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MONOVALENT COPPER COMPLEXES OF *N*-ARYL-PYRIDINE-2-ALDIMINE. SYNTHESIS, CHARACTERIZATION AND STRUCTURE

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Abstract—A direct synthetic route, based on silver(I) assisted metal exchange reaction, to cationic bis-ligand complexes of copper(I) involving *N*-aryl-pyridine-2-aldimines (L, **1**) has been studied. These complexes are obtained as their perchlorates, $[Cu(L)_2]ClO_4$ (**2**). They have been characterized with the help of spectroscopy and X-ray crystallography. The X-ray structure of $[Cu(L^2)_2]ClO_4$, where L^2 is *N*-*p*-tolyl-pyridine-2-aldimine is reported. There are two crystallographically independent molecules in the asymmetric unit. The ligand L^2 coordinates in a bidentate manner providing a highly distorted tetrahedral geometry about copper. The complexes show highly resolved symmetrical ^1H NMR spectra. Intense MLCT absorptions are observed in the visible range. In methanol the CuL_2^{2+}/CuL_2^{+} couple has $E_{1/2}$ *ca*, 0.35 V *vs* SCE at 298 K. The moderately high positive potential is brought about by the distortion in the geometry of CuL_2^{2+}. Copyright © 1996 Elsevier Science Ltd

Copper can adopt variable valence states and this ability is reflected[1,2] in its redox properties. The monovalent state of copper is important and requires special attention not only because it is difficult to stabilize and many of its complexes demonstrate[3] unusual structural features but also because some of them are well known for their efficient catalytic activities[4–6] in important photoredox reactions. Stable and well characterized copper(I) complexes are scarce in the literature. Accordingly, the synthesis of stable copper(I) complexes turn out to be essential prerequisites for further studies.

There have been reports that diimines like 2,2′-bipyridine(bpy) or 1,10-phenanthroline (phen) and their substituted derivatives will stabilize preferentially the cuprous state[7,8] especially when tetrahedral coordination is favoured by the presence of bulky substituents on the ligands. As a sequel to our continued endeavor to explore the transition metal chemistry of a neutral Schiff base, *N*-aryl-pyridine-2-carboxaldimine (L, **1**), we report herein synthesis, characterization, and properties of new cuprous complexes of L. Also incorporated in this

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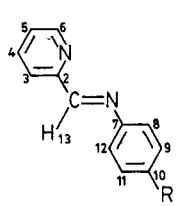
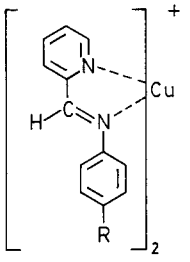


R = H : L^1
R = CH_3 : L^2
R = Cl : L^3

1, L



2

paper is the single crystal structure of $[Cu(L^2)_2](ClO_4)$. The ligand belongs to a α-diimine class and it differs in two major respects from bpy or phen. Firstly, its lowest π^* is at a lower energy[9] and as a result π-back bonding to L is stronger than for bpy or phen. This has notable influence on the spectroscopic and redox properties of these complexes. For example, the ruthenium(II) and iron(II) complexes of L absorb at much lower energy than the corresponding complexes of bpy and phen. Secondly, the ligand L is more flexible. Different modes of coordination of L have been best exemplified[10] in its organometallic complexes. Recently, we and others have reported some ruthenium,[11] rhenium[12] and silver[13] complexes of L. Multiple electron transfer, charge transfer absorption and emission, unusual chemical and photochemical reactions are some of the important observations in this area.

RESULTS AND DISCUSSION

Synthesis and formulation

The three ligands used in the present work are abbreviated as L^1–L^3 (**1**). These were generated *in situ* by reacting 2-pyridinecarboxaldehyde and the appropriate primary aromatic amine in ethanol. All of them reacted smoothly with $AgNO_3$ to produce cationic AgL_2^+ which were isolated[13] as their perchlorate salts. These silver complexes were used to synthesize the copper complexes.

The reaction of $[AgL_2]ClO_4$ in boiling aqueous ethanol with hydrated $CuCl_2$ in a 1:2 molar proportion afforded dark crystals of $[CuL_2](ClO_4)$ (**2**). The mechanism and the byproducts of the above reduction [Cu(II) → Cu(I)] are not yet known. However, we believe that complex formation followed by reduction would be a plausible path for the direct formation[14] of the cuprous complex. The cationic complexes were isolated as their perchlorate salts. These were formulated by elemental analyses (Table 1) and are 1:1 electrolytes in MeOH. The synthetic strategy, described above, based on[13,15] silver(I) assisted trans-metallation reaction. Here AgL_2^+ acts not only as a source of Ag^+ for complete removal of Cl^- from hydrated $CuCl_2$ but also supplies the L required for the formation of the desired complex.

