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THE METAL PROMOTED HYDRATION OF DI-2-PYRIDYL KETONE
and
THE CRYSTAL AND MOLECULAR STRUCTURES OF
Bis-2,2',N,N'-bipyridyl Ketone-hydrate Chromium(III) Chloride
and Ruthenium(III) Chloride

by
SHAUN SOMMERER

A Thesis Submitted in Partial
Fulfillment of the Requirements for the Degree
Master of Science, Major in Chemistry,
South Dakota State University

1987

THE METAL PROMOTED HYDRATION OF DI-2-PYRIDYL KETONE

and

CRYSTAL AND MOLECULAR STRUCTURES OF

Bis-2,2',N,N'-bipyridyl Ketone-hydrate Chromium(III) Chloride

and Ruthenium(III) Chloride

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply the conclusions reached by the candidate are necessarily the conclusions of the major department.

William P. Jensen
Major Advisor

Date

David C. Hilderbrand, Head
Department of Chemistry

Date

ACKNOWLEDGEMENTS

I would like to thank Dr. Robert A. Jacobson at Iowa State University for his help in this project as well as the use of his diffractometer.

Secondly, I would like to thank Pam Krage for typing this thesis and helping me to get this into final form.

Last on this list of thank you's but number one in my heart is Dr. William P. Jensen for his guidance and friendship while I was at South Dakota State University.

In the fury of the moment I can see the Masters hand, in every
leaf that trembles, in every grain of sand.

Bob Dylan

TABLE OF CONTENTS

	Page
Introduction	1
Historical Perspectives	4
N, N vs. N, O Coordination	4
Carbonyl Hydration and Tridentate Behavior	7
Driving Force Behind the DPK Hydration	12
Experimental Results	16
Isolation of DPK Complexes in the Solid State	16
UV-Visible Spectra of Metal-DPK Solutions	17
Aqueous Solution pH Study	21
Experiments Involving the Axial Position on the Metal Cation	25
Flash Evaporation of Solvent From Metal:DPK Solutions	27
X-Ray Powder Patterns	29
Calculation of d-Spacings	30
X-Ray Analysis of $\text{Cr}(\text{DPK-OH})_2(\text{OH})_2\text{Cl}\cdot\text{H}_2\text{O}$ and $\text{Ru}(\text{DPK-OH})_2(\text{OH})_3\cdot\text{H}_2\text{O}$	32
Data Collection	32
Structure Solutions and Refinement	34
Discussion of the Structures	47
Correlations of Solved DPK Structures	48
Conclusion	54
References	57
Appendix 1: UV-Visible Spectra	59
Appendix 2: UV-Visible Spectra (pH Study)	66
Appendix 3: Kodak d19-b Developer	68
Appendix 4: d-Spacings of Isolated Solid State DPK Compounds	69
Appendix 5: Basic Program for Determination of Bond Angles and Bond Distances in Crystal Space	71
Appendix 6: Basic Program for Calculating Aromatic Hydrogen Positions in Crystal Space	72

LIST OF FIGURES

	Page
Fig. 1: DP,DPK-hydrate	1
Fig. 2: Illustration of off axial coordination of the hydroxyl group	2
Fig. 3: 2-benzoylpyridine	5
Fig. 4: 2,2-bis(2-pyridyl)-1,3-dioxolane	11
Fig. 5: 2,2-bis(6-methyl-2-pyridyl)-1,3-dioxolane	11
Fig. 6: 2-pyridyl N-methyl-2-imidazolyl Ketone, PIK	15
Fig. 7: di(N-methyl-2-imidazolyl) Ketone, DIK	15
Fig. 8: 1690 cm^{-1} Region of Infrared Spectrum for Cu ⁻²⁺ :DPK and DPK	18
Fig. 9: PLUTO drawing of Cr ⁻³⁺ :DPK Structure	45
Fig. 10: PLUTO drawing of Ru ⁻³⁺ :DPK Structure	46
Fig. 11: Plot of M-O bond distance vs. angle of the normal	51
Fig. 12: Plot of Dist. of O off the equatorial plane vs. angle off the normal	52

LIST OF TABLES

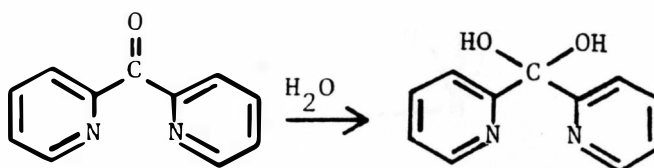
	Page
Table 1: Formulations of Newly Isolated DPK Compounds and Elemental Analysis Results	19
Table 2: pH Values of Cu(II)DPK Solutions	22
Table 3: pH Values of Cr(III)DPK Solutions	22
Table 4: Elemental Analysis for Cu(II):DPK Solid State	24
Table 5: Crystal Data for Cr(C ₁₁ H ₈ N ₂ (OH) ₂) ₂ (OH) ₂ Cl 3H ₂ O, I, Ru(C ₁₁ H ₈ N ₂ (OH) ₂ (OH) ₃ 4H ₂ O, II	33
Table 6: Final Positional Parameters for the Nonhydrogen Atoms, I & II	35
Table 7: Positional Parameters of the Hydrogen Atoms	37
Table 8: Thermal Parameters of Non-hydrogen Atoms I & II	39
Table 9: Interatomic Distances I & II	41
Table 10: Interatomic Angles I & II	43
Table 11: Combined Data for Correlations	49

Metal Promoted Hydration of Di-2-Pyridyl Ketone

Introduction

The metal promoted hydration of Di-2-Pyridyl Ketone (DPK), has been of interest for some time in that it falls into a rare class of ligands that undergo reaction upon coordination to a transition metal ion. Metal promoted hydration here means that the carbonyl linkage of the ketone has undergone hydration to the diol form because the DPK is coordinated to a metal. Fig. 1 illustrates the hydration process. This is of interest because it is well known that ketones do not normally undergo hydration unless they are flanked by very strong electron withdrawing groups such as chloride or fluoride.

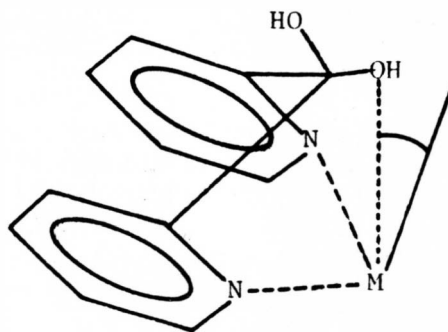
Fig. 1: DP,DPK-hydrate



Special mention must be made here about the role of the metal ion in that this hydration reaction should not be confused with a catalytic reaction. In this system, DPK becomes coordinated to the transition metal and remains in the complexed form throughout the hydration reaction of the ligand and remains attached thereafter.

It has also been found that when DPK is coordinated to a metal ion in the hydrated form, it behaves in a tridentate fashion in that one of the oxygen atoms from the diol group forms a bond to the metal in the "axial" position. This third bond is very interesting in that the oxygen bonds in an unusual off axis position making an angle with the line normal to the equatorial plane (see Fig. 2). In 1:2 complexes of metal ion with DPK there is the possibility of pseudo-octahedral coordination about the metal ion.

Fig. 2: Illustration of off axial coordination of the hydroxyl group



This study was undertaken in an attempt to gain additional insight into this intriguing system in hope that a better understanding of how this system works could be obtained. Work was undertaken in

Historical Perspective

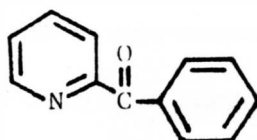
N,N vs. N,O-Coordination

From the first report of transition metal complexes of DPK to appear in the literature onwards, there has been discussion as to the mode of coordination for DPK. As can be seen from Fig. 1, DPK has the potential to bond either through one nitrogen atom and the carbonyl group (i.e. N,O coordination) or through both nitrogen atoms (i.e. N,N coordination). It is not obvious which mode is preferred or whether a mixture of both would result. R.R. Osborne and W.R. McWhinnie concluded in 1967 that a mixture of N,O and N,N coordinated complexes would result when they first reported compounds of DPK complexed to a metal ion (exclusively with copper).¹

By studying the shift of the DPK carbonyl stretching frequency in the infrared spectrum and comparing it with infrared data for 2-benzoylpyridine (see Fig. 3), a ligand which is known to chelate through the nitrogen and the oxygen of the carbonyl, M.C. Feller and R. Robson argued in 1968 that the infrared band for C=O had disappeared completely in the DPK complexes which they attributed to hydration or alcoholation across the ketonic double bond.² Since the band for C=O in 2-benzoylpyridine is (1663-1567 cm^{-1}), it followed that the band for N,O-coordination of DPK should be in this same neighborhood if indeed the DPK ligand was coordinating in such a fashion. They found no such band in the spectrum of the DPK compounds. In their work with copper they found that the infrared spectra along with the

e.s.r. spectra clearly indicated a copper environment of four equivalent nitrogen atoms leading them to conclude that DPK was bonding in a N,N-fashion rather than N,O- in aqueous solution.

Fig. 3: 2-benzoylpyridine



Included in a study of DPK coordination with Co, Ni, and Fe, V. Rattanaphani and W.R. McWhinnie in 1973 mention the possible N,O-coordination of DPK to a metal ion.³ In an Iron(III) perchlorate tris-DPK compound formulated as $[\text{Fe}(\text{pyCopy})(\text{pyC}(\text{OEt})\text{OHpy})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ they found no free carbonyl absorption at 1690 cm^{-1} but instead a band not previously observed in the spectrum of a DPK complex was observed at 1530 cm^{-1} . They argue that the only reasonable assignment for the observed vibrational mode at 1530 cm^{-1} is the carbonyl stretching frequency for a molecule of DPK that is N,O-coordinated to the metal ion. It must be noted that the solvent employed was absolute ethanol rather than water. They do assign N,N-coordination to other reported compounds using arguments similar to those of Feller et al.²

By means of potentiometry and spectrophotometry, Fischer and Sigel in 1975 were able to study the behavior of DPK in the absence and presence of metal ions and make the following conclusion: Indeed there is considerable evidence that in the low pH range metal ions coordinate in aqueous solution to the two nitrogen-atoms of DPK, facilitate the addition of water to the keto moiety, and coordinate at a somewhat higher pH also to a deprotonated hydroxy group of the geminal diol.⁴ Not only supporting the suggestion of N,N-coordination in aqueous solution that was previously outlined but also presenting two further suggestions of hydration and tridentate coordination (both of which will be discussed in following sections). Fischer and Sigel are the last to address the issue of N,N- vs. N,O-coordination directly.

