	80
H(11G)	271	2272	579	80
H(11H)	538	1572	1423	80
H(11I)	2331	2766	1542	80
H(11J)	-191	3606	1403	80
H(11K)	937	3853	1940	80
H(12A)	261	8230	1775	80
H(12B)	-202	6797	760	80
H(12C)	954	8561	921	80
H(12D)	-1561	8229	477	80
H(12E)	-1232	8964	1063	80
H(12F)	-3196	5787	716	80
H(12G)	-3855	6936	863	80
H(12H)	-2637	7220	1743	80
H(12I)	-3783	5463	1567	80
H(12J)	-1285	5759	2018	80
H(12K)	-1570	5053	1430	80
H(13A)	3439	9078	1328	80
H(13B)	3967	10170	2396	80
H(13C)	2784	10384	1963	80
H(13D)	5253	12740	2187	80
H(13E)	5008	12120	1589	80
H(13F)	7668	12726	2019	80
H(13G)	6907	11547	2416	80
H(13H)	6459	10619	1346	80
H(13I)	7669	10380	1761	80
H(13J)	5202	8008	1568	80
H(13K)	5472	8663	2162	80
H(21A)	536	5279	3846	80
H(21B)	-1003	4830	3006	80
H(21C)	-1716	5883	3205	80
H(21D)	-2192	3040	3589	80
H(21E)	-3519	3299	3247	80
H(21F)	-3517	4926	3938	80
H(21G)	-3749	3368	4153	80
H(21H)	-1838	5460	4764	80
H(21I)	-1105	4436	4561	80
H(21J)	-607	7333	4189	80

Table 60. (Continued)

H(21K)	702	7046	4533	80
H(22A)	2557	10127	3283	80
H(22B)	-757	8531	3151	80
H(22C)	175	8529	2696	80
H(22D)	-664	10542	2644	80
H(22E)	1163	11260	2684	80
H(22F)	-536	11351	3498	80
H(22G)	633	12708	3230	80
H(22H)	2777	12566	3669	80
H(22I)	1782	12563	4101	80
H(22J)	2651	10568	4189	80
H(22K)	802	9842	4073	80
H(23A)	3432	8756	4355	80
H(23B)	5049	10362	3804	80
H(23C)	5363	9025	3576	80
H(23D)	6508	10479	4639	80
H(23E)	7590	10699	4216	80
H(23F)	7041	8081	4214	80
H(23G)	7769	8926	4790	80
H(23H)	5519	6531	4780	80
H(23I)	5229	7875	5020	80
H(23J)	3957	6274	3966	80
H(23K)	2921	6166	4394	80
H(3A)	7519	337	-68	80
H(2A)	7247	2441	256	80
H(1A)	4633	2139	263	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 61. Bond Lengths [Å] and Angles [deg] for $CuI(P(C_6H_{11})_3)_2.C_6H_6$

I(1)-Cu(1)	2.626 (2)
Cu(1)-P(1)	2.296 (2)
Cu(1)-P(2)	2.279 (2)
P(1)-C(111)	1.858 (8)
P(1)-C(121)	1.883 (7)
P(1)-C(131)	1.887 (5)
P(2)-C(211)	1.885 (5)
P(2)-C(221)	1.891 (10)
P(2)-C(231)	1.880 (5)
C(111)-C(112)	1.538 (8)
C(111)-C(116)	1.555 (9)
C(112)-C(113)	1.573 (16)
C(113)-C(114)	1.532 (13)
C(114)-C(115)	1.512 (12)
C(115)-C(116)	1.534 (14)
C(121)-C(122)	1.549 (8)
C(121)-C(126)	1.549 (8)
C(122)-C(123)	1.533 (11)
C(123)-C(124)	1.531 (8)
C(124)-C(125)	1.509 (10)
C(125)-C(126)	1.546 (11)
C(131)-C(132)	1.526 (12)
C(131)-C(136)	1.553 (9)
C(132)-C(133)	1.553 (10)
C(133)-C(134)	1.553 (12)
C(134)-C(135)	1.506 (13)
C(135)-C(136)	1.574 (9)
C(211)-C(212)	1.551 (6)
C(211)-C(216)	1.546 (9)
C(212)-C(213)	1.531 (9)
C(213)-C(214)	1.517 (11)
C(214)-C(215)	1.531 (8)
C(215)-C(216)	1.562 (9)
C(221)-C(222)	1.559 (10)
C(221)-C(226)	1.506 (12)
C(222)-C(223)	1.586 (19)
C(223)-C(224)	1.448 (17)
C(224)-C(225)	1.505 (15)
C(225)-C(226)	1.559 (19)
C(231)-C(232)	1.563 (7)
C(231)-C(236)	1.551 (12)
C(232)-C(233)	1.544 (8)
C(233)-C(234)	1.520 (15)

Table 61. (Continued)

C(234)-C(235)	1.507 (9)
C(235)-C(236)	1.560 (8)
C(3)-C(2)	1.360 (35)
C(3)-C(1A)	1.383 (23)
C(2)-C(1)	1.370 (27)
C(1)-C(3A)	1.383 (23)
I(1)-Cu(1)-P(1)	105.8(1)
I(1)-Cu(1)-P(2)	117.3(1)
P(1)-Cu(1)-P(2)	136.2(1)
Cu(1)-P(1)-C(111)	108.3(2)
Cu(1)-P(1)-C(121)	119.0(2)
C(111)-P(1)-C(121)	111.4(3)
Cu(1)-P(1)-C(131)	109.7(2)
C(111)-P(1)-C(131)	105.3(3)
C(121)-P(1)-C(131)	102.1(3)
Cu(1)-P(2)-C(211)	114.1(2)
Cu(1)-P(2)-C(221)	111.4(2)
C(211)-P(2)-C(221)	111.7(3)
Cu(1)-P(2)-C(231)	112.2(2)
C(211)-P(2)-C(231)	104.3(2)
C(221)-P(2)-C(231)	102.4(3)
P(1)-C(111)-C(112)	120.4(6)
P(1)-C(111)-C(116)	112.6(4)
C(112)-C(111)-C(116)	110.1(5)
C(111)-C(112)-C(113)	109.2(7)
C(112)-C(113)-C(114)	112.3(7)
C(113)-C(114)-C(115)	111.4(7)
C(114)-C(115)-C(116)	111.1(8)
C(111)-C(116)-C(115)	110.9(6)
P(1)-C(121)-C(122)	118.2(4)
P(1)-C(121)-C(126)	112.5(6)
C(122)-C(121)-C(126)	109.4(4)
C(121)-C(122)-C(123)	111.6(5)
C(122)-C(123)-C(124)	111.8(7)
C(123)-C(124)-C(125)	111.7(4)
C(124)-C(125)-C(126)	111.2(6)
C(121)-C(126)-C(125)	111.3(7)
P(1)-C(131)-C(132)	110.1(4)
P(1)-C(131)-C(136)	110.9(5)
C(132)-C(131)-C(136)	110.4(4)
C(131)-C(132)-C(133)	113.2(6)
C(132)-C(133)-C(134)	109.6(8)
C(133)-C(134)-C(135)	111.7(5)

Table 61. (Continued)

C(134)-C(135)-C(136)	110.5(6)
C(131)-C(136)-C(135)	110.7(7)
P(2)-C(211)-C(212)	112.8(4)
P(2)-C(211)-C(216)	115.4(4)
C(212)-C(211)-C(216)	111.1(5)
C(211)-C(212)-C(213)	110.8(5)
C(212)-C(213)-C(214)	112.0(7)
C(213)-C(214)-C(215)	111.2(5)
C(214)-C(215)-C(216)	111.3(6)
C(211)-C(216)-C(215)	109.4(6)
P(2)-C(221)-C(222)	111.1(6)
P(2)-C(221)-C(226)	120.0(6)
C(222)-C(221)-C(226)	110.8(8)
C(221)-C(222)-C(223)	107.7(7)
C(222)-C(223)-C(224)	111.8(9)
C(223)-C(224)-C(225)	113.9(12)
C(224)-C(225)-C(226)	111.3(9)
C(221)-C(226)-C(225)	110.8(7)
P(2)-C(231)-C(232)	109.7(4)
P(2)-C(231)-C(236)	111.6(4)
C(232)-C(231)-C(236)	111.0(6)
C(231)-C(232)-C(233)	111.4(5)
C(232)-C(233)-C(234)	111.5(6)
C(233)-C(234)-C(235)	110.7(7)
C(234)-C(235)-C(236)	112.3(6)
C(231)-C(236)-C(235)	110.5(6)
C(2)-C(3)-C(1A)	122.0(17)
C(3)-C(2)-C(1)	117.8(15)
C(2)-C(1)-C(3A)	120.0(22)

Table 62. Anisotropic Displacement Parameters (A^2 x 10^3) for $CuI(P(C_6H_{11})_3)_2.C_6H_6$