Structural studies

A summary of the crystallographic data for one of the cuprous compounds, $[Cu(L^2)_2](ClO_4)$ is presented in Table 2. Important bond lengths and bond angles are collected in Table 3. The structural analysis reveals that the asymmetric unit consists of two crystallographically independent molecules, with only slightly different bond lengths and bond angles. The structure consists of monomeric $Cu(L^2)_2^+$ cation and uncoordinated ClO_4^- anion. The closest distance between Cu and O of ClO_4^- is 4.41 Å. The ORTEP diagram of the cation with the atom numbering scheme is shown in Fig. 1. The ligand, L^2 coordinates in a bidentate manner *via* two nitrogen atoms, as shown in **2**, providing a distorted tetrahedral arrangement about copper. The dihedral angle between the two planes defined by the copper and the two chelate rings is *ca* 81° and is appreciably smaller than the expected angle (90°) between the two planes for a regular tetrahedral geometry. Notably, similar distortion (dihedral angle 80.9°) has been observed[16] for $Cu(dmbp)_2^+$ (dmpb = 6,6′-dimethyl-2,2′-bipyridine). The aryl and the pyridine rings are not

Table 1. Microanalytical data

Compound	Anal. data[a] (%)			
	C	H	N	Cu
$[Cu(L^1)_2]ClO_4$	54.2 (54.6)	3.9 (3.8)	10.5 (10.6)	12.1 (12.0)
$[Cu(L^2)_2]ClO_4$	56.5 (56.2)	4.4 (4.3)	10.2 (10.0)	11.2 (11.4)
$[Cu(L^3)_2]ClO_4$	48.2 (48.3)	2.9 (3.0)	9.2 (9.4)	10.4 (10.6)

[a]Calculated values are in parentheses.

Table 2. Crystallographic data for $[Cu(L^2)]ClO_4$

Chemical formula	$CuClO_4N_4C_{26}H_{24}$
fw	555.49
Crystal system	monoclinic
Space group	*P*2 1/*c*
a (Å)	24.904(6)
b (Å)	16.359(3)
c (Å)	12.819(3)
β (°)	98.720 (20)
V (Å^3)	5162.2(19)
Z	8
D_{calcd} (gm cm^{-3})	1.430
μ (cm^{-1})	9.935
Crystal size (mm)	0.15 × 0.22 × 0.55
λ (Å)	0.7107
T (K)	298
R_f, *Rw*	0.077, 0.082
GOF	2.95

coplanar. The dihedral angle between the tolyl ring and the planar (mean deviation : 0.02–0.03 Å) (pyridylmethylene)amino functionality[12c] is 30–31°. The Cu—N_{py} bond lengths are very similar to those found[16,17] in typical tetracoordinated copper(I) complexes. The Cu—N_{imine} bonds are slightly longer than Cu—N_{py} bond lengths. This observation is qualitatively similar[12c] to that observed in a mixed ligand rhenium(I) complex of L^1. Solution properties of the cuprous complexes of another two ligands, namely, L^1 and L^3, agree well (Tables 4–6) with those of structurally analysed $[Cu(L^2)_2](ClO_4)$. This implies that the gross structures of all the cuprous compounds, reported here, are identical.

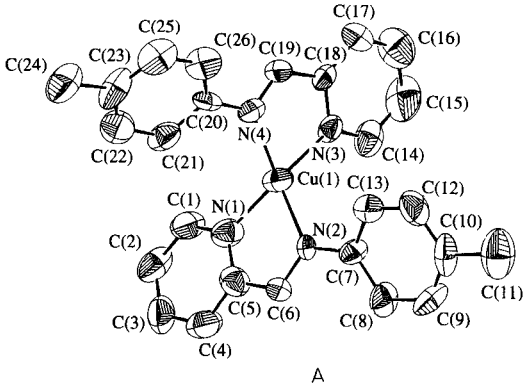
Optical spectra

Selected infrared frequencies are collected in Table 4. All the copper complexes show characteristic absorptions for coordinated L in their IR