Following this paper, N,N-coordination of DPK is presented only indirectly by three sets of authors, each group working independently.^{5,6,7} Each of these three papers report DPK molecular structures determined by X-ray diffraction and though it is not directly noted, the structures themselves show DPK coordinated to the metal ion via N,N-coordination which once again supports the premise of N,N-coordination of DPK to a metal ion.

As can be seen from the literature, there is considerable support for N,N-coordination being the preferred mode of chelation for DPK. One instance of N,O-coordination was mentioned above, however that particular species with a few others reported appear to be

isolated cases that are not well documented. Although most reports of N,N-coordination were from systems where the solvent contained water, there were also several reports of N,N-coordination in non-aqueous systems too. Hence, N,O-coordination of DPK is no longer thought to take place to any great extent with metal ions in solution.

Carbonyl Hydration and Tridentate Behavior

By virtue of DPK's ability to undergo a hydration reaction with coordination to a metal ion, which was illustrated in the introduction (see Fig. 1), the DPK ligand can become tridentate after initially being bidentate. The first to suggest that a reaction such as hydration may be possible after coordination for the DPK ligand was M.C. Feller and R. Robson in 1968.² As stated in the previous section, they observed the complete disappearance of the carbonyl band at 1690 cm^{-1} which they attributed to hydration or solvation across the ketone double bond. In a paper that followed from their laboratory, also on the DPK system, they suggested that it is possible for one of the hydroxy groups of >C(OH)_2 to coordinate to the metal cation, the DPK ligand now behaving in a tridentate fashion.⁸

In a follow-up study Feller and co-workers investigated DPK complexed with several transition metals including Co, Fe, and Ni. They found the disappearance of the carbonyl stretching frequency at 1690 cm^{-1} in the infrared spectrum to be characteristic of several of these complexes and led them to state in their conclusion that DPK can function as a tridentate ligand. Therefore, the metal cation may

possess a pseudo-octahedral trans N_4O_2 ligand field by virtue of the hydration reaction.⁹

Concurring with Feller and Robson, Fischer and Sigel state in a 1975 paper that DPK exists in aqueous solution as the ketone and not the diol.⁴ They arrived at this conclusion from an I.R. spectrum of DPK (5%) in D_2O (a neutral solution) which showed a band at 1667 cm^{-1} (i.e. $C=O$). This evidence along with Feller and Robson's observation of the similarity of the U.V. spectra of DPK in H_2O and in anhydrous diethyl ether² helps confirm the idea that only in the presence of a metal does the carbonyl of DPK hydrate to a significant extent and that the presence of H_2O alone will not cause DPK to hydrate. Hence, a most interesting feature of the DPK ligand can be seen in that it undergoes a transformation under the influence of a metal ion to a species more suitable for metal coordination. Possessing three sites for coordination each, two hydrated-DPK ligands could produce an N_4O_2 octahedral coordination sphere for a metal cation.

A paper by Annibale et al. in 1981 reported two quite important details.⁵ First, concerning the hydration reaction they reported an experiment in which they attempted to ascertain whether hydration occurs only after coordination of DPK to the metal ion or whether it could also occur during the process of coordination. By monitoring the progress of the reaction spectrophotometrically they determined that the complex with the ligand in its keto-form was found first and then reacted with water to give the hydrated species quantitatively.

Second, concerning the tridentate behavior of DPK, they present the first molecular structures of a Pd(DPK) complex and a Au(DPK) complex determined by single crystal X-ray diffraction. Each metal ion is shown to be involved in a weak long-range interaction with the oxygen of one of the hydroxyl groups (e.g. [Au - O = 2.77(1)Å] and [Pd - O = 2.824(6)Å]) resultant from the hydration of the carbonyl of DPK. Thus, the DPK ligand is bonded in a tridentate rather than bidentate fashion. An interesting observation points out that the metal ion-oxygen interactions are not exactly in the coordination plane of these two complexes. In fact there is quite a bit of distortion in that an angle of 29.9° is made by the Pd - O vector to the equatorial coordination plane in the Pd(DPK) complex and an angle of 27.2° is made by the Au - O vector in the Au(DPK) complex. Although the tridentate behavior of the hydrated DPK may not be surprising, it is surprising to see the oxygen coordination manifested in such an unusual off axis manner.

Reporting the next molecular structure involving DPK, P.K. Byers and co-workers present an AuMe₂ complex similar to the Au(III) complex mentioned previously.⁶ There again appears to be a weak coordination interaction between the Au(III) center and one of the hydroxy groups resulting from the hydration of the carbonyl, even though the Au - O = 2.850(8)Å distance here which is slightly longer than the Au - O = 2.77(1)Å distance in the Au(III) complex reported by Annibale et al.⁵ Hence, DPK is shown to bond in a tridentate fashion and upon

examination of the experimental section of the study one can see that the oxygen coordination is in an unusual off axis position.

The first reported structures of DPK were 1:1 metal ion to DPK ligand, however, in 1986 there were three 1:2 complexes reported involving DPK with NiSO_4 , CuCl_2 , and $\text{Cu}(\text{NO}_3)_2$.⁷ The structures, determined by single crystal X-ray diffraction, show that in all cases the keto group of the DPK has undergone hydration and that each hydrated DPK bonds with the metal in a tridentate fashion to form a complex which contains an octahedral trans N_4O_2 ligand field. These authors not only point out the tridentate behavior of the hydrated DPK but also the apparent distortion of the octahedral symmetry by the coordination of one of the hydroxyl groups from each ligand in an unusual off axis position forming an angle between the line from the metal to the oxygen and normal to the equatorial plane of about 41° and 25° in the nickel and copper complexes, respectively. In addition to the steric requirements imposed by the ligands, these authors argue that the Jahn-Teller effect usually inhibits the formation of ideal octahedral configurations in d^9 systems must be considered.

The most recent paper published in which complexes of DPK in the hydrated form are discussed is by Newkome et al.¹⁰ Discussion is centered around the comparison of the ligands 2,2-bis(6-methyl-2-pyridyl)-1,3-dioxolane (Fig. 5) and 2,2-bis(2-pyridyl)-1,3-dioxolane (Fig. 4) with that of DPK in the hydrated form since Fig. 4 and Fig. 5 possess a spiroketal function that can mimic the hydrated form of DPK.

They found that indeed these analogues behaved in a similar manner as far as coordination though obviously hydration did not take place. Isolated from non-aqueous solvents were twelve different compounds of which only four were stable enough for single crystal studies. Upon examination of the four structures presented (formulated as A: $\text{CuCl}_2\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$, B: $\text{CuCl}_2\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$, C: $\text{CoCl}_2\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$, D: $[\text{Ni}(\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2) \cdot (\text{H}_2\text{O})_3]\text{Cl}_2$) each metal cation has an oxygen from the dioxolane ligand occupying a position near the axial site, hence providing the metal ion with a pseudo-octahedral geometry. Although the focus of the study was to investigate the structural features of Ni(II), Co(II), and Cu(II) with ligands 4 and 5, these analogues of DPK show a marked resemblance in tridentate behavior with the coordination of the oxygen in an unusual off axis position on the metal ion.

Fig. 4: 2,2-bis(2-pyridyl)-1,3-dioxolane

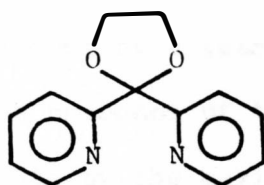
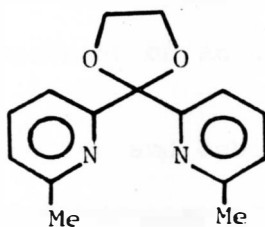


Fig. 5: 2,2-bis(6-methyl-2-pyridyl)-1,3-dioxolane



Thus with DPK analogues exhibiting similar coordination behavior, the final area to explore will be the possible driving force behind this unique system.

The Driving Force Behind the DPK Hydration

As a possible driving force for the hydration of the DPK ligand, Feller and Robson first postulated that the replacement of the sp^2 carbon by an sp^3 (tetrahedral) allows the ligand to adopt a more deformed but nevertheless angle - strain-free configuration in which the alpha hydrogen atoms are raised further above the copper N_2 plane than is possible in the ketonic ligand thereby reducing interference with other ligands.² Though not directly stated, they were obviously concerned with 1:2 metal to ligand complexes since there would be no steric interaction between alpha hydrogens in 1:1 complexes. This postulate was restated in their next publication on the DPK system as follows: a process, such as ketone hydration, in which the trigonal ketonic carbon of DPK is replaced by a tetrahedral center may be thermodynamically favored in the presence of the metal ion in that it enables the ligand to coordinate by the maximum number of strong metal-nitrogen bonds without introducing at the same time the serious non-bonded repulsive interactions with trans ligands or angle strain which would accompany similar attachment of an unhydrated DPK unit.⁸

Taking issue with Feller and Robson, Fischer and Sigel argued that interaction of the alpha-hydrogens of the pyridyl moieties cannot be the actual reason for hydration as it occurs also in 1:1 complexes,

and there is no such steric interaction present.⁴ Atomic models reveal that the formation of a planar 6-membered ring between DPK and a metal ion is difficult, while the formation of the chelate in a boat form with the metal ion and the carbonyl group above the plane defined by the other four members of the ring is more easily achieved (see Fig. 2). Should the coordination occur in this way, the planarity is destroyed by its coordination and as a result the hydration of the carbonyl would be facilitated. In addition, if the sp^2 carbon of the carbonyl is replaced by an sp^3 carbon of the geminal diol the strain within the 6-membered chelate is reduced.⁴

Supporting this proposal of Fischer and Sigel were the first two structures of metals with DPK determined by single crystal X-ray diffraction published by Annibale et al.⁵ Both structures show that the metal ion ring is indeed a six membered ring in the boat form. The Pd(DPK) and Au(DPK) complexes are 1:1 in metal to ligand which also refutes the alpha-hydrogen argument for there is not a steric problem and hydration has also occurred. The authors also postulate that an additional driving force for the metal promoted hydration might result from an interaction of the hydroxyl-group or the X-group of C(OH)X with the central metal, (i.e. tridentate coordination).