	U11	U22	U33	U23	U13	U12
I(1)	101(1)	104(1)	57(1)	81(1)	15(1)	20(1)
Cu(1)	47(1)	48(1)	39(1)	25(1)	10(1)	9(1)
P(1)	38(1)	36(1)	36(1)	18(1)	5(1)	5(1)
P(2)	44(1)	47(1)	35(1)	23(1)	7(1)	8(1)
C(111)	44(2)	28(6)	44(3)	15(2)	7(2)	3(3)
C(112)	84(4)	65(9)	48(3)	38(4)	10(3)	3(4)
C(113)	85(5)	66(10)	72(4)	32(4)	20(4)	-15(5)
C(114)	66(4)	60(9)	103(6)	27(4)	10(4)	-26(5)
C(115)	73(4)	23(8)	124(7)	17(4)	28(4)	-2(5)
C(116)	58(3)	18(7)	88(5)	12(3)	25(3)	-1(4)
C(121)	44(2)	61(7)	45(3)	27(3)	8(2)	11(3)
C(122)	46(3)	71(7)	56(3)	31(3)	8(2)	24(4)
C(123)	59(3)	70(9)	61(4)	37(4)	1(3)	19(4)
C(124)	47(3)	56(7)	70(4)	26(3)	0(2)	12(4)
C(125)	47(3)	83(8)	83(4)	34(4)	15(3)	21(4)
C(126)	45(3)	63(7)	66(4)	26(3)	15(2)	23(4)
C(131)	39(2)	41(6)	41(2)	19(3)	6(2)	10(3)
C(132)	53(3)	40(7)	88(5)	22(3)	22(3)	15(4)
C(133)	72(4)	31(9)	99(6)	20(4)	26(4)	15(5)
C(134)	51(3)	56(8)	98(5)	7(3)	19(3)	12(5)
C(135)	52(3)	45(7)	72(4)	20(3)	18(3)	15(4)
C(136)	39(2)	52(7)	71(4)	22(3)	11(2)	6(4)
C(211)	47(2)	41(6)	43(3)	18(3)	9(2)	10(3)
C(212)	57(3)	60(8)	47(3)	17(3)	4(2)	4(4)
C(213)	55(3)	62(8)	63(4)	14(3)	6(3)	9(4)
C(214)	51(3)	77(8)	77(4)	19(3)	14(3)	19(5)
C(215)	66(4)	76(9)	56(4)	20(4)	22(3)	25(4)
C(216)	55(3)	62(7)	46(3)	21(3)	15(2)	10(3)
C(221)	75(3)	61(8)	52(3)	44(4)	12(3)	21(4)
C(222)	97(5)	89(11)	63(4)	65(6)	-10(4)	6(5)
C(223)	125(6)	112(14)	90(6)	88(8)	2(5)	23(7)
C(224)	144(7)	92(13)	124(8)	92(8)	48(7)	47(8)
C(225)	148(7)	43(14)	91(6)	56(7)	13(5)	-2(7)
C(226)	112(5)	74(12)	60(4)	52(6)	6(4)	-2(5)
C(231)	45(3)	49(6)	41(3)	19(3)	5(2)	8(3)
C(232)	52(3)	52(7)	58(3)	20(3)	11(2)	16(4)
C(233)	46(3)	82(9)	68(4)	20(3)	5(3)	-5(4)
C(234)	53(3)	104(10)	69(4)	42(4)	4(3)	14(5)
C(235)	67(3)	94(9)	55(3)	46(4)	-2(3)	16(4)
C(236)	57(3)	64(7)	46(3)	28(3)	10(2)	21(4)
C(3)	88(7)	172(22)	128(9)	58(10)	32(6)	45(11)

Table 62. (Continued)

C(2)	105(8)	168(25)	102(8)	41(9)	14(6)	65(11)
C(1)	197(13)	150(26)	109(8)	126(15)	26(9)	53(11)

The anisotropic displacement factor exponent takes the form:
$-2 \text{ pi}^2 [h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

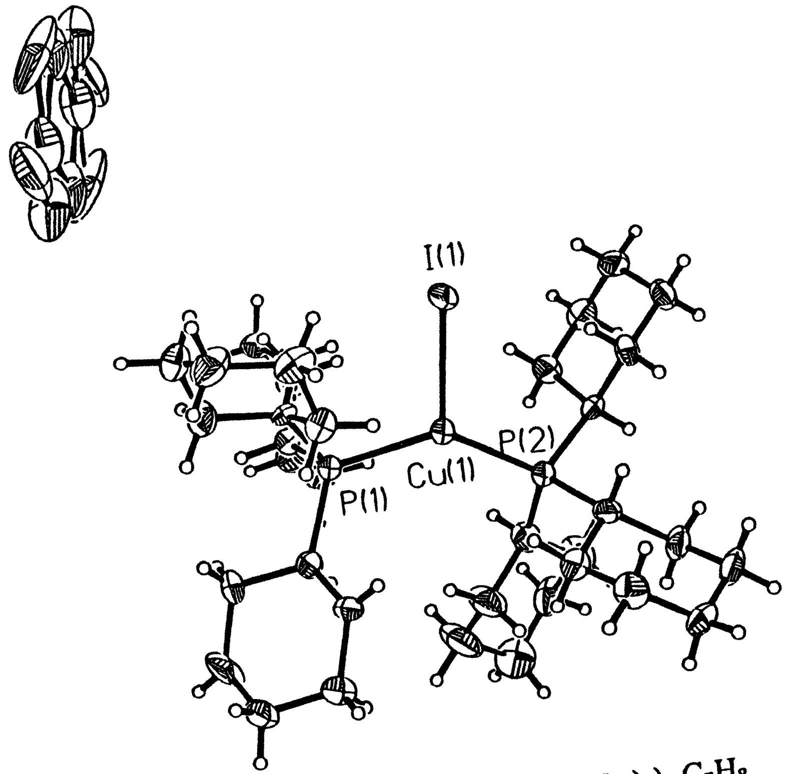


Figure 34 Projection View of $CuI(P(C_6H_{11})_3)_2.C_7H_8$

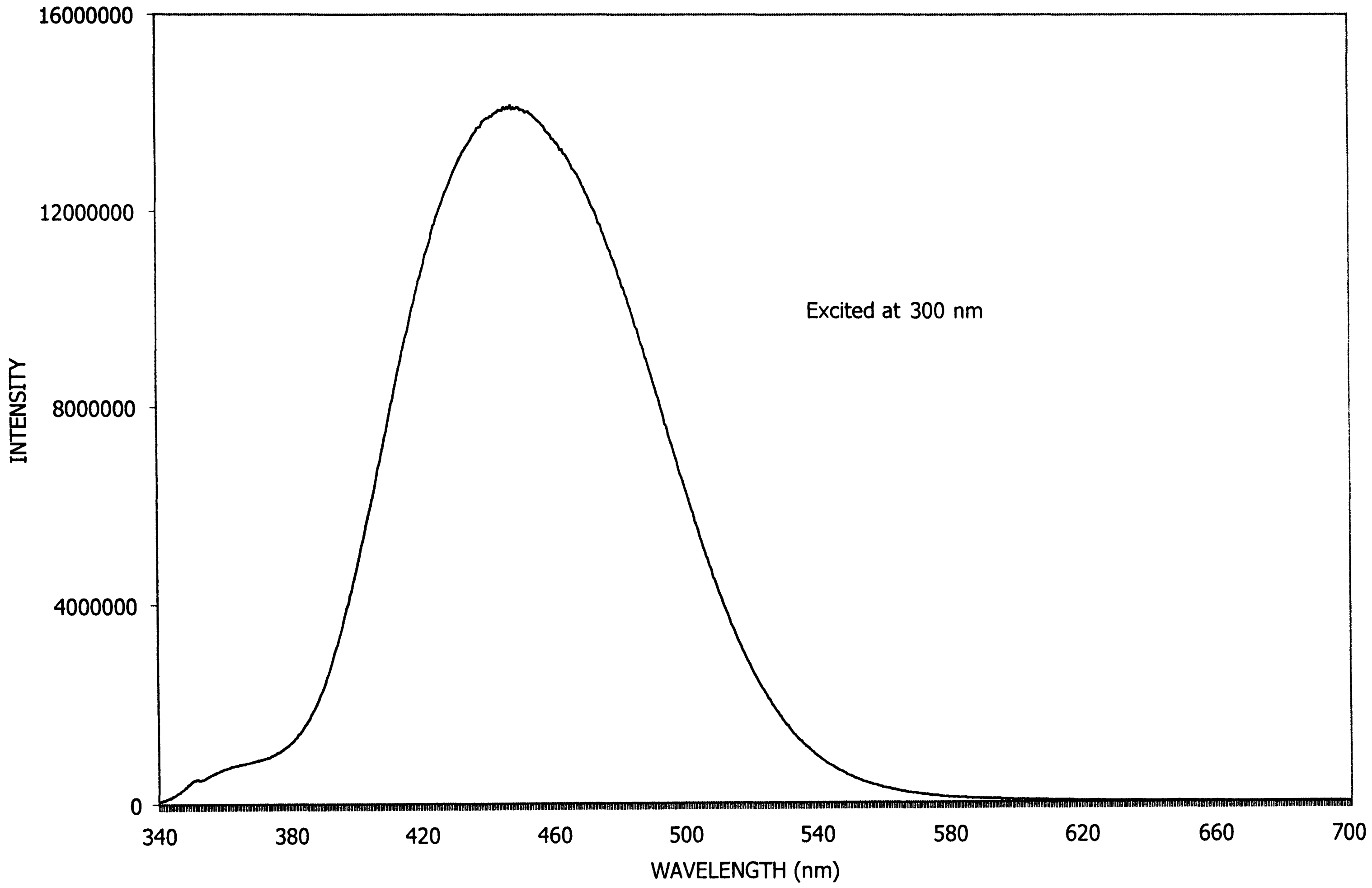


Figure 35 Emission Spectrum of $CuI(P(C_6H_{11})_3)_2.C_7H_8$

Table 63. Crystal Data and Structure Refinement for $CuI(P(C_6H_{11})_3)_2.C_7H_8$