Table 3. Selected bond distances and bond angles of $[Cu(L^2)_2]ClO_4$[a]

Bond distances (Å)			
Cu(1A)—N(1A)	2.013(11)	Cu(1B)—N(1B)	1.977(11)
Cu(1A)—N(2A)	2.033(9)	Cu(1B)—N(2B)	2.105(10)
Cu(1A)—N(3A)	2.002(10)	Cu(1B)—N(3B)	1.890(15)
Cu(1A)—N(4A)	2.066(9)	Cu(1B)—N(4B)	2.069(10)
Bond angles (°)			
N(1A)—Cu(1A)—N(2A)	81.8(4)	N(1B)—Cu(1B)—N(2B)	82.5(4)
N(1A)—Cu(1A)—N(3A)	131.4(4)	N(1B)—Cu(1B)—N(3B)	134.7(5)
N(1A)—Cu(1A)—N(4A)	122.0(4)	N(1B)—Cu(1B)—N(4B)	124.5(4)
N(2A)—Cu(1A)—N(3A)	119.2(4)	N(2B)—Cu(1B)—N(3B)	110.2(5)
N(2A)—Cu(1A)—N(4A)	127.4(4)	N(2B)—Cu(1B)—N(4B)	128.4(4)
N(3A)—Cu(1A)—N(4A)	81.5(4)	N(3B)—Cu(1B)—N(4B)	82.4(4)

[a]There are two crystallographically independent molecules in the asymmetric unit (see text).



A

Fig. 1. ORTEP plot and atom labelling scheme of $[Cu(L^2)_2](ClO_4)$ [one (molecule A) of two chemically similar but crystallographically independent molecules].

spectra. The very structureless ν_3 band near 1100 cm^{-1} indicates[18] the presence of ionic perchlorate in the solid state rather than in solution. The IR spectra of the complexes also show consistent appearance of two strong bands at *ca* 1620 and 1590 cm^{-1} assignable[19] to C=N(imine) and C=N(pyridine), respectively. It may be noted that in the free ligand these absorptions occur at 1630 and 1600 cm^{-1}. Similar IR spectra were also reported[13,20] for the corresponding iron(II) and cobalt(II) complexes of L.

The solution electronic spectra of copper(I) complexes were recorded in the range 860–220 nm in methanol. The electronic spectral data are presented in Table 4 and representative spectra are displayed in Fig. 2. The visible range spectrum of **2** is dominated by a metal-to-ligand charge transfer

Table 4. Optical spectral data of complexes

Compound	IR[a] (cm^{-1}) $\nu_{C=N(pyridine)}$	$\nu_{C=N(imine)}$	$\nu_{ClO_4^-}$	UV-vis[b] λ^{max}[nm (ε, $M^{-1}\,cm^{-1}$)]
$[Cu(L^1)_2]ClO_4$	1580	1620	1100[c], 620	620[d], 490(2325), 310(14,580), 235(22,270)
$[Cu(L^2)_2]ClO_4$	1590	1610	1100[c], 620	620[d], 495(2450), 320(15,220), 235(22,270)
$[Cu(L^3)_2]ClO_4$	1590	1625	1100[c], 620	620[d], 485(2380), 310(15,500), 245(23,560)

[a]In KBr disk.
[b]Solvent.
[c]Very broad band.
[d]Ill-defined shoulder.

Table 5. ^1H NMR spectral data for $[CuL_2]ClO_4$[a,b] in $CDCl_3$

Compound	δ[c] [ppm(J, Hz)] 3-H	4-H	5-H	6-H	8-H	9-H	10-H	11-H	12-H	13-H	10-Me
$[Cu(L^1)_2]ClO_4$	8.13d (7.50)	8.10t (7.60)	7.66t (6.70)	8.66d (5.60)	7.47d (7.60)	7.34t (7.40)	7.27t (7.20)	7.34t (7.40)	7.47d (7.60)	9.00s	
$[Cu(L^2)_2]ClO_4$	8.20d (7.45)	8.08t (7.20)	7.61t (6.68)	8.50d (5.50)	7.40d (7.50)	7.14d (7.40)		7.14d (7.40)	7.40d (7.50)	9.22s	2.28s

[a]Solubility of $[Cu(L^3)_2]ClO_4$ in $CDCl_3$ is very low for any meaningful measurement.
[b]Abbreviations: s, singlet; d, doublet; t, triplet. Tetramethylsilane is the internal standard.
[c]Spin–spin coupling amongst nearest neighbour protons only.