Providing further rationale for the coordination behavior of DPK and the driving force behind the hydration reaction, P.K. Byers and co-workers in 1985⁶ investigated the coordination behavior of DPK as it compares with 2-pyridyl N-methyl-2-imidazolyl ketone, (PIK), and

di(N-methyl-2-imidazolyl) ketone, (DIK) (Fig. 6 and Fig. 7). They found that DPK reacts with Au(III)Me_2 and Ni(II)NO_3 in water to form complexes involving hydration of DPK and coordination as $\text{DPK H}_2\text{O}$. However, the ketone containing the imidazolyl rings (i.e. DIK and PIK) react with Au(III)Me_2 , Ni, and Cu nitrate under identical conditions to form complexes of ketones without hydration. Metal-nitrogen distances of about 2.0\AA require the disruption of planarity of the ketone with loss of the carbonyl conjugation^{4,5} or retention of planarity with poor overlap of the nitrogen lone pairs with the metal orbitals. Replacement then of the pyridyl rings with the imidazolyl rings, having smaller angles within the ring, is expected to increase the distance between the nitrogen donor atoms, and to give direction of nitrogen lone pairs more consistent with metal-nitrogen distances of about 2.0\AA and nitrogen-metal-nitrogen angles of about 90.0° .⁶ Thus, with ligands that are near the correct bite size, no conformational change (e.g. hydration of the carbonyl) is necessary for chelation to occur. These results are again consistent with the proposal that DPK readily hydrates so that a six-membered chelate ring in the stable boat configuration can be obtained.

Finally, the three 1:2 DPK structures reported by Wang et al.⁷ which show the prominent off axis distortion of the hydroxy group in the axial positions, demonstrates that the driving force behind the hydration of the carbonyl may not simply lie in conformational change. Other effects such as the Jahn-Teller effect for d^9 species as well as

Fig. 6: 2-pyridyl N-methyl-2-imidazolyl Ketone, PIK

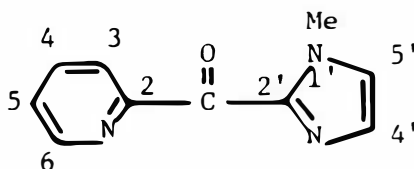
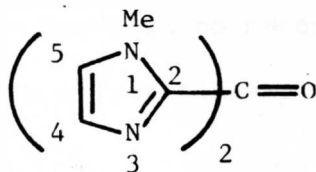


Fig. 7: di(N-methyl-2-imidazolyl) Ketone, DIK



other interactions peculiar to the metal cation may need to be considered.⁷

Experimental Results

At the outset it was decided that this study would concentrate on 1:2 metal ion to DPK complexes combined in aqueous solution since the literature to date has been at best sketchy on this type of DPK system. To achieve this UV-visible spectroscopy, infrared spectroscopy, elemental analysis, X-ray powder patterns, and single crystal X-ray diffraction were all employed. Experiments were performed in each of these areas and the results will be reported in the text that follows. It will be noted that all of the solution work is focused around Cu^{2+} and Cr^{3+} . Copper(II) was selected for study because extensive solution work has been reported^{1,2,8} and also because the molecular structure (1:2) in the solid state is known.⁷ Chromium(III) was selected because there has been no report in the literature of it complexed with DPK under any circumstances.

Isolation of DPK Complexes in the Solid State

Four new complexes of transition metal cations which included Cr^{3+} , Ru^{3+} and Al^{3+} , 1:2, and Ag^{1+} , 1:1, with DPK were isolated. The method used for isolation follows: DPK was mixed with metal salt in a 1:2 ratio in distilled water and the water was allowed to slowly evaporate. Upon the formation of crystals, the remaining solution was removed and the crystals were washed with distilled water. The metal salts were analytical reagent grade and the DPK was purchased from Aldrich Chemicals #12,772-1.

To determine whether the complex isolated had undergone hydration, an infrared spectrum was taken of a KBr/DPK (complex) pellet using a Perkin-Elmer 1420 Ratio Recording Infrared Spectrophotometer. Disappearance of the 1690 cm^{-1} carbonyl band indicated that hydration had occurred. Fig. 8 provides a general illustration of this by comparing the 1690 cm^{-1} region of uncomplexed DPK with the same region of the hydrated Cu(DPK) complex.

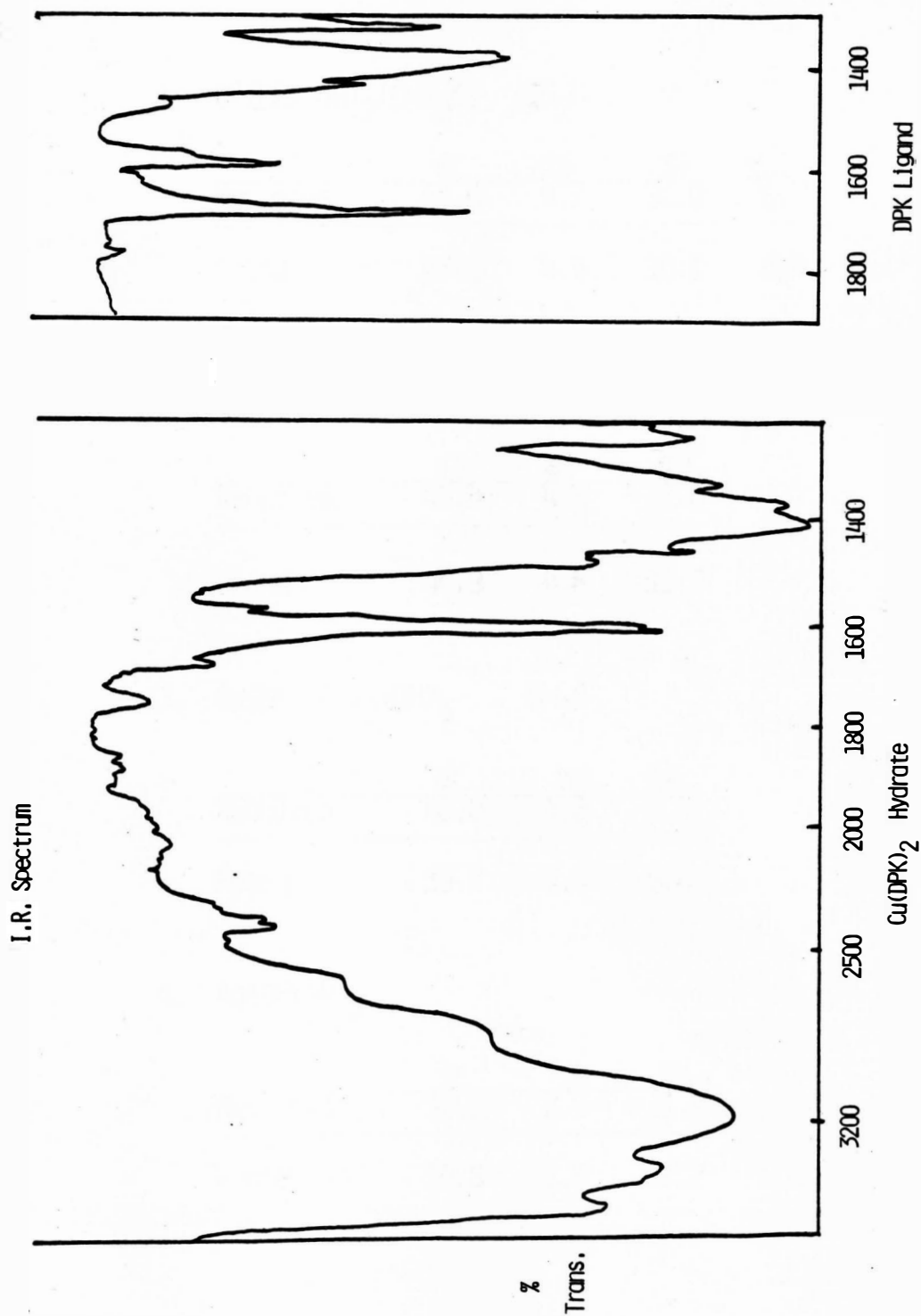
A 50 mg sample of each compound was sent to Galbraith Laboratories, Inc., Knoxville, TN, for carbon, hydrogen and nitrogen elemental analysis and chlorine in case of the Cr complex. A listing of the results as well as formulations for the isolated compounds is found in Table 1.

UV-Visible Spectra of Metal - DPK Solutions

Aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ and CrCl_3 with DPK were studied spectrophotometrically under a variety of conditions. A summary of the spectra is found in Appendix 1 each being referred to by spectrum number. The spectra were recorded on the Perkin-Elmer 330 UV-Visible spectrophotometer and ground glass cuvetts were used to hold the sample solutions.