Empirical formula	$C_{26.3333}H_{42.6667}Cu_{0.6667}I_{0.6667}P_{1.33330}$	
Formula weight	527.5	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, *P*$\bar{1}$	
Unit cell dimensions	a = 9.62(3) Å	α = 92.72(3) deg.
	b = 9.622(10) Å	β = 94.900(0) deg.
	c = 25.473(16) Å	γ = 116.05(2) deg.
Volume	2100(6) $Å^3$	
Z, Calculated density	3, 1.251 Mg/m^3	
Absorption coefficient	1.355 mm^{-1}	
F(000)	826	
Crystal size	0.1 x 0.1 x 0.1 mm	
Theta range for data collection	3.5 to 22.5 deg.	
Index ranges	$-1 \leq h \leq 13, -13 \leq k \leq 12, -35 \leq l \leq 35$	
Reflections collected / unique/ observed	13647 / 11694 [R(int) = 0.2251]/ 3256(8.0>σ(F))	
Goodness-of-fit	2.65	
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.1131	
R indices (all data)	R1 = 0.2164, wR2 = 0.1524	
Extinction coefficient	-0.0003(3)	
Largest diff. peak and hole	1.94 and –1.22 $eÅ^{-3}$	

Table 64. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for $CuI(P(C_6H_{11})_3)_2.C_7H_8$

	x	y	z	U(eq)
I(1)	5219(2)	4306(2)	2155(1)	77(1)
Cu(1)	7172(2)	3059(2)	2252(1)	48(1)
P(1)	7477(5)	2773(5)	3135(1)	43(2)
P(2)	7817(5)	2299(5)	1491(2)	45(2)
C(111)	5832(19)	994(21)	3278(6)	47(9)
C(112)	5733(23)	-481(21)	2951(7)	67(11)
C(113)	4344(23)	-2068(27)	3022(9)	86(13)
C(114)	2760(24)	-1900(27)	2912(9)	86(12)
C(115)	2805(22)	-562(26)	3256(7)	73(12)
C(116)	4167(17)	954(18)	3164(6)	44(8)
C(121)	7317(17)	4411(19)	3516(5)	41(8)
C(122)	8512(24)	5955(26)	3386(7)	78(13)
C(123)	8128(23)	7269(22)	3583(8)	72(10)
C(124)	7994(27)	7267(28)	4172(9)	89(14)
C(125)	6898(26)	5758(28)	4311(7)	81(13)
C(126)	7185(24)	4354(23)	4112(6)	66(10)
C(131)	9268(18)	2606(23)	3424(6)	54(9)
C(132)	9288(22)	2175(26)	4000(6)	70(11)
C(133)	10726(26)	1890(32)	4164(8)	100(14)
C(134)	12243(24)	3019(27)	4032(7)	76(13)
C(135)	12195(22)	3446(26)	3463(7)	73(11)
C(136)	10811(22)	3736(29)	3290(7)	84(13)
C(211)	9582(20)	3855(23)	1249(6)	63(10)
C(212)	10124(20)	3414(24)	729(6)	64(10)
C(213)	11483(22)	4853(27)	545(7)	78(12)
C(214)	12835(21)	5675(27)	957(8)	78(12)
C(215)	12395(22)	6169(23)	1467(7)	70(11)
C(216)	11016(23)	4751(27)	1671(7)	80(13)
C(221)	8054(23)	485(22)	1548(6)	63(10)
C(222)	8001(32)	-512(29)	1075(8)	97(15)
C(223)	7983(32)	-2057(27)	1206(8)	99(15)
C(224)	9340(35)	-1787(30)	1620(10)	116(18)
C(225)	9288(36)	-894(34)	2095(9)	124(19)
C(226)	9388(28)	708(27)	1977(8)	92(14)
C(231)	6226(17)	1699(19)	935(5)	42(8)
C(232)	4622(20)	506(23)	1092(7)	63(10)
C(233)	3210(22)	-8(23)	660(7)	67(10)
C(234)	3020(21)	1340(26)	479(7)	71(11)
C(235)	4592(20)	2586(25)	300(7)	68(10)
C(236)	5970(20)	3065(20)	733(6)	54(9)
C(100)	3621(60)	8541(64)	4790(14)	153(36)

Table 64. (Continued)

C(101)	2503(80)	7560(126)	4624(30)	148(55)
C(102)	4330(97)	10794(89)	5018(15)	189(82)
C(103)	3304(149)	9753(104)	4804(30)	127(61)
C(104)	4940(203)	8208(137)	4816(40)	184(86)
H(11A)	5975	859	3647	80
H(11B)	6675	-574	3044	80
H(11C)	5668	-329	2582	80
H(11D)	4461	-2252	3387	80
H(11E)	4341	-2921	2810	80
H(11F)	1927	-2877	2971	80
H(11G)	2618	-1727	2547	80
H(11H)	2912	-740	3622	80
H(11I)	1849	-485	3177	80
H(11J)	4024	1091	2796	80
H(11K)	4165	1824	3364	80
H(12A)	6351	4374	3365	80
H(12B)	8608	5940	3014	80
H(12C)	9493	6127	3572	80
H(12D)	7190	7161	3381	80
H(12E)	8963	8256	3533	80
H(12F)	7687	8038	4294	80
H(12G)	8977	7487	4368	80
H(12H)	5901	5566	4133	80
H(12I)	6819	5766	4685	80
H(12J)	8158	4495	4297	80
H(12K)	6381	3374	4184	80
H(13A)	9172	1685	3228	80
H(13B)	8349	1252	4027	80
H(13C)	9311	3001	4233	80
H(13D)	10631	986	4333	80
H(13E)	12995	2620	4089	80
H(13F)	12580	3940	4270	80
H(13G)	12174	2622	3230	80
H(13H)	13126	4369	3428	80
H(13I)	10910	4639	3120	80
H(21A)	9247	4623	1154	80
H(21B)	9258	2995	455	80
H(21C)	10462	2627	790	80
H(21D)	11105	5588	446	80
H(21E)	11818	4533	237	80
H(21F)	13621	6576	829	80
H(21G)	13275	4976	1037	80
H(21H)	12043	6937	1391	80
H(21I)	13278	6635	1734	80

Table 64. (Continued)

H(21J)	11411	4050	1793	80
H(21K)	10690	5134	1968	80
H(22A)	7145	-199	1699	80
H(22B)	8944	67	922	80
H(22C)	7137	-683	818	80
H(22D)	8076	-2580	891	80
H(22E)	6978	-2682	1314	80
H(22F)	10346	-1333	1496	80
H(22G)	9133	2804	1719	80
H(22H)	10095	-789	2366	80
H(22I)	8309	-1422	2234	80
H(22J)	9373	1281	2294	80
H(22K)	10361	1272	1839	80
H(23A)	6483	1231	640	80
H(23B)	4390	955	1397	80
H(23C)	4735	-393	1190	80
H(23D)	2263	-751	776	80
H(23E)	3421	-483	357	80
H(23F)	2817	1818	784	80
H(23G)	2153	1042	210	80
H(23H)	4473	3477	196	80
H(23I)	4811	2110	-1	80
H(23J)	6920	3804	618	80
H(23K)	5749	3556	1030	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 65. Bond Lengths [Å] and Angles [deg] for $CuI(P(C_6H_{11})_3)_2.C_7H_8$

I(1)-Cu(1)	2.637 (9)
Cu(1)-P(1)	2.289 (8)
Cu(1)-P(2)	2.269 (9)
P(1)-C(111)	1.828 (16)
P(1)-C(121)	1.882 (21)
P(1)-C(131)	1.889 (22)
P(2)-C(211)	1.880 (17)
P(2)-C(221)	1.868 (26)
P(2)-C(231)	1.860 (16)
C(111)-C(112)	1.572 (29)
C(111)-C(116)	1.586 (27)
C(112)-C(113)	1.557 (26)
C(113)-C(114)	1.604 (37)
C(114)-C(115)	1.504 (36)
C(115)-C(116)	1.518 (23)
C(121)-C(122)	1.500 (25)
C(121)-C(126)	1.536 (22)
C(122)-C(123)	1.539 (38)
C(123)-C(124)	1.517 (30)
C(124)-C(125)	1.454 (31)
C(125)-C(126)	1.563 (39)
C(131)-C(132)	1.544 (24)
C(131)-C(136)	1.485 (24)
C(132)-C(133)	1.551 (39)
C(133)-C(134)	1.465 (29)
C(134)-C(135)	1.528 (27)
C(135)-C(136)	1.511 (37)
C(211)-C(212)	1.570 (26)
C(211)-C(216)	1.553 (23)
C(212)-C(213)	1.557 (25)
C(213)-C(214)	1.484 (24)
C(214)-C(215)	1.518 (30)
C(215)-C(216)	1.576 (26)
C(221)-C(222)	1.488 (32)
C(221)-C(226)	1.544 (31)
C(222)-C(223)	1.533 (42)
C(223)-C(224)	1.524 (40)
C(224)-C(225)	1.468 (40)
C(225)-C(226)	1.547 (45)
C(231)-C(232)	1.566 (22)
C(231)-C(236)	1.542 (30)
C(232)-C(233)	1.550 (25)
C(233)-C(234)	1.475 (36)