Table 6. Cyclic voltammetric data[a–c] for the complexes in MeOH at 298 K

Compound	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	n[d]
$[Cu(L^1)_2]ClO_4$	0.41	0.29	120	0.35	1.06
$[Cu(L^2)_2]ClO_4$	0.41	0.27	140	0.34	1.05
$[Cu(L^3)_2]ClO_4$	0.42	0.28	140	0.35	0.98

[a]Meanings of the symbols used are the same as in the text; all E values are quoted *vs* the SCE.
[b]Supporting electrolyte TBAP (0.1 mol); solute concentration *ca* 10^{-3} mol; scan rate 50 mV s^{-1}.
[c]The responses are oxidative in nature.
[d]$n = Q/Q'$; where Q' is the calculated coulomb count after exhaustive electrolysis; oxidations were performed at 0.50 V *vs* SCE in CH_3OH (0.10 M $[NBu^t_4][ClO_4]$).

(MLCT) occurring at *ca* 490 nm associated with an ill defined shoulder at *ca* 620 nm. A similar situation[14,21] in the bis-2-arylazopyridine and bis-arylazooximates of copper(I) occurs. In the bis-complexes of copper(I) with bpy and related ligands the lowest energy charge transfer occurs[22] at a relatively high energy, near 450 nm. Absorptions of **2** in the UV region were characterized by two high energy intraligand transitions occurring at *ca* 300 and 240 nm, respectively.

Magnetic resonance spectra

All the cuprous chelates show highly resolved ^1H NMR spectra in $CDCl_3$ at 400 MHz. The spectral data are collected in Table 5. A representative spectrum is shown in Fig. 3. Assignment of individual proton resonances are made by a comparison of the spectra of 2 with those of reported[11a] ruthenium(II) complexes of L. An examination of the ^1H NMR data reveals the following: (i) pyridyl, aryl and

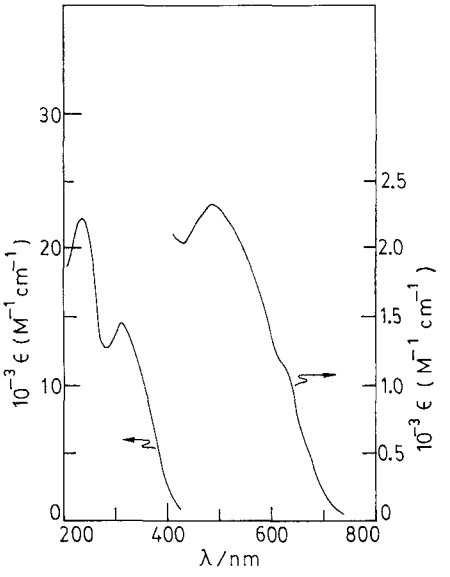


Fig. 2. Electronic spectrum of $[Cu(L^1)_2](ClO_4)$ in CH_3OH.

imine proton resonances of the ligand L shift on coordination, indicating in **2** coordination of L to Cu^+; (ii) in the present group of complexes each kind of proton gives rise to one signal (singlet or multiplet). It may be concluded, therefore, that each of the compounds exists as a single isomer and two chelate rings in CuL_2^+ are magnetically equivalent. A two-fold axis of symmetry is thus required. The ^1H NMR data therefore conform, at least in solution, to the tetrahedral geometry of 2.

Redox properties

The results of cyclic voltammetric scans for CuL_2^+ are shown in Fig. 4. In methanol with TBAP as the supporting electrolyte **2** undergoes a quasi-reversible oxidation–reduction reaction at *ca* 0.35 V *vs* SCE (at 50 mV s^{-1} scan rate, $\Delta E_p =$

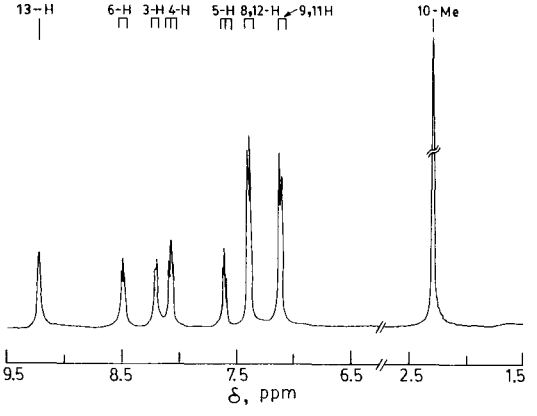


Fig. 3. ^1H NMR spectrum of $[Cu(L^2)_2](ClO_4)$ in $CDCl_3$.