The spectra in 1 illustrates the shift of the absorption peak for Cu^{2+} towards higher energy upon the addition of DPK 1:2 and 1:1. A rapid darkening of the combined solution accompanied this spectral

Fig. 8: 1690 cm^{-1} Region of Infrared Spectrum for
 $\text{Cu}^{2+}:\text{DPK}$ and DPK



**Table 1: Formulations of Newly Isolated DPK Compounds
and Elemental Analysis Results**

1.	$\text{Cr}(\text{DPK-OH})_2(\text{OH})_2\text{Cl} \cdot 2\text{H}_2\text{O}$			
		%C	%H	%N
	Requires	47.0	4.7	10.0
	Found	47.1	4.6	10.1
				%Cl
	Requires			6.3
	Found			6.4
2.	$\text{Al}(\text{DPK-OH})_2(\text{OH})_2(\text{NO}_3) \cdot 3\text{H}_2\text{O}$			
		%C	%H	%N
	Requires	45.4	4.8	12.0
	Found	44.8	4.8	11.9
3.	$\text{Ru}(\text{DPK-OH})_2(\text{OH})_3 \cdot 6\text{H}_2\text{O}$			
		%C	%H	%N
	Requires	40.0	4.8	8.5
	Found	39.7	4.4	8.4
4.	$\text{Ag}(\text{DPK})\text{NO}_3$			
		%C	%H	%N
	Requires	37.3	2.3	11.9
	Found	39.8	2.5	12.7

movement. As can be seen from Spectra 2 & 3 this shift is normal for the coordination of either two or four nitrogen atoms per Cu^{2+} . These ligands (en = ethylenediamine, dpyamine = dipyridylamine, and 2,2-bpy = 2,2 bipyridyl) were employed since they are similar to DPK in that they chelate with two nitrogen atoms and do so immediately upon addition to a Cu^{2+} solution.

An interesting phenomenon observed in the spectrum of the Cu^{2+} - DPK solution after a period of 5 weeks is shown in Spectra 4. Not only does the absorption peak broaden out but it also shifts back towards lower energy. This phenomenon was then investigated quite closely and it was found that there was indeed a reverse movement of the peak within one week of the metal -DPK combination. A summary of the total movement of the Cu-DPK, 1:2, over time is presented in Spectra 5. Very small crystals were visible in the time study solution only after twelve days. Elemental analysis and infrared spectral evidence showed these to be $\text{Cu}(\text{DPK-OH})_2\text{X}_2$ crystals, the structure of which is known.

Chromium(III) spectra were recorded in parallel with those of Cu^{2+} although it was observed from the outset that changes in the Cr^{3+} -DPK solution spectra were much slower. Upon the addition of DPK to the Cr^{3+} solution, the color slowly changed from green to red over a period of about twenty five minutes. The spectra in 6 shows the final position of the Cr^{3+} -DPK absorption peak. Spectra were also recorded for Cr^{3+} with ethylenediamine, dipyridylamine, and

2,2-bipyridyl and results parallel those for the Cu^{2+} -DPK system, i.e. equal shifts towards higher energy of the absorption peak for all ligands and for DPK in both 1:1 and 1:2 ratios. Again as the spectra in 7 illustrate a reverse shift was observed for the Cr^{3+} -DPK however, it was not as pronounced as that for the Cu^{2+} -DPK system.

This reverse shift towards lower energy observed after the initial peak shift towards higher energy was found to be unique to the DPK systems of Cu:DPK and Cr:DPK. The solutions containing either Cu^{2+} or Cr^{3+} with bpyamine, 2,2 bpy, and en showed only the initial shift towards higher energy with no reverse shift back towards lower energy over time.

Aqueous Solution pH Study

The pH of the aqueous solutions of Cu^{2+} and Cr^{3+} with DPK, 1:2, were recorded as UV-Vis spectra were being recorded as discussed in the previous section. A Chemitrix type 40E pH meter and magnetic stirrer were employed for determining the pH of the solutions before the respective solutions were placed in the cuvetts. The pH meter was standardized with commercial pH 4 and pH 10 buffers.

For Cr^{3+} in H_2O with the addition of DPK 1:2: *Note: Since the reaction takes about 30 min. to complete the pH was recorded every 5 min. as noted.

Table 2: pH Values of Cu(II) Solutions

pH		Solution
7.1	:	H ₂ alone
7.0	:	DPK in H ₂
4.2	:	Cu(NO ₃) ₂ in H ₂ O
7.0 → 4.2	:	DPK + Cu(NO ₃) ₂ upon addition

Table 3: pH Values of Cr(III) Solution

pH		Solution
7.1		H ₂ O alone
7.2		DPK in H ₂ O
2.8		CrCl ₃ in H ₂ O
7.2 → 4.0		CrCl ₃ + DPK upon addition
3.5		after 5 min.
3.2		after 10 min.
3.0		after 15 min.
2.7		after 20 min.
2.6		after 25 min.
2.5		after 30 min.
2.5		after 1 hour

The pH of these solutions were then taken daily after the initial measurements and it was found that the solutions remained acidic becoming slightly more acidic with time. Upon visible observation of crystal formation the Cu:DPK solution was at a pH of 3.2 and the Cr:DPK solution was at a pH of 1.9. Thus the systems natural tendency is towards an acidic medium.

Following these observations an attempt was made to vary the pH of the solutions by adding either acid or base with counter ions common to those already in solution i.e. HNO_3/NaOH for $\text{Cu}(\text{NO}_3)_2:\text{dpk}$ system and HCl/NaOH for $\text{CrCl}_3:\text{DPK}$ system. UV-Vis spectra were again taken of the respective solutions to see if any adsorption peak shift occurred. As can be seen by the respective spectra in Appendix 2 there is indeed movement of the absorption peaks with an induced change in pH. In the Cu-2+:DPK system the peak is shown at pH = 4.0. This is where the absorption peak initially moves upon the addition of DPK. With the addition of 6N NaOH there is a reverse shift of the absorption peak towards lower energy as shown by the position of the peak at pH = 12.2 Addition of 6N HCl brought the absorption peak back to the position where pH = 4.0. For the Cr-3+:DPK system 6N HNO_3 was used to adjust the pH instead of the 6N HCl in a parallel procedure giving similar results. The spectra for the Cu-2+:DPK and Cr-3+:DPK systems appear to be cyclic in the sense that the absorption peak, after the initial shift toward higher energy, was shifted back to lower energy and then was returned to the position to where it had moved originally.

It is interesting to note that a similar reverse shift (discussed in the previous section) in the UV-Vis spectrum for Cu-2+ and Cr-3+ with DPK was not accompanied by a rise in the pH of the system. Hence it appears that the previously reported reverse shift in the UV-Vis spectrum was not due to a change in pH.

A Cu-2+:DPK solution with pH adjusted to 11.4 and a Cr-3+:DPK solution with pH adjusted to 11.7 were set aside for slow evaporation in order to isolate the respective crystals out of the basic solution. After five days (much sooner than when additional acidic or basic solutions are not added) crystals were visible in both solutions. The pH = 9.8 for the Cu-2+:DPK and pH = 8.8 for the Cr-3+:DPK at this point. A sample of the Cu-2+:DPK solid was sent to Galbraith Laboratories for elemental analysis with the following results returned:

**Table 4: Results of Elemental Analysis for
Cu²⁺:DPK Solid**

Formulation: $\text{Cu}(\text{DPK-OH})_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$

	%C	%H	%N

(calculated) :	47.5	5.1	10.1
(observed) :	47.2	4.4	10.1

By comparing this formulation with one reported previously⁷ it appears that the two nitrate anions were replaced with two hydroxide ions and

there is an additional water molecule associated with this compound isolated from basic solution. Infrared spectra of both compounds isolated from basic solution evidence a disappearance of the 1690 cm^{-1} band indicating that hydration of the carbonyl had taken place. Although the Cr-3+DPK crystals isolated from the basic solution were not sent for elemental analysis, similar findings could be expected, i.e. replacement of the chloride anion by a hydroxide ion. Evidence for this is suggested by the similarity of the infrared spectra of these crystals isolated from basic solution with those isolated at low pH.

Experiments Involving the Axial Position on the Metal Cation

Metal cations such as Cu^{2+} or Cr^{3+} are believed to possess an octahedral coordination sphere containing six water molecules when in aqueous solution. The axial positions of these complexes are quite interesting (see the historical section). The solid state structures of metal-DPK hydrate compounds show unusual off axis coordination. Two questions arise: first, could both axial positions on the metal be blocked by ligands stronger in ligand field strength according to the spectrochemical series than hydroxide ion or H_2O which would not allow DPK to coordinate in a tridentate fashion, i.e. coordination in the axial position with one of the hydroxyl groups from the newly formed diol. Second, does the hydration of the carbonyl carbon atom occur via an intramolecular or intermolecular process, that is, does the H_2O molecule that became involved in the hydration reaction with

the carbonyl to form the diol the H_2O already in the axial position and coordination sphere of the metal cation due to initial solvation or a H_2O from outside the coordination sphere, i.e. the surrounding solution.

Although the instrumentation was not readily available to definitively answer these questions, several experiments were performed with the equipment available in an attempt to gain some insight.

Ammonia and pyridine were chosen to attempt to block the axial positions on the metal cations for both Cu^{2+} and Cr^{3+} in a 1:2, metal to ligand ratio. In this situation one would expect to find the ammonia and pyridine to be occupying the axial positions to a great extent replacing the H_2O from the initial solvation. The choice of ammonia as one of the blocking ligands was intentional for it was a means to address the second question of where the H_2O molecule comes from that participates in the hydration reaction. If the H_2O in the axial position was the H_2O involved in the hydration reaction one may observe amination rather than hydration at the carbonyl. These ideas were investigated in the following manner.

Both ammonia and pyridine (reagent grade) were added separately to individual aqueous solution of Cu^{2+} and Cr^{3+} in aqueous solution in a 1:2 metal to ligand ratio. After the addition of the axial blocking agents, DPK was added in a 1:2 metal to ligand ratio. UV-Vis spectra were taken after each addition and afterward for an extended time period. No significant effects were observed in these respective

spectra opposed to those spectra taken previously in the absence of the axial blocking agents. Upon evaporation of the solution, solid compounds were obtained though they did not appear to be good crystalline material. Samples of these were sent to Galbraith Laboratories for elemental analysis. The percentage of C, H, and N found did not lead to any recognizable formulations, hence we report that the results for these particular experiments were inconclusive. Conclusive results might be obtained by implementing Raman spectroscopy experiments and ^{18}O isotopes as tracers for the H_2O in the axial position.