Table 65. (Continued)

C(234)-C(235)	1.584 (24)
C(235)-C(236)	1.533 (24)
C(100)-C(101)	1.105 (85)
C(100)-C(102)	2.004 (100)
C(100)-C(103)	1.328 (152)
C(100)-C(104)	1.436 (219)
C(100)-C(10B)	1.797 (103)
C(101)-C(103)	1.917 (146)
C(102)-C(103)	1.124 (108)
C(102)-C(10A)	1.797 (103)
C(102)-C(10C)	0.955 (137)
C(104)-C(10B)	0.955 (137)

I(1)-Cu(1)-P(1)	105.3(3)
I(1)-Cu(1)-P(2)	116.7(2)
P(1)-Cu(1)-P(2)	137.5(3)
Cu(1)-P(1)-C(111)	108.7(5)
Cu(1)-P(1)-C(121)	108.0(6)
C(111)-P(1)-C(121)	105.8(8)
Cu(1)-P(1)-C(131)	119.2(6)
C(111)-P(1)-C(131)	104.9(9)
C(121)-P(1)-C(131)	109.5(8)
Cu(1)-P(2)-C(211)	113.8(6)
Cu(1)-P(2)-C(221)	111.6(6)
C(211)-P(2)-C(221)	110.6(10)
Cu(1)-P(2)-C(231)	112.4(6)
C(211)-P(2)-C(231)	105.7(7)
C(221)-P(2)-C(231)	102.1(8)
P(1)-C(111)-C(112)	111.8(12)
P(1)-C(111)-C(116)	115.6(13)
C(112)-C(111)-C(116)	106.0(12)
C(111)-C(112)-C(113)	116.8(18)
C(112)-C(113)-C(114)	108.2(21)
C(113)-C(114)-C(115)	111.4(16)
C(114)-C(115)-C(116)	111.0(17)
C(111)-C(116)-C(115)	115.0(17)
P(1)-C(121)-C(122)	110.9(14)
P(1)-C(121)-C(126)	119.2(15)
C(122)-C(121)-C(126)	112.4(13)
C(121)-C(122)-C(123)	110.7(18)
C(122)-C(123)-C(124)	110.8(20)
C(123)-C(124)-C(125)	112.2(17)
C(124)-C(125)-C(126)	115.3(21)
C(121)-C(126)-C(125)	108.1(17)

Table 65. (Continued)

P(1)-C(131)-C(132)	116.5(14)
P(1)-C(131)-C(136)	118.3(16)
C(132)-C(131)-C(136)	113.9(14)
C(131)-C(132)-C(133)	111.1(17)
C(132)-C(133)-C(134)	117.7(23)
C(133)-C(134)-C(135)	113.3(16)
C(134)-C(135)-C(136)	113.6(18)
C(131)-C(136)-C(135)	117.1(21)
P(2)-C(211)-C(212)	117.0(12)
P(2)-C(211)-C(216)	116.1(11)
C(212)-C(211)-C(216)	109.8(16)
C(211)-C(212)-C(213)	111.3(16)
C(212)-C(213)-C(214)	114.0(16)
C(213)-C(214)-C(215)	113.2(18)
C(214)-C(215)-C(216)	110.8(16)
C(211)-C(216)-C(215)	114.4(15)
P(2)-C(221)-C(222)	122.1(16)
P(2)-C(221)-C(226)	112.2(14)
C(222)-C(221)-C(226)	111.6(23)
C(221)-C(222)-C(223)	113.6(18)
C(222)-C(223)-C(224)	110.9(18)
C(223)-C(224)-C(225)	109.9(30)
C(224)-C(225)-C(226)	112.4(21)
C(221)-C(226)-C(225)	109.7(17)
P(2)-C(231)-C(232)	112.0(10)
P(2)-C(231)-C(236)	113.5(10)
C(232)-C(231)-C(236)	106.4(16)
C(231)-C(232)-C(233)	115.6(14)
C(232)-C(233)-C(234)	111.4(15)
C(233)-C(234)-C(235)	110.8(19)
C(234)-C(235)-C(236)	111.9(15)
C(231)-C(236)-C(235)	114.4(14)
C(101)-C(100)-C(102)	135.2(86)
C(101)-C(100)-C(103)	103.6(91)
C(102)-C(100)-C(103)	31.9(52)
C(101)-C(100)-C(104)	114.8(90)
C(102)-C(100)-C(104)	109.7(56)
C(103)-C(100)-C(104)	139.8(72)
C(101)-C(100)-C(10B)	146.7(88)
C(102)-C(100)-C(10B)	78.0(53)
C(103)-C(100)-C(10B)	109.2(60)
C(104)-C(100)-C(10B)	31.9(52)
C(100)-C(101)-C(103)	42.3(71)
C(100)-C(102)-C(103)	102.0(53)

Table 65. (Continued)

C(103)-C(102)-C(10A)	139.4(111)
C(100)-C(102)-C(10C)	154.0(145)
C(103)-C(102)-C(10C)	167.3(157)
C(10A)-C(102)-C(10C)	52.7(125)
C(100)-C(103)-C(101)	34.0(39)
C(100)-C(103)-C(102)	109.3(120)
C(101)-C(103)-C(102)	143.0(125)
C(100)-C(104)-C(10B)	95.4(142)

Table 66. Anisotropic Displacement Parameters (A^2 x 10^3) for $CuI(P(C_6H_{11})_3)_2.C_7H_8$

	U11	U22	U33	U23	U13	U12
I(1)	112(1)	116(1)	51(1)	93(1)	12(1)	18(1)
Cu(1)	55(1)	65(2)	37(1)	36(1)	11(1)	10(1)
P(1)	46(3)	56(3)	35(2)	29(3)	8(2)	8(2)
P(2)	50(3)	57(3)	36(2)	32(3)	9(2)	9(2)
C(111)	48(11)	58(13)	39(8)	27(10)	1(8)	6(8)
C(112)	89(15)	49(14)	86(13)	50(13)	24(12)	10(10)
C(113)	76(15)	82(20)	95(16)	31(15)	18(13)	9(13)
C(114)	68(15)	69(18)	96(15)	5(13)	21(13)	11(13)
C(115)	67(14)	104(19)	63(11)	55(15)	-7(10)	-10(11)
C(116)	43(10)	15(11)	72(10)	6(9)	23(9)	13(8)
C(121)	25(9)	56(12)	47(9)	20(9)	15(7)	9(8)
C(122)	84(15)	111(20)	58(11)	59(15)	18(11)	13(12)
C(123)	69(14)	46(13)	97(15)	21(11)	22(12)	-2(11)
C(124)	105(18)	85(20)	97(16)	54(16)	39(15)	9(14)
C(125)	102(17)	104(21)	50(11)	57(17)	15(12)	-6(11)
C(126)	91(15)	64(15)	49(10)	43(13)	6(10)	-4(9)
C(131)	38(11)	71(15)	50(9)	20(10)	14(8)	23(9)
C(132)	78(14)	104(18)	40(9)	49(14)	14(10)	28(10)
C(133)	78(17)	127(23)	100(16)	45(17)	-1(13)	79(16)
C(134)	79(16)	105(19)	67(12)	64(16)	-7(11)	6(12)
C(135)	64(13)	97(18)	72(12)	49(14)	2(11)	8(11)
C(136)	57(14)	151(22)	73(12)	67(15)	26(11)	59(14)
C(211)	66(13)	107(17)	39(9)	63(13)	-1(9)	-4(9)
C(212)	59(12)	93(17)	33(8)	27(12)	11(9)	0(9)
C(213)	66(15)	114(19)	50(11)	31(14)	30(12)	17(12)
C(214)	42(13)	114(19)	76(13)	27(13)	30(12)	27(13)
C(215)	68(14)	65(16)	62(11)	19(12)	-3(11)	-4(10)
C(216)	82(15)	130(21)	52(11)	67(16)	15(11)	11(12)
C(221)	78(13)	65(14)	57(10)	44(12)	3(10)	0(9)
C(222)	150(22)	100(20)	76(13)	88(19)	9(14)	-2(12)
C(223)	158(23)	92(19)	92(15)	86(18)	57(17)	27(14)
C(224)	185(26)	99(21)	135(20)	118(22)	52(20)	39(17)
C(225)	167(25)	168(29)	89(16)	134(25)	-36(17)	-7(17)
C(226)	122(19)	110(20)	80(13)	89(18)	-10(13)	3(13)
C(231)	37(10)	55(12)	39(8)	23(9)	13(8)	6(8)
C(232)	61(13)	74(15)	55(10)	34(12)	-2(10)	3(10)
C(233)	60(13)	73(16)	64(11)	25(12)	13(11)	1(10)
C(234)	50(13)	106(19)	60(11)	40(13)	-2(10)	0(12)
C(235)	52(13)	91(16)	52(10)	24(12)	-1(10)	27(10)
C(236)	66(12)	48(13)	51(9)	25(10)	12(9)	24(9)
C(100)	203(47)	237(60)	81(24)	141(41)	55(30)	78(29)