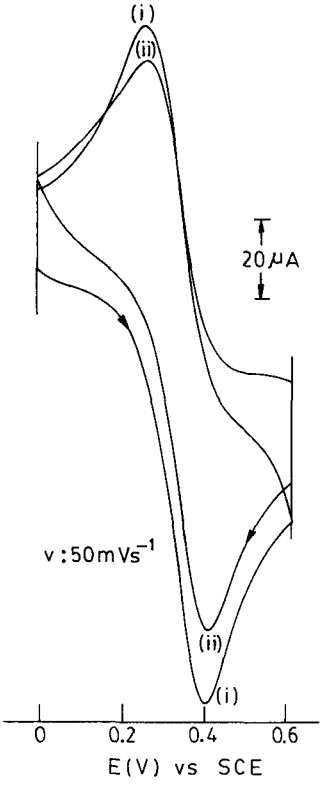


Fig. 4. Cyclic voltammograms in CH_3OH: (i) $[Cu(L^1)_2](ClO_4)$ and (ii) electrogenerated $Cu(L^1)_2^{2+}$.

$E_{pa} - E_{pc} = 100$ mV and $i_{pa}/i_{pc} = 1$) at a platinum working electrode. This response is attributed to copper(II)/copper(I) couple in **2**:

$$\mathbf{2}^+ + e \rightleftharpoons \mathbf{2} \quad E_{1/2} = 0.35\,V$$

Controlled potential coulometry at 0.50 V fully corroborates the one-electron stoichiometry of the couple. The electrochemical data are presented in Table 6. The copper(II) congener, formed by electrolysis, shows an identical response, but reductive in nature (Fig. 4). This implies that although the electron transfer for the present copper(II)/copper(I) couple is quasireversible, it is chemically reversible. A close examination of $E_{1/2}$ data, presented in Table 6, reveals that the redox process in CuL_2^{n+} (n = 1, 2) occurs at a moderately high positive potential. In fact it is much higher than the formal potential[23] for $Cu(bpy)_2^{2+}/Cu(bpy)_2^+$ couple. It may be noted here that, among CuN_4 species, the examples of copper(II)/copper(I) couple occurring at a positive potential, especially more positive than 0.25 V *vs* SCE, is very limited. In general, the cuprous state in those complexes is stabilized either by soft donors[14] or sterically hindered ligands[24,25] which favour tetrahedral geometry. Thus, high potentials for copper(II)/copper(I) couple are observed in the com-

plexes of sterically hindered substituted bpy, tripod ligands or strong π-acids, 2-(arylazo)pyridines. Since the electrochemical parameter[26] of L (E_L) is only slightly higher than those for bpy, the large difference between the formal potentials of CuL_2^+ and $Cu(bpy)_2^+$ cannot be attributed only to the stronger $d\pi$–$p\pi$ interactions. We believe that the deviation from square planar geometry of CuL_2^{2+} has a definite influence on the higher reduction potential for the present diimine complexes.

Properties of CuL_2^{2+}

The light brown solution of CuL_2^{2+}, generated by electroxidation, showed a broad band near 700 nm. In view of low intensity (ε, *ca* 125 M^{-1} cm^{-1}), this band has been assigned to a *d–d* transition. It may be noted here that the near-infrared and visible absorption spectra of square planar copper(II) complexes containing N_4 donor atom sets mostly have *d–d* bands in the range[27] 18,500–20,000 cm^{-1}. The *d–d* transition in CuL_2^{2+} lies well below the lower limit of this range. Moreover, the intensity of the above transition in **2** is higher than that for square planar cupric complexes. Both the observations on the *d–d* transitions for the present group of cupric complexes indicate distortion to tetrahedral geometry. This has been further supported by the EPR data. The EPR spectra of CuL_2^{2+} were obtained in a fluid solution and in a glass solution at 77 K. At room temperature (298 K) in methanol four lines in the EPR spectrum for **3** with g_{av}, *ca* 2.07 are observed. The spectra in methanol glass show two identifiable magnetic g values ($g_\parallel$, 2.271; $A_\parallel$ Cu, 175 cm^{-1} and $g_\perp$, 2.060) along with corresponding copper ($I_{cu} = 3/2$) hyperfine splittings. The axial EPR spectrum of the complexes with $g_\parallel > g_\perp > 2.0$ is consistent[28] with a distortion from square planar to tetrahedral geometry. This distortion in **3** is not unexpected since in the *trans* planar arrangement of the CuL_2 moiety the pyridyl group of one L would be in a close proximity to the aryl group of the other ligand which most likely results in steric interactions leading to deviation from a planar arrangement.