Flash Evaporation of Solvent from the Metal:DPK Solution

Having noted the color changes associated with both Cu-2+ and Cr-3+ upon the addition of DPK in aqueous solution, we also noted the substantial difference in time required for the color changes to occur. For Cu-2+:DPK the color change is immediate upon the addition of the ligand where Cr-3+:DPK takes 25-30 min. to reach its final color after the addition of the ligand. We believe that this color change has something to do with the progress of the coordination of the ligand to the metal cation. Since we could not take the infrared spectrum of the aqueous metal:DPK solution due to the severe O-H interference, we attempted to isolate solids at points through the color changes.

A round bottom flask to which either Cu-2+ or Cr-3+ with DPK solution was added was sealed and connected to a vacuum pump with a liquid nitrogen cold finger trap placed in line to freeze out the H₂O solvent. DPK was added (1:2 metal to ligand ratio) to the respective metal cation and allowed to react for an allotted time and then the solvent was flash evaporated as rapidly as possible taking from 10-15 min.

In the case of Cu-2+ with DPK, the apparatus used did not allow for the solvent to be pulled off before the color change had become complete. Hence only after the complete color change were we able to obtain a solid compound of which an infrared spectrum could be obtained. Though it was after the color change, this solid was obtained well ahead of the normal 10-14 days for the first appearance of crystals. The infrared spectra displayed no 1690 cm⁻¹ band which indicates that hydration of the carbonyl had taken place.

The Cr-3+ with DPK was much more interesting in that our apparatus allowed us to obtain a solid compound at several points along the 25-30 min. color transition pathway. It was found that there was evidence of the carbonyl, again determined from infrared spectra, in all the solid compounds each to a lesser degree, until the final red colored solution was evaporated in which there was no evidence of the 1690 cm⁻¹ band.

This evidence would then suggest that along with the initial color change and the movement of the absorption peak in the UV-Visible spectrum there is also hydration of the carbonyl of DPK. Two points need to be noted: first, what is found in the solid state is not necessarily the same thing that is present in the solution state, and second, we forced the metal:DPK complex into the solid state well in advance of the normal time required for precipitation to occur naturally. Both of these could have some unforeseen effect on the respective complexes.

X-ray Powder Patterns

To augment our characterization of the solid state of metal:DPK compounds, X-ray powder photographs were taken of each compound. These compounds contained Co^{3+} , Cd^{2+} , Ru^{3+} , Fe^{3+} , Cu^{2+} , Mn^{2+} , Al^{3+} , Cr^{3+} in a 1:2 ratio and Ag^{1+} in a 1:1 ratio as the cations. Hydration was indicated by the respective infrared spectra. Although several of these compounds have been previously reported in the literature, no attempt at X-ray powder pattern characterization has been reported.

Though X-ray powder photographs are of limited value in crystal structure analysis, they can be useful in determining whether two compounds are isostructural. With a series of very similar compounds such as these DPK-hydrate complexes, such characterization could prove to be useful reference at some future date in the identification of a particular compound.

other, then by determining d we will know the interplanar spacings peculiar to that compound.

A listing of d -spacings can be found in Appendix 4 for each compound that was isolated.

X-ray Analysis of
Cr(DPK-OH)₂(OH)₂Cl·H₂O
and Ru(DPK-OH)₂(OH)₃·H₂O

Data Collection

Crystals suitable for an X-ray crystal structure analysis were obtained by allowing the aqueous solvent to slowly evaporate from a 1:2, metal cation to ligand ratio, solutions of both Cr-3+ and Ru-3+. The resulting crystals were rectangular in shape with approximate dimensions of 0.18 X 0.19 X 0.38 mm for the Cr-3+ complex and 0.10 X 0.12 X 0.11 mm for the Ru-3+ complex. These crystals were transported to The Ames Laboratory-USDOE at Iowa State University, Ames, Iowa for data collection. The crystals were attached to glass fibers and mounted on standard X, Y, Z translation goniometers. All intensity data were collected at 22°C. The unit cell parameters were initially calculated using the automatic indexing procedure BLIND.¹¹ The space group C2/C for the Cr-3+ complex and P $\bar{1}$ for the Ru-3+ complex were consistent with the systematic absences observed in the data. Table 5 contains a tabulation of the pertinent information relevant to the data collected.

Table 5: Crystal Data for $\text{Cr}(\text{C}_{11}\text{H}_8\text{N}_2$ $(\text{OH})_2)_2(\text{OH})_2\text{Cl} \cdot 3\text{H}_2\text{O}$, I, $\text{Ru}(\text{C}_{11}\text{H}_8\text{N}_2$ $(\text{OH})_2)_2(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, II

	I	II
Empirical formula	$\text{CrC}_{22}\text{H}_{28}\text{N}_4\text{O}_9\text{Cl}$	$\text{RuC}_{22}\text{H}_{30}\text{N}_4\text{O}_{10}$
Formula weight	579.0	611.1
Crystal system	Monoclinic	Ticlinic
Space group	C2/C	$\text{P}\bar{1}$
a(Å)	11.19(1)	8.680(7)
b(Å)	14.67(1)	9.829(9)
c(Å)	17.12(1)	8.908(7)
Alpha(deg)	90.0	99.79(6)
Beta(deg)	104.06(1)	103.04(6)
Gamma(deg)	90.0	76.30(7)
V(Å ³)	2810(1)	714(1)
Z	4	1
Calculated density (g cm ⁻³)	1.37	1.42
Diffractometer	Datex	Syntex-LT-1
Monochromator	Oriented graphite crystal	
Radiation	Mo($\lambda=0.71034\text{Å}$)	Cu($\lambda=1.5418$)
Scan type	ω scan	ω scan
Number of unique refl.	1848	2406
Max. # of parameters refined	179	193
Linear Abs. Coef.	5.66 cm ⁻¹	5.95 cm ⁻¹
R	8.6	5.0
Rw	11.7	6.6

Structure Solutions and Refinement

The heavy atom method was employed in solving the two structures. Analysis of the three-dimensional Patterson maps revealed the appropriate positions for the heavy atoms and electron density maps¹² generated from the structure factors phased by the metal atom yielded the probable locations for all of the other non-hydrogen atoms. A basic computer program, written by the author, to calculate atom positions relative to each other in crystal space was used to determine atom positions from the electron density map. A listing of this program is found in Appendix 5. These positions and the associated anisotropic thermal parameters were refined first by using diagonal block matrix least-squares calculations¹¹ and the final refinement was done using full matrix least squares techniques. Positions for hydrogen atoms were calculated assuming a C-H distance of 1.05Å (Appendix 6). Final positional parameters for the non-hydrogen atoms in the two structures are listed in Table 6, positional parameters for the hydrogen atoms, Table 7, thermal parameters of non-hydrogen atoms, Table 8, interatomic distances, Table 9, and interatomic angles, Table 10. Figures 9 and 10 are PLUTO drawings of the solved Cr:DPK and RU:DPK structures respectively.

**Table 6: Final Positional Parameters for the
Non-hydrogen Atoms, I**

(X 10⁴)

ATOM	X	Y	Z
Cr	0	0	0
N1	862 (5)	296 (4)	1180 (3)
C1	886 (7)	1064 (5)	1596 (4)
C2	1548 (8)	1106 (6)	2384 (5)
C3	2188 (8)	369 (7)	2755 (4)
C4	2136 (7)	-444 (6)	2331 (4)
C5	1458 (6)	-436 (5)	1525 (4)
C11	1231 (6)	-1276 (5)	956 (4)
O1	1247 (4)	-949 (3)	196 (2)
O2	2106 (4)	-1947 (4)	1250 (3)
N2	-912 (5)	-992 (4)	474 (3)
C21	-2116 (7)	-1106 (5)	422 (5)
C22	-2525 (9)	-1827 (7)	820 (5)
C23	-1660 (9)	-2415 (6)	1279 (6)
C24	-423 (8)	-2294 (5)	1338 (4)
C25	-80 (7)	-1572 (5)	934 (4)
C1	54 (4)	4903 (3)	602 (3)
O3	1854 (6)	6523 (4)	424 (4)
O4	-264 (6)	3234 (5)	1662 (4)
O5	4654 (20)	52 (11)	1235 (9)
O6	5000 (0)	1100 (0)	2500 (0)

Table 6 (cont.): Final Positional Parameters for the Non-hydrogen Atoms, II

($\times 10^4$)

ATOM	X	Y	Z
Ru	0	0	0
N1	328 (5)	1878 (4)	1319 (5)
C1	-652 (7)	3156 (6)	1294 (8)
C2	-186 (8)	4314 (6)	2269 (9)
C3	1310 (8)	4157 (6)	3238 (9)
C4	2313 (7)	2831 (6)	3248 (7)
C5	1789 (6)	1725 (5)	2269 (6)
C11	2698 (6)	199 (6)	2123 (6)
O1	2382 (4)	-324 (6)	532 (4)
O2	4334 (4)	50 (4)	2753 (4)
N2	454 (5)	-795 (4)	2094 (5)
C21	-443 (7)	-1463 (6)	2630 (7)
C22	105 (8)	-1968 (6)	4077 (7)
C23	1574 (8)	-1774 (6)	4947 (7)
C24	2504 (7)	-1070 (6)	4381 (7)
C25	1904 (6)	-603 (5)	2940 (6)
O3	3748 (6)	4202 (5)	386 (5)
O4	5751 (6)	1570 (5)	1568 (6)
O5	6275 (6)	7321 (6)	2731 (8)
O6	5478 (12)	5034 (10)	3683 (9)

Table 7: Positional Parameters of the Hydrogen Atoms, I

($\times 10^4$)