Table 66. (Continued)

C(101)	104(52)	252(105	69(48)	61(52)	-9(40)	60(56)
C(102)	433(130	252(104	59(26)	303(112	72(38)	50(36)
C(103)	253(103	62(69)	89(48)	86(73)	47(56)	8(40)
C(104)	371(148	117(99)	139(73)	147(97)	178(94)	49(59)

The anisotropic displacement factor exponent takes the form:

$-2\ \mathrm{pi}^2\ [\ h^2 a^{*2}\ U_{11} + \dots + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

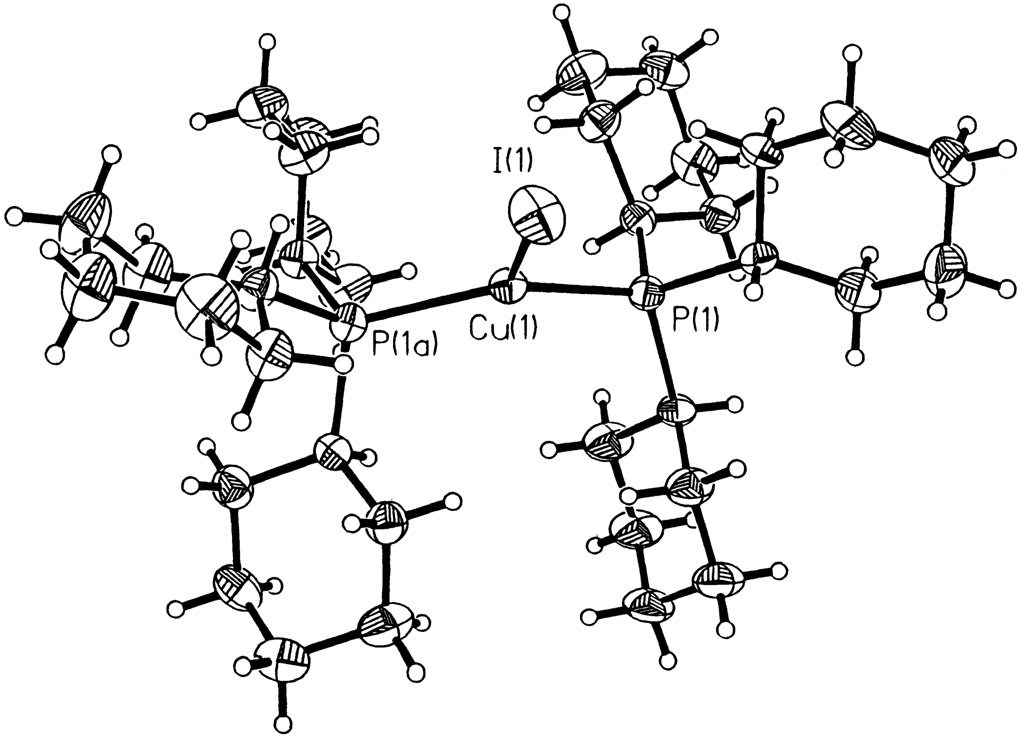


Figure 36 Projection View of $CuI(P(C_6H_{11})_3)_2$ (hex)

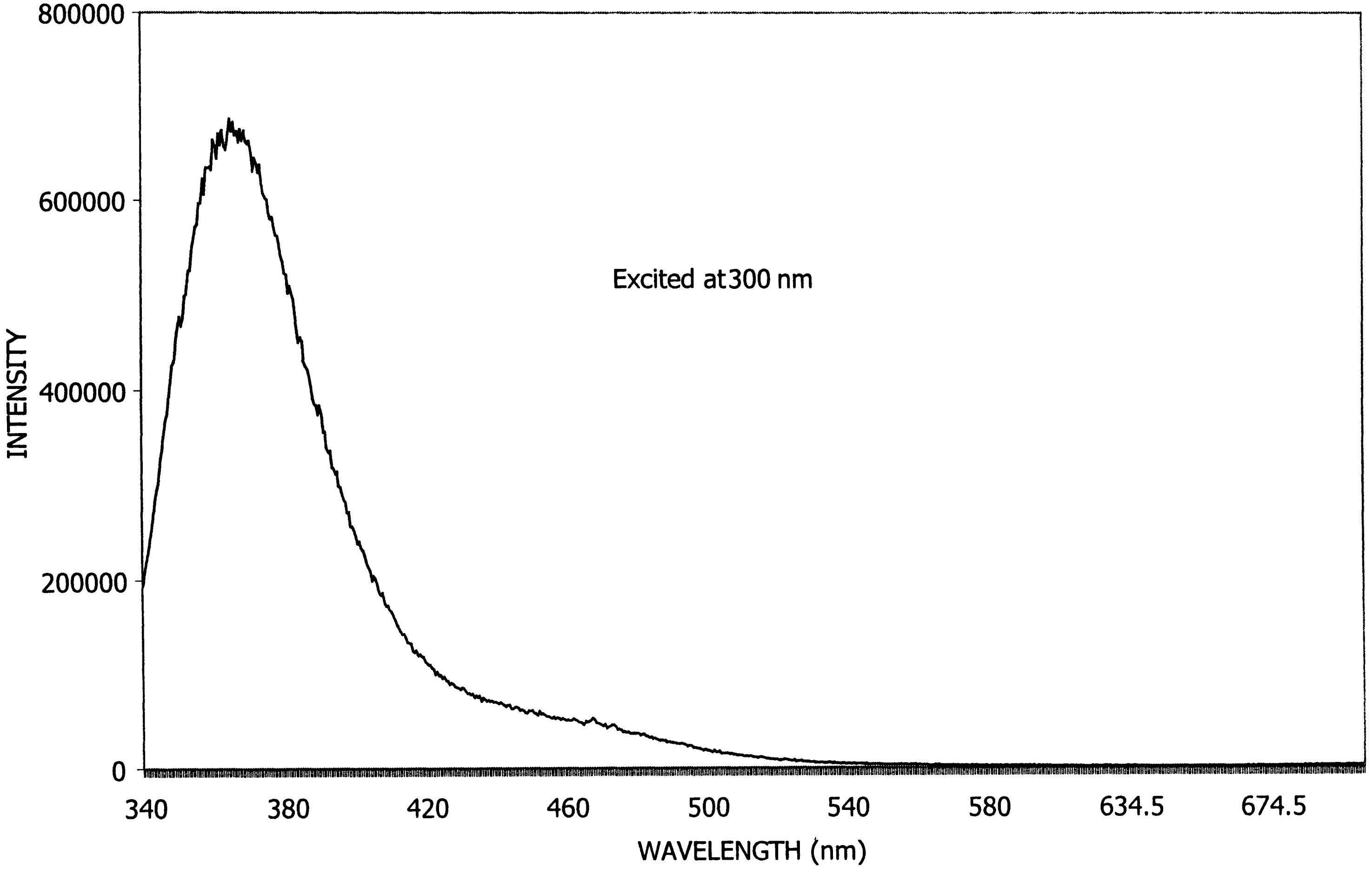


Figure 37 Emission Spectrum of $CuI(P(C_6H_{11})_3)_2$ (hex)

Table 67. Crystal Data and Structure Refinement for CuI(P(C_6H_{11})$_3$)$_2$ (hex)

Empirical formula	$C_{18}H_{33}Cu_{0.5}I_{0.5}P$
Formula weight	375.6
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C2/c*
Unit cell dimensions	a = 18.441(9) Å α = 90.0 deg.
	b = 9.276(6) Å β = 97.03(5) deg.
	c = 22.51(2) Å γ = 90.0 deg.
Volume	3820(5) Å^3
Z, Calculated density	8, 1.306 Mg/m^3
Absorption coefficient	1.485 mm^{-1}
F(000)	1576
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	2.14 to 29.98 deg.
Index ranges	$-1 \leq h \leq 25$, $-13 \leq k \leq 1$, $-31 \leq l \leq 31$
Reflections collected / unique/ observed	6735 / 5580 [R(int) = 0.0663]/ 2025(6.0>σ(F))
Goodness-of-fit	1.64
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.0794
R indices (all data)	R1 = 0.1561, wR2 = 0.1065
Extinction coefficient	-0.00028
Largest diff. peak and hole	1.38 and –0.96 e. Å^{-3}