EXPERIMENTAL

Materials

The salts, $CuCl_2 \cdot 2H_2O$ and $AgNO_3$ were obtained, respectively, from E. Merck, Bombay and S. D., Boisar, and used without further purification. 2-Pyridinecarboxaldehyde was obtained from Fluka. The free ligand,[16] *N-p*-tolyl-pyridine-2-aldimine (L^2) and silver(I) compounds, $(AgL_2)ClO_4$ were prepared as before.[17]

Physical measurements

Elemental analyses were carried out on a Heraeus Elemental Analyser, CHN-O-RAPID. Copper was estimated gravimetrically as CuSCN. Infrared spectra were obtained using KBr disks (4000–600 cm^{-1}) with a Perkin–Elmer IR-297 spectrophotometer. Solution electronic spectra were recorded on a Hitachi-330 spectrophotometer. Solution electrical conductivity measurements were performed on an Elico-CM 82T conductivity bridge with a solute concentration of *ca* 10^{-3} M. ^1H NMR spectra were recorded in $CDCl_3$ using Bruker WM-400 FT-NMR spectrometer. X-band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K. The spectra were calibrated with the help of diphenylpicryl-hydrazyl (dpph) ($g = 2.0037$). Electrochemical measurements were done with the help of a PAR model 370-4 Electrochemistry system as described before.[11] All results were collected at 298 ± 1 K, are referenced to a saturated calomel electrode (SCE). The reported potentials were uncorrected for junction contributions.

Preparation of compounds

Bis(2-N-*phenyl-pyridine-2-aldimine*)copper(I) *perchlorate* $[Cu(L^1)_2]ClO_4$. $CuCl_2 \cdot 2H_2O$ (0.100 g, 0.60 mmol) was dissolved in 30 cm^3 of 1:1 (v/v) ethanol–water and $[Ag(L^1)_2]ClO_4$ (0.685 g, 1.2 mmol) was added then the mixture was heated to reflux for 0.5 h. The brown solution, thus obtained, was cooled and filtered through a G-4 sintered glass funnel. The filtrate was then concentrated to 10 cm^3 and left overnight for crystallization. The dark crystals, thus deposited, were filtered and washed with hexane and finally dried *in vacuo*. Yield, 78%; Λ_M(MeOH) = 110 cm^2 ohm^{-1} mol^{-1}.

Bis(N-p-*tolyl-pyridine-aldimine*)*copper(I) perchlorate*, $[Cu(L^2)_2]ClO_4$ *and bis*(N-p-*chlorophenyl-pyridine-aldimine*)*copper(I) perchlorate*, $[Cu(L^3)_2]ClO_4$. These two compounds were prepared similarly using appropriate $[AgL_2]ClO_4$. $[Cu(L^2)_2]ClO_4$: Yield, 72%; $\Lambda_M = 115$ cm^2 ohm^{-1} mol^{-1}. $[Cu(L^3)_2]ClO_4$: Yield, 75%, $\Lambda_M = 115$ cm^2 ohm^{-1} mol^{-1}.

Crystallography

Single crystals of $[Cu(L^2)_2]ClO_4$, suitable for X-ray diffraction, were grown by slow evaporation of a saturated aqueous ethanolic solution of the

compound at 20°C. Diffraction measurements were carried out on a Nonius CAD-4 fully automated four-circle diffractometer. The unit cell was determined and refined using setting angles of 25 reflections, with 2θ angles in the range 19.16–25.08°. The unit cell dimensions are listed in Table 2. Data were collected by $\theta-2\theta$ scans with in the angular range 3.0–45.0°. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The structure was solved by the Patterson method. Final cycles of least-square refinement converged with discrepancy indices of $R_f = 0.077$ and $Rw = 0.082$. Tables containing full listings of atom positions, anisotropic thermal parameters and hydrogen atom locations are available as supplementary material.

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