ATOM	X	Y	Z
H1	404	1,637	1,314
H2	1,578	1,713	2,712
H3	2,700	388	3,356
H4	2,620	-1,019	2,613
H5	-2,759	-657	76
H6	-3,470	-1,918	775
H7	-1,943	-2,962	1,584
H8	220	-2,744	1,687

Table 7 (cont.): Final Positional Parameters for the Hydrogen Atoms,

II

($\times 10^4$)

ATOM	X	Y	Z
H1	-1,830	3,289	532
H2	-993	5,354	2,248
H3	1,694	5,061	3,987
H4	3,496	2,693	4,011
H5	-1,612	-1,615	1,950
H6	-622	-2,513	4,513
H7	2,030	-2,166	6,061
H8	3,670	-924	5,060

Table 8: Thermal Parameters of Non-hydrogen Atoms, I

ATOM	(x 10 ⁴)					
	B11	B22	B33	B12	B13	B23
Cr	49 (1)	28 (1)	21 (1)	-1 (1)	5 (1)	3 (1)
N1	55 (5)	32 (3)	24 (2)	-7 (3)	8 (3)	-5 (2)
C1	79 (7)	45 (4)	33 (3)	-15 (4)	20 (4)	-7 (3)
C2	105 (9)	55 (5)	36 (3)	-12 (6)	20 (5)	-21 (3)
C3	99 (9)	67 (5)	26 (3)	-24 (6)	5 (4)	-9 (3)
C4	71 (7)	58 (5)	32 (3)	-7 (5)	5 (4)	-9 (3)
C5	69 (7)	37 (4)	26 (3)	-1 (4)	10 (3)	2 (3)
C11	68 (7)	35 (4)	26 (2)	-7 (4)	4 (3)	-2 (2)
O1	66 (4)	38 (2)	38 (2)	25 (2)	5 (3)	-4 (2)
O2	72 (5)	42 (3)	37 (2)	8 (3)	0 (3)	6 (2)
N2	59 (5)	35 (3)	32 (2)	-3 (3)	13 (3)	-4 (2)
C21	76 (8)	46 (4)	39 (3)	-11 (5)	18 (4)	-6 (3)
C22	100 (9)	62 (6)	48 (4)	-32 (6)	32 (5)	-15 (4)
C23	113 (10)	53 (5)	42 (4)	-24 (6)	20 (5)	2 (3)
C24	112 (9)	40 (4)	32 (3)	-12 (5)	12 (4)	7 (3)
C25	83 (7)	36 (4)	28 (3)	-3 (4)	10 (4)	-2 (3)
C1	93 (4)	61 (3)	48 (2)	-20 (3)	8 (2)	3 (2)
O3	115 (7)	54 (3)	53 (3)	-7 (4)	33 (3)	-10 (3)
O4	112 (7)	73 (4)	57 (3)	9 (4)	5 (4)	9 (3)
O5	307 (31)	70 (9)	60 (8)	-44 (14)	18 (12)	-1 (7)

Table 8 (cont.): Thermal Parameters of Non-hydrogen Atoms, II

ATOM	(x 10 ⁴)					
	B11	B22	B33	B12	B13	B23
Ru	74(1)	70(1)	74(1)	-18(1)	14(1)	7(1)
N1	89(6)	68(5)	92(6)	-16(5)	17(5)	5(5)
C1	131(10)	86(7)	142(10)	-13(7)	15(8)	6(7)
C2	182(12)	69(7)	205(13)	-13(7)	29(10)	2(8)
C3	186(12)	92(8)	183(12)	-43(8)	16(10)	-15(8)
C4	142(10)	107(8)	105(9)	-52(7)	18(8)	-6(7)
C5	96(8)	78(6)	88(8)	-29(6)	11(6)	5(6)
C11	83(8)	92(6)	78(7)	-26(6)	2(6)	11(6)
O1	71(5)	92(4)	82(5)	-20(4)	12(4)	6(4)
O2	77(5)	125(5)	110(6)	-26(4)	-9(5)	15(5)
N2	106(7)	70(5)	80(6)	-20(5)	20(5)	11(5)
C21	126(9)	81(6)	116(9)	-28(6)	49(7)	8(6)
C22	187(12)	93(7)	120(9)	-33(7)	60(9)	20(7)
C23	199(13)	105(8)	105(9)	-18(8)	39(9)	32(7)
C24	133(10)	95(7)	104(9)	-10(7)	8(8)	18(6)
C25	99(8)	72(6)	88(8)	-22(6)	16(6)	9(6)
O3	297(11)	123(6)	117(7)	46(6)	48(7)	43(6)
O4	186(9)	188(8)	157(8)	-41(6)	78(7)	6(6)
O5	197(10)	176(8)	330(14)	-47(7)	5(10)	66(9)
O6	685(30)	458(20)	254(15)	-359(21)	8(17)	110(15)

Table 9: Interatomic Distances, I

ATOMS	Distance
Cr-O1	1.941 (5)
Cr-N1	2.062 (5)
Cr-N2	2.055 (6)
N1-C1	1.330 (9)
N1-C5	1.325 (10)
C1-C2	1.374 (11)
C2-C3	1.365 (13)
C3-C4	1.391 (13)
C4-C5	1.404 (10)
C5-C11	1.553 (11)
C11-O2	1.393 (9)
C11-O1	1.390 (8)
C11-C25	1.523 (11)
N2-C21	1.339 (9)
N2-C25	1.361 (9)
C21-C22	1.394 (12)
C22-C23	1.389 (13)
C23-C24	1.375 (13)
C24-C25	1.370 (10)

Table 9 (cont.): Interatomic Distances, II

ATOMS	Distance
Ru-O1	1.975(4)
Ru-N1	2.057(4)
Ru-N2	2.065(5)
N1-C1	1.340(7)
N1-C5	1.347(7)
C1-C2	1.391(9)
C2-C3	1.378(10)
C3-C4	1.386(8)
C4-C5	1.372(8)
C5-C11	1.519(7)
C11-O2	1.387(6)
C11-O1	1.411(6)
C11-C25	1.519(7)
N2-C21	1.335(7)
N2-C25	1.351(7)
C21-C22	1.401(9)
C22-C23	1.372(9)
C23-C24	1.396(9)
C24-C25	1.384(8)

Table 10: Interatomic Angles, I

ATOMS	Angle
N1-Cr-N2	94.54 (21)
N1-Cr-O1	99.44 (19)
N2-Cr-O1	99.85 (21)
Cr-N1-C1	130.33 (47)
Cr-N1-C5	109.34 (46)
N1-C1-C2	119.99 (69)
C1-C2-C3	121.24 (78)
C2-C3-C4	119.05 (69)
C3-C4-C5	116.72 (76)
C4-C5-N1	122.61 (74)
N1-C5-C11	112.03 (57)
Cr-N2-C21	130.57 (49)
Cr-N2-C25	109.61 (45)
C21-N2-C25	119.75 (61)
N2-C21-C22	120.44 (73)
C21-C22-C23	118.73 (86)
C22-C23-C24	120.86 (81)
C23-C24-C25	117.56 (73)
C24-C25-N2	122.64 (70)
C5-C11-C25	104.54 (58)
C5-C11-O1	106.01 (56)
C5-C11-O2	109.90 (57)
C25-C11-O1	107.87 (55)
C25-C11-O2	113.29 (59)
O1-C11-O2	114.52 (57)

Table 10 (cont.): Interatomic Angles, II

ATOMS	Angle
N1-Ru-N2	94.42(17)
N1-Ru-O1	101.02(17)
N2-Ru-O1	78.89(17)
Ru-N1-C1	129.31(38)
Ru-N1-C5	111.04(31)
N1-C1-C2	120.44(55)
C1-C2-C3	119.93(55)
C2-C3-C4	119.00(57)
C3-C4-C5	118.63(55)
C4-C5-N1	122.39(46)
N1-C5-C11	111.10(42)
Ru-N2-C21	129.07(37)
Ru-N2-C25	110.65(33)
C21-N2-C25	120.24(46)
N2-C21-C22	120.47(53)
C21-C22-C23	119.69(56)
C22-C23-C24	119.55(56)
C23-C24-C25	118.13(53)
C24-C25-N2	121.91(47)
C5-C11-C25	106.62(41)
C5-C11-O1	106.62(42)
C5-C11-O2	112.81(44)
C25-C11-O1	106.40(42)
C25-C11-O2	110.78(43)
O1-C11-O2	113.17(40)