Table 68. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters
($Å^2$x 10^3) for CuI(P(C_6H_{11})$_3$)$_2$ (hex)

	x	y	z	U(eq)
I(1)	0	5847(1)	2500	78(1)
Cu(1)	0	3059(1)	2500	42(1)
P(1)	594(1)	2126(2)	3366(1)	43(1)
C(11)	901(5)	3563(10)	3923(4)	50(3)
C(12)	1493(6)	4536(10)	3725(4)	61(3)
C(13)	1601(7)	5899(12)	4109(5)	91(5)
C(14)	1742(7)	5582(12)	4773(5)	89(5)
C(15)	1153(8)	4612(13)	4960(5)	95(5)
C(16)	1059(7)	3222(11)	4580(4)	80(4)
C(21)	1404(5)	1021(9)	3231(4)	46(3)
C(22)	1880(6)	1760(10)	2798(4)	63(4)
C(23)	2479(8)	770(11)	2622(5)	84(5)
C(24)	2957(6)	155(12)	3168(5)	75(4)
C(25)	2477(6)	-618(11)	3565(5)	76(4)
C(26)	1881(6)	366(11)	3771(4)	64(4)
C(31)	39(5)	906(8)	3789(4)	46(3)
C(32)	-650(6)	1631(10)	3949(5)	68(4)
C(33)	-1092(6)	659(11)	4321(5)	77(4)
C(34)	-1284(6)	-771(11)	4001(5)	77(4)
C(35)	-606(7)	-1496(11)	3838(5)	82(5)
C(36)	-169(7)	-502(10)	3468(5)	74(4)
H(11A)	490	4203	3904	80
H(12A)	1387	4779	3309	80
H(12B)	1940	3996	3778	80
H(13A)	1163	6464	4034	80
H(13B)	1998	6460	3993	80
H(14A)	1769	6464	4998	80
H(14B)	2204	5099	4854	80
H(15A)	700	5133	4919	80
H(15B)	1274	4359	5373	80
H(16A)	1502	2668	4640	80
H(16B)	670	2643	4698	80
H(21A)	1205	193	3013	80
H(22A)	2114	2578	3001	80
H(22B)	1575	2102	2450	80
H(23A)	2779	1279	2373	80
H(23B)	2247	-15	2395	80
H(24A)	3211	935	3383	80
H(24B)	3315	-500	3047	80
H(25A)	2780	-992	3907	80
H(25B)	2240	-1417	3351	80

Table 68. (Continued)

H(26A)	1579	-163	4014	80
H(26B)	2111	1141	4006	80
H(31A)	330	664	4159	80
H(32A)	-953	1862	3584	80
H(32B)	-525	2515	4159	80
H(33A)	-1527	1140	4410	80
H(33B)	-796	453	4693	80
H(34A)	-1597	-571	3638	80
H(34B)	-1542	-1393	4245	80
H(35A)	-728	-2389	3635	80
H(35B)	-300	-1709	4203	80
H(36A)	263	-986	3374	80
H(36B)	-471	-288	3101	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 69. Bond Lengths [Å] and Angles [deg] for
$CuI(P(C_6H_{11})_3)_2$ (hex)

Cu(1)-I(1)	2.587 (3)
Cu(1)-P(1)	2.285 (3)
Cu(1)-P(1A)	2.285 (3)
P(1)-C(11)	1.871 (9)
P(1)-C(21)	1.867 (9)
P(1)-C(31)	1.864 (9)
C(11)-C(12)	1.524 (14)
C(11)-C(16)	1.504 (13)
C(12)-C(13)	1.531 (14)
C(13)-C(14)	1.514 (17)
C(14)-C(15)	1.509 (19)
C(15)-C(16)	1.545 (16)
C(21)-C(22)	1.549 (13)
C(21)-C(26)	1.537 (12)
C(22)-C(23)	1.525 (17)
C(23)-C(24)	1.532 (16)
C(24)-C(25)	1.514 (17)
C(25)-C(26)	1.543 (15)
C(31)-C(32)	1.520 (14)
C(31)-C(36)	1.519 (12)
C(32)-C(33)	1.532 (16)
C(33)-C(34)	1.530 (15)
C(34)-C(35)	1.504 (17)
C(35)-C(36)	1.536 (17)
I(1)-Cu(1)-P(1)	112.2(1)
I(1)-Cu(1)-P(1A)	112.2(1)
P(1)-Cu(1)-P(1A)	135.5(1)
Cu(1)-P(1)-C(11)	112.1(3)
Cu(1)-P(1)-C(21)	112.3(3)
C(11)-P(1)-C(21)	108.5(4)
Cu(1)-P(1)-C(31)	115.5(3)
C(11)-P(1)-C(31)	103.3(4)
C(21)-P(1)-C(31)	104.5(4)
P(1)-C(11)-C(12)	113.2(6)
P(1)-C(11)-C(16)	121.0(7)
C(12)-C(11)-C(16)	110.7(8)
C(11)-C(12)-C(13)	111.8(9)
C(12)-C(13)-C(14)	113.0(9)
C(13)-C(14)-C(15)	110.4(10)
C(14)-C(15)-C(16)	112.3(11)
C(11)-C(16)-C(15)	111.3(8)
P(1)-C(21)-C(22)	112.7(6)

Table 69. (Continued)

P(1)-C(21)-C(26)	118.7(6)
C(22)-C(21)-C(26)	111.0(7)
C(21)-C(22)-C(23)	112.4(8)
C(22)-C(23)-C(24)	112.3(10)
C(23)-C(24)-C(25)	109.2(10)
C(24)-C(25)-C(26)	112.8(8)
C(21)-C(26)-C(25)	110.8(8)
P(1)-C(31)-C(32)	112.3(6)
P(1)-C(31)-C(36)	113.7(7)
C(32)-C(31)-C(36)	108.9(8)
C(31)-C(32)-C(33)	112.7(8)
C(32)-C(33)-C(34)	111.2(10)
C(33)-C(34)-C(35)	110.6(9)
C(34)-C(35)-C(36)	111.8(9)
C(31)-C(36)-C(35)	112.2(9)

Table 70. Anisotropic Displacement Parameters ($A^2 \times 10^3$) for $CuI(P(C_6H_{11})_3)_2$ (hex)

	U11	U22	U33	U23	U13	U12
I(1)	97(1)	33(1)	99(1)	0	-5(1)	0
Cu(1)	42(1)	38(1)	47(1)	0	8(1)	0
P(1)	49(1)	37(1)	44(1)	-6(1)	7(1)	2(1)
C(11)	53(6)	54(5)	45(5)	-14(5)	13(4)	0(4)
C(12)	59(6)	61(5)	62(5)	-33(5)	7(5)	-8(5)
C(13)	88(9)	72(7)	111(10)	-42(7)	4(7)	-17(7)
C(14)	101(10)	84(8)	80(7)	-46(8)	6(7)	-21(7)
C(15)	124(12)	98(9)	67(7)	-31(9)	20(7)	-28(7)
C(16)	97(9)	73(7)	70(7)	-40(7)	14(6)	-4(6)
C(21)	43(5)	45(4)	49(5)	1(4)	3(4)	-1(4)
C(22)	69(7)	64(6)	58(6)	7(6)	12(5)	11(5)
C(23)	94(9)	76(7)	90(8)	12(7)	39(7)	2(7)
C(24)	58(7)	65(6)	105(8)	1(5)	17(7)	-9(6)
C(25)	67(7)	62(6)	96(8)	17(6)	-4(6)	14(6)
C(26)	61(6)	69(6)	60(6)	-3(5)	4(5)	14(5)
C(31)	50(5)	38(4)	52(5)	-11(4)	10(4)	6(4)
C(32)	69(7)	58(6)	79(7)	-14(5)	23(6)	-3(5)
C(33)	62(7)	80(7)	93(7)	-18(6)	29(6)	-2(7)
C(34)	61(7)	79(7)	94(8)	-27(6)	15(6)	13(6)
C(35)	92(9)	52(6)	108(9)	-36(6)	33(7)	-2(6)
C(36)	87(8)	49(5)	91(7)	-23(6)	34(7)	-14(5)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