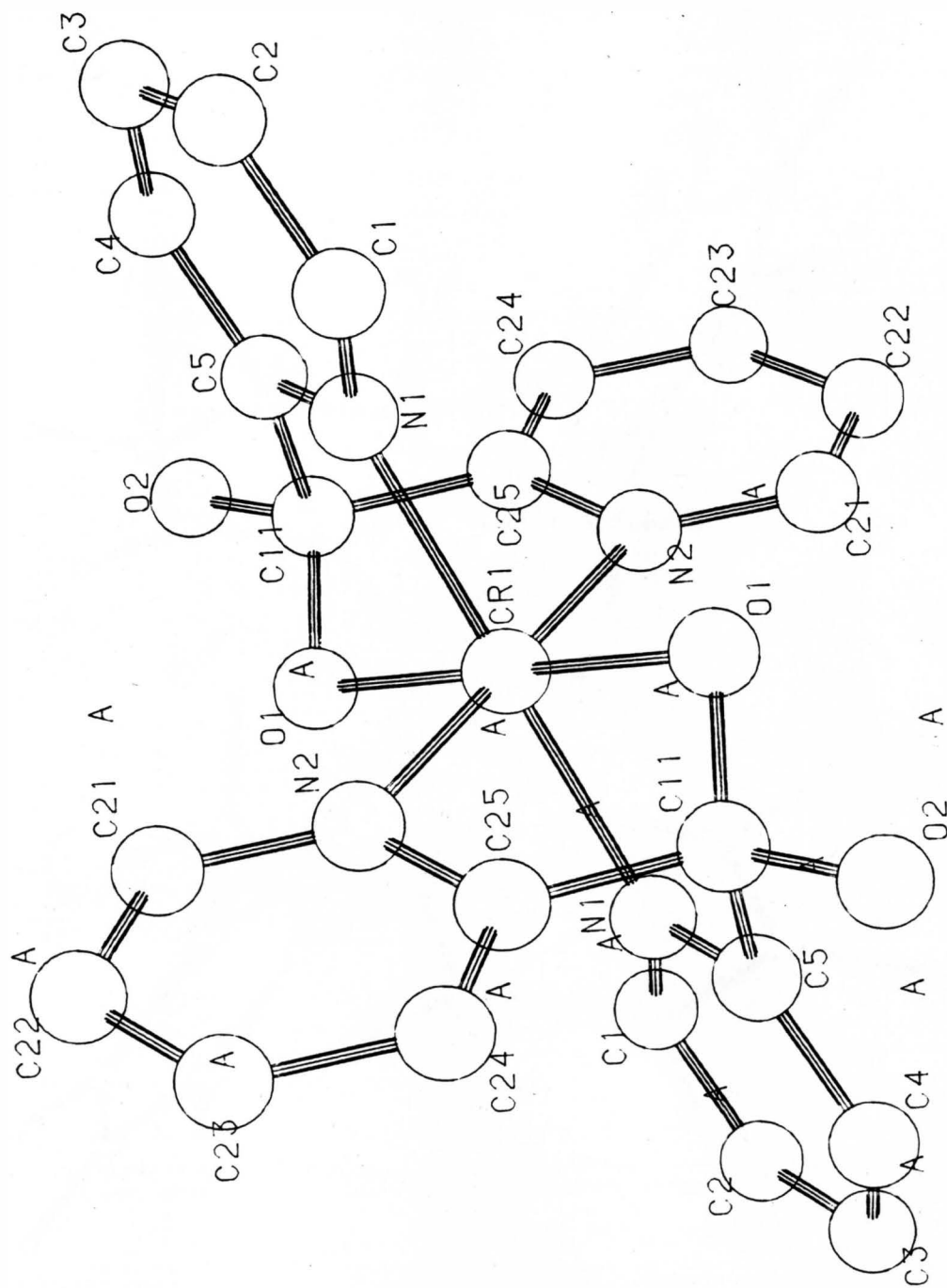
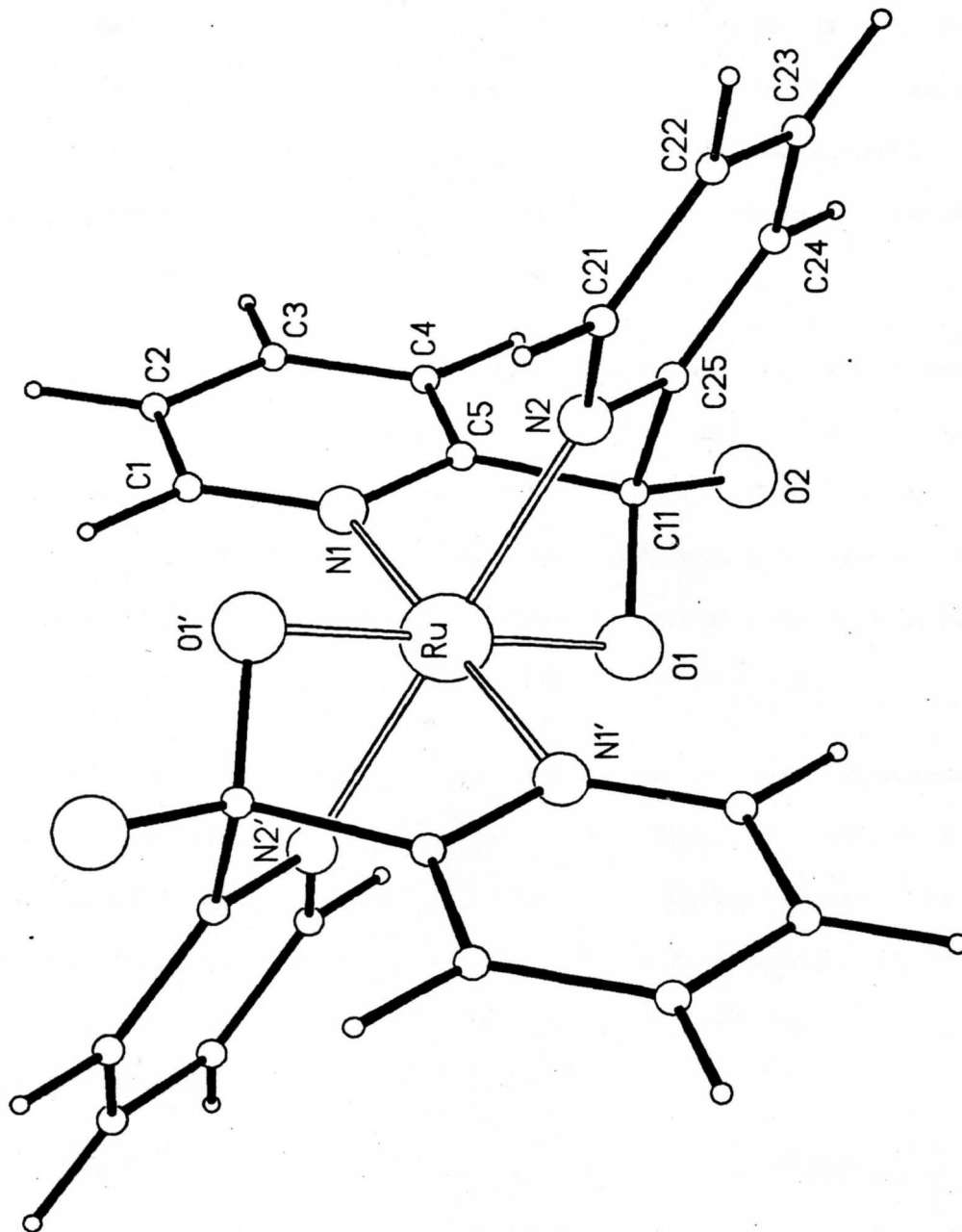
Fig. 9: PLUTO drawing of Cr³⁺:DPK Structure

Fig. 10: PLUTO drawing of Ru-3+:DPK Structure

Discussion of the Structures

The PLUTO drawings of both the Cr-3+ and Ru-3+ complexes show the two DPK ligands bonded to the metal cation in a tridentate fashion. The geometry about the metal atom can be described as a distorted octahedron due to the unusual off axis coordination of the hydroxyl groups. In these two aspects, both structures are quite similar to the previously reported 1:2 complexes.⁷

In the Ru complex, the metal-ligand bond distances are very similar (Ru-N avg. = 2.061Å, Ru-O = 1.975Å) which indicates similar bond strength within the coordination sphere. The off axis angle formed between the Ru-O bond and the line normal to the equatorial plane was found to be about 15°. There are three hydroxide groups as the anions to complete the structure and charge balance.

For the Cr complex, the metal-ligand bond distances are similar (Cr-N avg. = 2.058Å, Cr-O = 1.941Å). The off axis angle formed between the Cr-O bond and the line normal to the equatorial plane was found to be about 12 (deg). This is the smallest off axis angle yet reported. One chloride (disordered) and two hydroxide groups are present as the anions.

The bond distances and angles in the DPK ligands are quite normal in both structures. The average C-C bond distances within the rings are 1.385Å and 1.383Å for the Ru(III) and Cr(III) structures respectively which are quite close to the accepted value for pyridine

of $1.395(1)\text{\AA}$.¹³ Likewise the average C-N bond distances, 1.343\AA and 1.339\AA are very close to the accepted value of $1.340(1)\text{\AA}$ as well as the average bond angles within the rings of 120.0° , and 120.0° . Hence, there is no apparent strain or distortion within the pyridine rings.

It is interesting to note that the intra-ligand pyridyl ring dihedral angles are 101° for Cr and 109° for Ru as compared to 180° for a planar DPK ligand. These are quite significant deviations from planarity for the DPK ligand. Upon the examination of models reflecting the structures, it is evident that with the additional M-O coordination there would be a significant deviation of the pyridyl rings from co-planarity though the extent to which this would occur is probably dependent on a number of factors.

Correlations of Solved DPK Structures

Observing the similar coordination behavior (i.e. N_4O_2 pseudo-octahedral coordination sphere with off axial distortion) for the Cr and Ru DPK complexes, the question arose as to whether the off axis phenomenon could be correlated with some parameter of the complex. Data for all known structures of transition metal cations with DPK were collected. A summary of the combined data used for these correlations is found in Table 11.

<u>Metal</u>	<u>Off Axis Angle</u>	<u>Pyr. Ring Angle</u>	<u>M - O(A)</u>	<u>Dist. Off Plane (A)</u>
Ni (dioxolane)+2	24.9	66.2	2.113	1.916
Cu (dioxolane)+2	19.2	69.5	2.400	2.267
Cu (dioxolane)+2	28.31	70.5	2.678	2.358
Au (1:1)+3	18.294	116.6	2.77	2.630
Pd (1:1)+2	29.4	114.5	2.824	2.461
Au (1:1)+3	31.28	86.4	2.850	2.436
Cu (1:2)+2	22.6	83.0	2.464	2.275
Cu (1:2)+2	21.5	65	2.465	2.294
Cr (1:2)+3	12.5	101	1.940	1.894
Ru (1:2)+3	15.0	71	1.980	1.911

Table 11: Combined Data for Correlations

The following properties were considered in the correlations: ionic radii of the metal cation, number of d electrons, M-O bond distance, distance of the off axis oxygen atom from the equatorial plane, atomic number, and atomic weight. By plotting each of these properties vs. the angle (in degrees) formed with the line normal to the equatorial plane, two trends appear to develop. As can be seen by the plots in Figures 11 and 12, there is a correlation between the off axis angle formed in the complexes and both the M-O bond distance and the distance of the oxygen off the equatorial plane. The remaining plots show no evidence of any trends developing and hence are not included here.