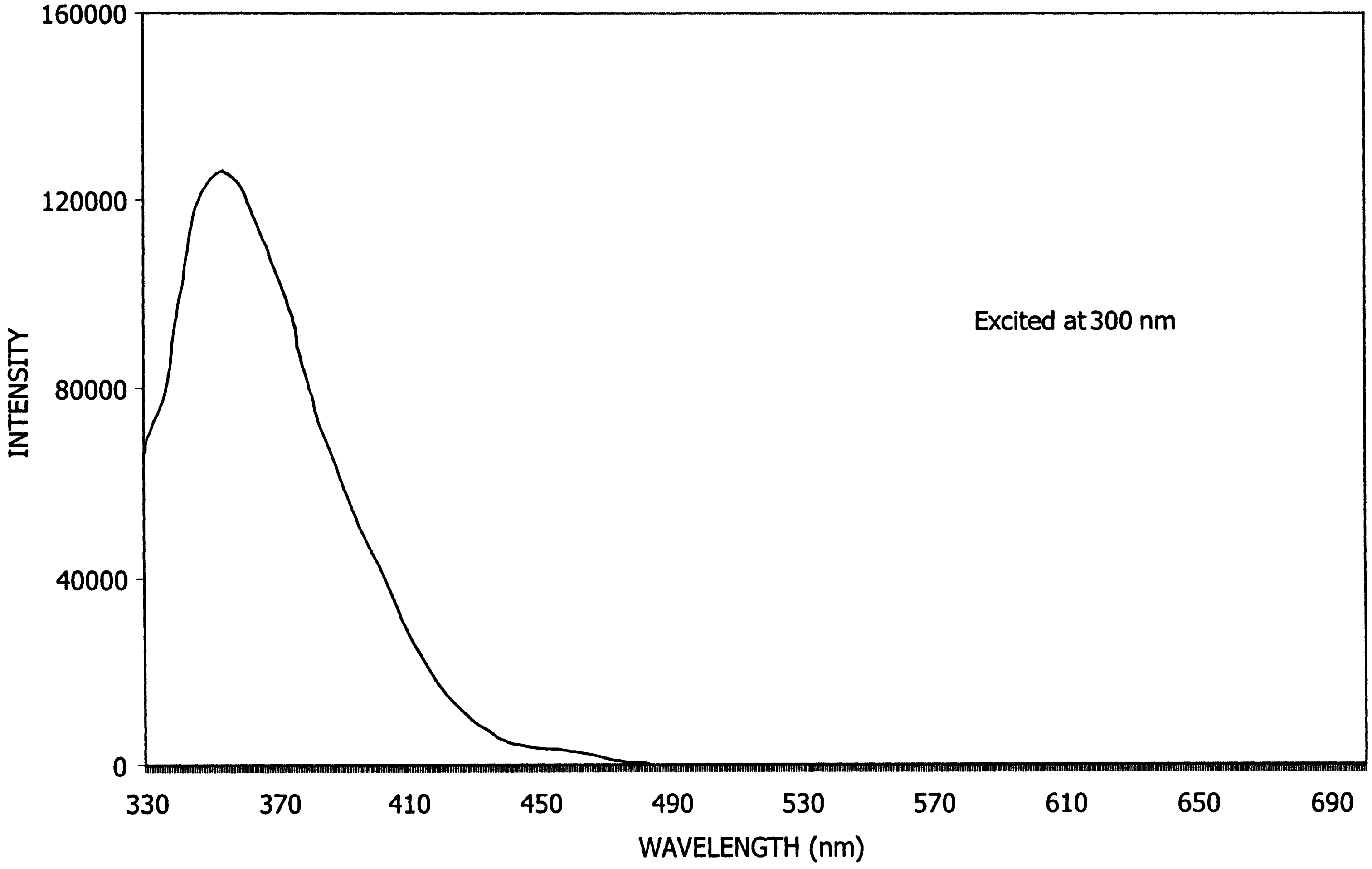


Figure 38 Emission Spectrum of $CuI(P(C_6H_{11})_3)_2$ (mix)

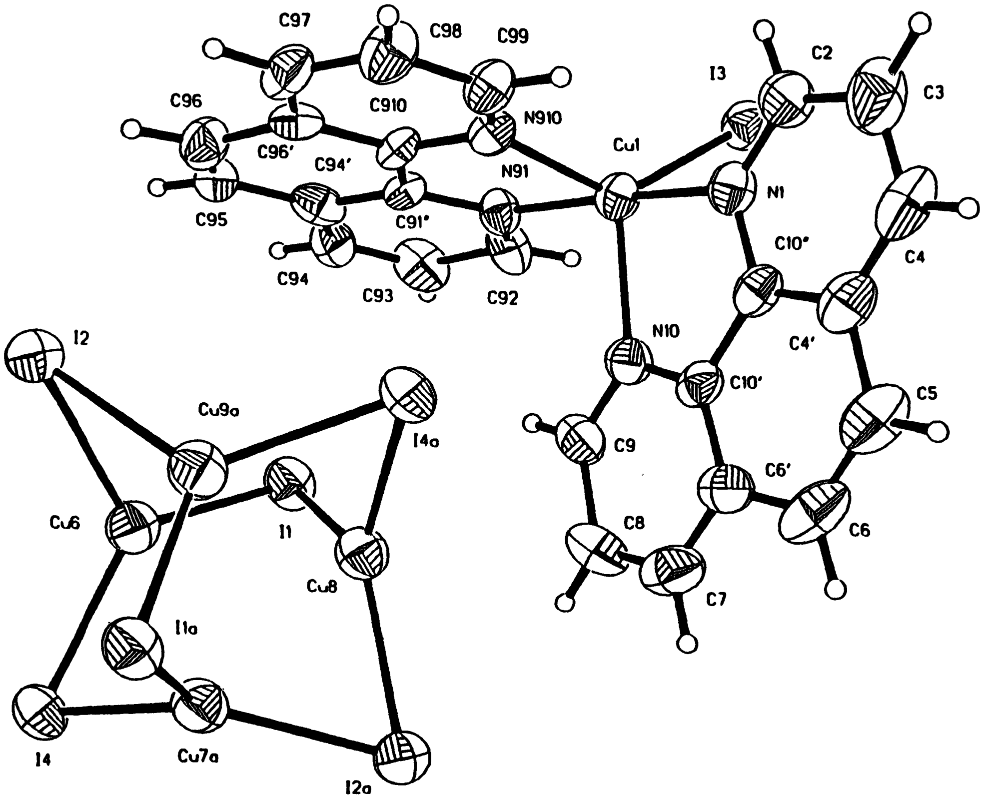


Figure 39 Projection View of Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide$]_2$

Table 71. Crystal Data and Structure Refinement for
Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$

Empirical formula	$C_{24}\ H_{16}\ Cu_3\ I_4\ N_4$	
Formula weight	1058.63	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\bar{1}$	
Unit cell dimensions	a = 10.640(15) Å	α = 77.51(9) deg.
	b = 12.060(11) Å	β = 84.13(13) deg.
	c = 12.838(19) Å	γ = 82.92(9) deg.
Volume	1591(4) A^3	
Z, Calculated density	2, 2.209 Mg/m^3	
Absorption coefficient	5.885 mm^{-1}	
F(000)	974	
Crystal size	0.2 x 0.2 x 0.2 mm	
Theta range for data collection	1.93 to 30.01 deg.	
Index ranges	$-14 \le h \le 1, -16 \le k \le 16, -18 \le l \le 18$	
Reflections collected / unique	10580 / 9210 [R(int) = 0.1862]	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R1 = 0.0872, wR2 = 0.2085	
R indices (all data)	R1 = 0.2061, wR2 = 0.2849	
Extinction coefficient	0.0003(6)	
Largest diff. peak and hole	1.404 and -1.526 $eÅ^{-3}$	

Table 72. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$x 10^3) for Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$

	x	y	z	U(eq)
I(1)	2576(1)	5389(1)	3706(1)	76(1)
I(2)	3163(1)	5143(1)	7154(1)	77(1)
I(3)	435(1)	11637(1)	965(1)	74(1)
I(4)	4886(1)	2309(1)	5467(1)	76(1)
Cu(1)	1842(2)	10201(1)	2406(1)	62(1)
Cu(6)	3708(3)	4318(3)	5380(3)	74(1)
Cu(7)	3677(3)	6029(3)	5211(3)	76(1)
Cu(8)	4911(3)	5919(3)	3698(3)	74(1)
Cu(9)	4778(4)	4216(3)	4117(3)	78(1)
N(1)	3243(10)	11235(9)	2144(9)	65(3)
C(2)	3170(14)	12301(13)	2288(15)	84(5)
C(3)	4180(2)	12984(18)	2075(17)	119(7)
C(4)	5404(18)	12463(18)	1732(14)	98(6)
C(4')	5515(14)	11352(15)	1534(13)	81(4)
C(5)	6687(15)	10780(18)	1127(14)	94(6)
C(6)	6761(16)	9668(19)	954(14)	96(6)
C(6')	5639(16)	9065(14)	1213(12)	75(4)
C(7)	5654(18)	7993(17)	1056(14)	96(6)
C(8)	4500(2)	7398(15)	1222(19)	123(8)
C(9)	3385(16)	8039(12)	1632(14)	83(5)
N(10)	3371(11)	9087(9)	1810(9)	64(3)
C(10')	4497(13)	9570(11)	1609(10)	60(3)
C(10")	4416(13)	10721(12)	1768(11)	63(3)
N(91)	587(10)	9019(8)	2800(9)	60(3)
C(92)	-45(15)	8652(12)	2107(15)	83(5)
C(93)	-787(16)	7661(13)	2495(16)	88(5)
C(94)	-900(14)	7186(12)	3549(14)	76(4)
C(94')	-226(11)	7598(10)	4282(14)	67(4)
C(95)	-234(14)	7104(11)	5436(12)	68(4)
C(96)	429(13)	7505(13)	6044(14)	77(4)
C(96')	1203(11)	8481(10)	5661(12)	61(3)
C(97)	1879(14)	8951(13)	6315(12)	74(4)
C(98)	2591(15)	9881(14)	5847(13)	81(4)
C(99)	2566(13)	10287(12)	4747(12)	65(3)
N(910)	1897(9)	9853(9)	4105(9)	58(3)
C(910)	1226(10)	8958(10)	4553(10)	52(3)
C(91")	507(11)	8501(10)	3860(11)	53(3)
H(2A)	2363	12607	2571	80
H(3A)	4055	13766	2151	80
H(4A)	6142	12871	1629	80

Table 72. (Continued)

H(5A)	7439	11170	992	80
H(6A)	7539	9314	667	80
H(7A)	6443	7613	818	80
H(8A)	4484	6652	1074	80
H(9A)	2611	7680	1803	80
H(92A)	-24	9035	1369	80
H(93A)	-1177	7346	1999	80
H(94A)	-1426	6578	3810	80
H(95A)	-749	6496	5741	80
H(96A)	428	7139	6787	80
H(97A)	1853	8656	7073	80
H(98A)	3075	10211	6271	80
H(99A)	3062	10903	4422	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 73. Bond Lengths [Å] and Angles [deg] for
Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$

I(1)-Cu(6)	2.585(6)
I(1)-Cu(9)	2.624(5)
I(1)-Cu(8)	2.639(5)
I(1)-Cu(7)	2.651(5)
I(2)-Cu(7)	2.525(6)
I(2)-Cu(8)'	2.557(5)
I(2)-Cu(6)	2.661(6)
I(2)-Cu(9)'	2.683(6)
I(3)-Cu(1)	2.684(4)
I(4)-Cu(9)	2.561(5)
I(4)-Cu(6)	2.573(5)
I(4)-Cu(7)'	2.616(5)
I(4)-Cu(8)'	2.629(4)
Cu(1)-N(1)	2.017(10)
Cu(1)-N(91)	2.022(10)
Cu(1)-N(910)	2.135(12)
Cu(1)-N(10)	2.166(12)
Cu(6)-Cu(9)	1.901(7)
Cu(6)-Cu(8)'	1.935(6)
Cu(6)-Cu(7)	2.024(5)
Cu(6)-Cu(9)'	2.747(5)
Cu(6)-Cu(7)'	2.812(7)
Cu(6)-Cu(8)	2.875(7)
Cu(7)-Cu(9)'	1.896(6)
Cu(7)-Cu(8)	2.250(7)
Cu(7)-Cu(8)'	2.807(6)
Cu(7)-Cu(9)	2.914(7)
Cu(8)-Cu(9)	2.027(5)
Cu(8)-Cu(9)'	2.825(7)
N(1)-C(2)	1.329(19)
N(1)-C(10")	1.410(18)
C(2)-C(3)	1.40(2)
C(3)-C(4)	1.45(3)
C(4)-C(4')	1.41(2)
C(4')-C(10")	1.44(2)
C(4')-C(5)	1.45(2)
C(5)-C(6)	1.40(3)
C(6)-C(6')	1.45(2)
C(6')-C(7)	1.35(2)
C(6')-C(10')	1.39(2)
C(7)-C(8)	1.47(3)
C(8)-C(9)	1.45(3)

Table 73. (Continued)

C(9)-N(10)	1.330(18)
N(10)-C(10')	1.373(17)
C(10')-C(10")	1.438(19)
N(91)-C(91")	1.368(17)
N(91)-C(92)	1.343(18)
C(92)-C(93)	1.48(2)
C(93)-C(94)	1.35(2)
C(94)-C(94')	1.44(2)
C(94')-C(91")	1.398(17)
C(94')-C(95)	1.47(2)
C(95)-C(96)	1.30(2)
C(96)-C(96')	1.487(19)
C(96')-C(910)	1.413(18)
C(96')-C(97)	1.405(19)
C(97)-C(98)	1.42(2)
C(98)-C(99)	1.39(2)
C(99)-N(910)	1.363(16)
N(910)-C(910)	1.358(15)
C(910)-C(91")	1.462(17)
N(1)-Cu(1)-N(91)	172.5(4)
N(1)-Cu(1)-N(910)	93.8(4)
N(91)-Cu(1)-N(910)	81.1(4)
N(1)-Cu(1)-N(10)	80.4(5)
N(91)-Cu(1)-N(10)	95.7(5)
N(910)-Cu(1)-N(10)	106.4(4)
N(1)-Cu(1)-I(3)	92.3(3)
N(91)-Cu(1)-I(3)	95.2(3)
N(910)-Cu(1)-I(3)	136.0(3)
N(10)-Cu(1)-I(3)	117.6(3)
N(1)-C(2)-C(3)	124.9(17)
C(2)-C(3)-C(4)	117.2(19)
C(4')-C(4)-C(3)	119.7(14)
C(4)-C(4')-C(10")	118.8(15)
C(4)-C(4')-C(5)	123.9(15)
C(10")-C(4')-C(5)	117.4(16)
C(6)-C(5)-C(4')	122.1(14)
C(5)-C(6)-C(6')	118.6(16)
C(7)-C(6')-C(10')	117.2(16)
C(7)-C(6')-C(6)	121.1(17)
C(10')-C(6')-C(6)	121.7(16)
C(6')-C(7)-C(8)	122.1(17)
C(9)-C(8)-C(7)	113.9(16)

Table 73. (Continued)

N(10)-C(9)-C(8)	124.1(16)
C(9)-N(10)-C(10')	117.1(12)
N(10)-C(10')-C(6')	125.4(13)
N(10)-C(10')-C(10")	114.8(12)
C(6')-C(10')-C(10")	119.7(13)
N(1)-C(10")-C(10')	119.2(11)
N(1)-C(10")-C(4')	120.2(13)
C(10')-C(10")-C(4')	120.6(14)
C(91")-N(91)-C(92)	119.9(11)
N(91)-C(92)-C(93)	119.5(14)
C(94)-C(93)-C(92)	120.0(13)
C(93)-C(94)-C(94')	119.6(13)
C(91")-C(94')-C(94)	117.5(14)
C(91")-C(94')-C(95)	118.5(12)
C(94)-C(94')-C(95)	124.0(12)
C(96)-C(95)-C(94')	120.3(13)
C(95)-C(96)-C(96')	124.4(15)
C(910)-C(96')-C(97)	119.3(12)
C(910)-C(96')-C(96)	115.8(12)
C(97)-C(96')-C(96)	124.9(14)
C(98)-C(97)-C(96')	119.4(14)
C(97)-C(98)-C(99)	117.3(12)
N(910)-C(99)-C(98)	124.0(12)
C(910)-N(910)-C(99)	118.6(11)
N(910)-C(910)-C(96')	121.4(10)
N(910)-C(910)-C(91")	118.2(11)
C(96')-C(910)-C(91")	120.3(11)
N(91)-C(91")-C(94')	123.3(11)
N(91)-C(91")-C(910)	116.0(10)
C(94')-C(91")-C(910)	120.6(12)

Symmetry transformations used to generate equivalent atoms: 1-x, 1-y, 1-z.

Table 74. Anisotropic Displacement Parameters (A^2 x 10^3) for Cu_4I_6[di-1,10-phenanthrolino copper(II) iodide]$_2$

	U11	U22	U33	U23	U13	U12
I(1)	67(1)	70(1)	90(1)	-8(1)	-10(1)	-12(1)
I(2)	73(1)	78(1)	82(1)	-23(1)	-1(1)	-8(1)
I(3)	73(1)	82(1)	63(1)	-11(1)	-6(1)	-4(1)
I(4)	86(1)	56(1)	88(1)	-15(1)	-12(1)	-11(1)
Cu(1)	59(1)	68(1)	58(1)	-10(1)	-3(1)	-15(1)
Cu(6)	74(2)	72(2)	79(3)	-18(2)	-1(2)	-15(2)
Cu(7)	72(2)	68(2)	86(3)	-14(2)	-2(2)	-7(2)
Cu(8)	77(2)	66(2)	79(3)	-17(2)	-4(2)	-11(2)
Cu(9)	84(2)	70(2)	82(3)	-19(2)	-6(2)	-16(2)
N(1)	62(6)	73(7)	61(8)	-10(6)	-6(5)	-19(5)
C(2)	59(8)	81(10)	107(14)	-17(9)	11(8)	-12(7)
C(3)	148(18)	121(15)	106(16)	-37(12)	21(13)	-86(14)
C(4)	86(12)	149(17)	64(12)	-24(11)	10(9)	-52(11)
C(4')	60(9)	110(12)	71(12)	-17(9)	0(7)	-14(8)
C(5)	60(9)	150(16)	82(13)	-34(12)	-5(8)	-34(10)
C(6)	63(9)	166(19)	61(12)	-35(11)	-3(8)	-1(10)
C(6')	91(11)	78(9)	48(9)	-12(7)	-14(8)	23(8)
C(7)	93(12)	121(15)	65(12)	-20(10)	-14(9)	38(11)
C(8)	150(2)	57(9)	150(2)	-21(11)	10(16)	10(11)
C(9)	81(10)	59(8)	98(14)	-2(8)	1(9)	0(7)
N(10)	76(7)	61(6)	53(8)	-9(5)	-7(6)	2(5)
C(10')	64(8)	74(8)	39(8)	-6(6)	-5(6)	3(6)
C(10")	63(8)	82(9)	42(8)	-10(6)	-2(6)	-9(6)
N(91)	71(7)	56(6)	52(7)	-5(5)	-13(5)	-13(5)
C(92)	84(10)	66(8)	94(13)	9(8)	-28(9)	-11(7)
C(93)	99(11)	78(9)	100(15)	-28(9)	-43(10)	-18(8)
C(94)	79(9)	64(8)	84(13)	-6(8)	-6(8)	-16(7)
C(94')	46(6)	57(7)	103(13)	-23(7)	-15(7)	1(5)
C(95)	76(9)	59(7)	64(11)	-8(7)	6(7)	-4(6)
C(96)	62(8)	85(10)	75(11)	-6(8)	12(7)	-9(7)
C(96')	52(7)	60(7)	72(11)	-26(7)	1(6)	10(5)
C(97)	80(9)	96(10)	45(9)	-16(8)	1(7)	-5(8)
C(98)	86(10)	105(11)	62(11)	-28(9)	-7(8)	-28(9)
C(99)	65(8)	82(9)	50(9)	-17(7)	-6(6)	-14(6)
N(910)	50(5)	67(6)	56(7)	-16(5)	1(5)	-6(5)
C(910)	46(6)	71(7)	39(8)	-15(6)	6(5)	-5(5)
C(91")	47(6)	60(7)	51(8)	-14(6)	7(5)	-4(5)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

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