To pursue these correlations further, the regions that lack data would be of interest to see if either of these trends continue. By choosing metal cation:DPK complexes that have M-O bond distances in these areas of interest (these distances could be calculated from ionic radii), one could determine whether these correlations are continued.

We have searched the chemical literature referenced by several methods in an attempt to acquire complete data for this study. We have also searched the Cambridge Crystallographic Data File with the help of Dr. G. Palenik of the University of Florida. The data reported in Table 11 appears to be complete to the present time. Consequently, more structures need to be solved to pursue this study of correlations further.

Fig. 11: Plot of M-O bond distance vs. angle of the normal

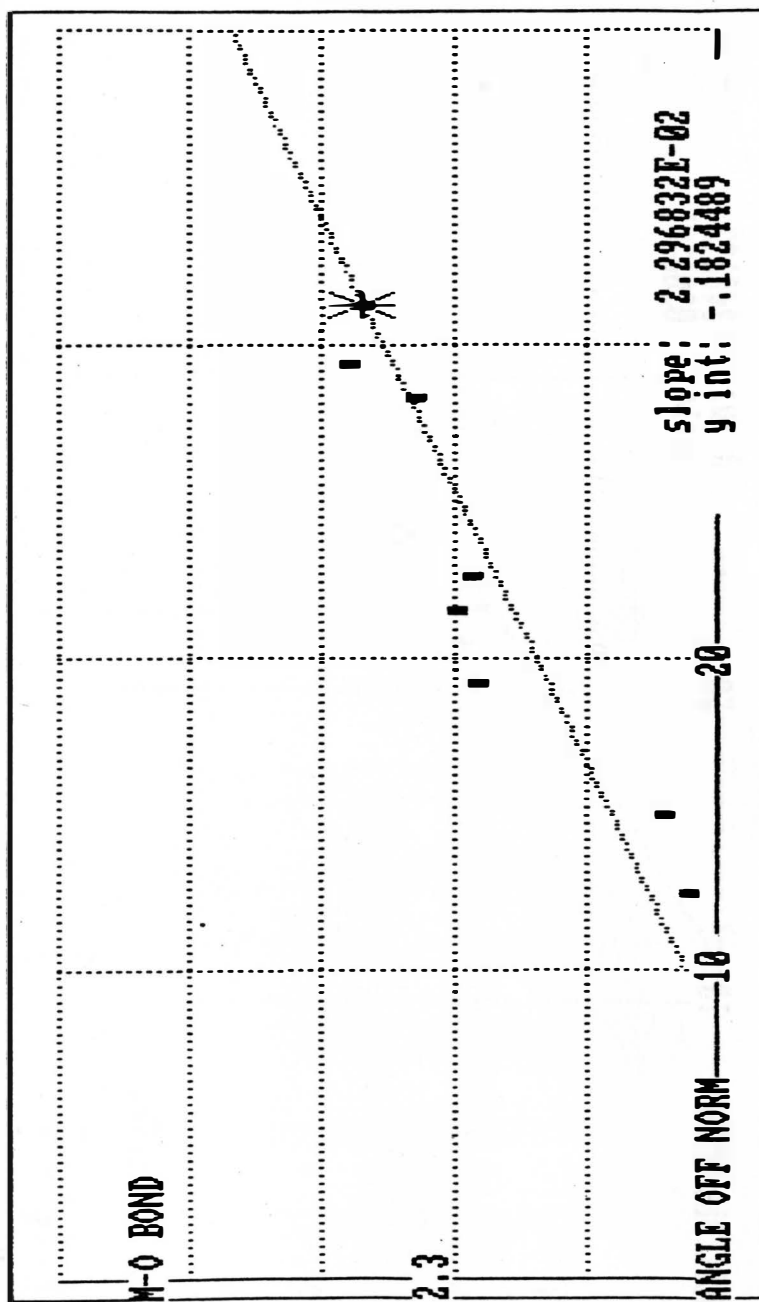
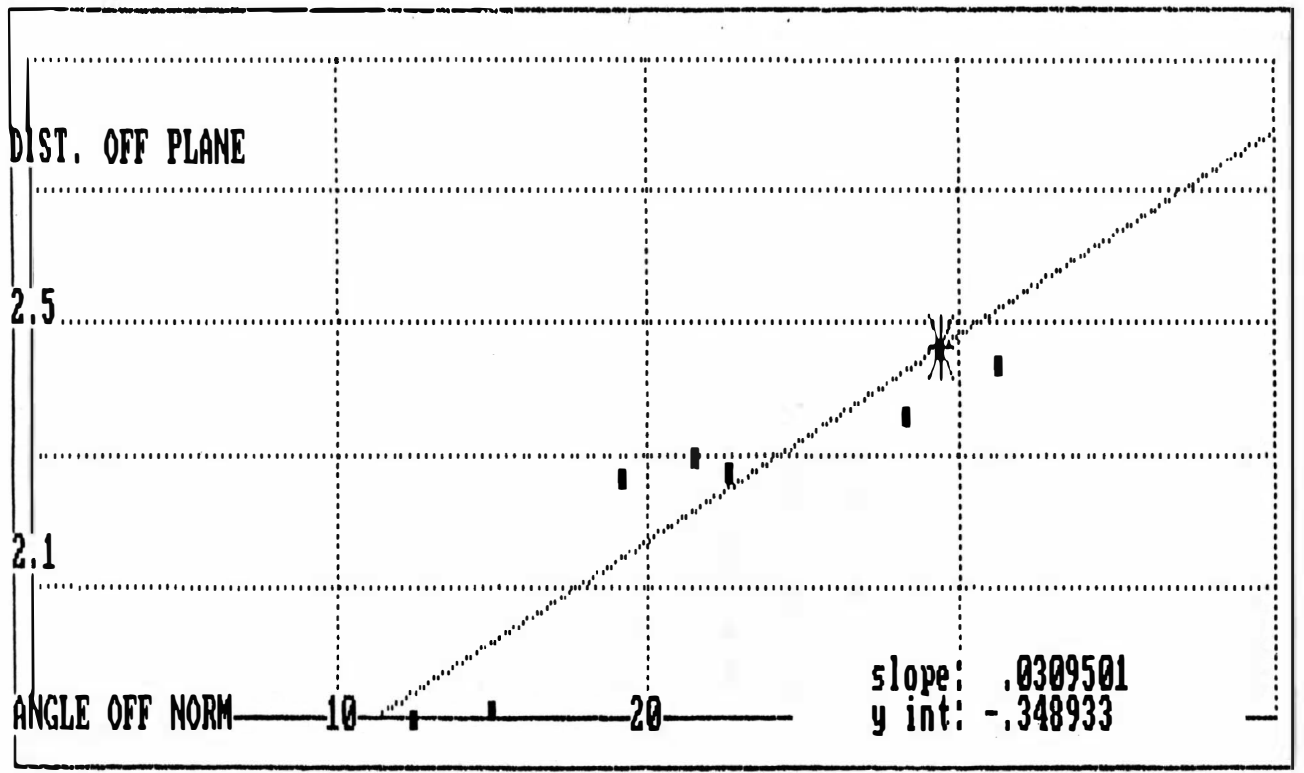


Fig. 12: Plot of Dist. of 0 off the equatorial plane vs. angle off the normal



Even though these two correlations are in no way the final word on this system, they do direct us towards further investigation of the off axis behavior observed in these metal:DPK complexes since there does appear to be some intrinsic relationship between the off axis angle formed and the structure itself. If developed further, these correlations could lead to a diagnostic technique or help to predict the off axis distortion for a given M-O bond distance. Also widening the spectrum of metal cations complexed with DPK may also lead to correlations not yet explored. Though many metals are reported to complex with DPK, relatively few are in a 1:2 metal to ligand ratio and solvent containing water, hence more crystal structures resulting from these chemical conditions need to be solved to pursue these correlations further.

Conclusion

In assessing the achievements of this project, I would like to focus on three areas. First, as reported in the experimental section of this text, four new metal:DPK complexes were isolated and characterized. In addition, the Cr:DPK and the Ru:DPK solid state structures were solved and hence this data can be added to that of previously solved structures thereby augmenting the reported information of this unique system.

Second, after assembling the data from all reported solid state structures, two correlations were observed relating both the metal-oxygen bond distance and the distance of the oxygen atoms (from the diol) from the equatorial plane of the complex formed by the metal and four nitrogen atoms with the angle formed between the M-O bond and the line normal to the equatorial plane. Though the correlations are not a final pronouncement, they do demonstrate possible direct relationships. Further development of these relationships could lead to a diagnostic tool for predicting the extent of axial distortion for a given metal:DPK complex.

Third and finally, a survey of the literature and the results presented in this study has helped to identify several significant features of this DPK system which when viewed collectively leads to a final thesis on the mechanism of this system.

From the solid state structures reported here and in the literature we know generally the features of the final product resulting from the addition of DPK to a transition metal cation in aqueous solution. One immediately notes in the solid state structures the unusual off axis coordination of the hydroxyl groups. The progress of coordination about the transition metal cation was investigated in this study by means of UV-Visible spectroscopy. A very interesting reverse shift in the spectrum of the two metal cations was noted. After accounting for the movements of the adsorption peak due to the coordination of the four nitrogen atoms (1:2 metal to ligand) initially, it would appear that the reverse shift would be due to the coordination of the hydroxyl groups in the "off axial position." A shift toward lower energy would result because the hydroxyl group replacing the water molecule already in the axial position due to solvation is lower in the spectrochemical series than water and the fact that the coordination is not exactly in the axial position but rather off axis, evidenced by the solid state structures, would lead to a lowering in the average ligand field strength resulting in a movement toward lower energy.

However, before the coordination of the hydroxyl can take place, DPK must undergo hydration across the carbonyl. The results reported in the flash evaporation experiments showed that hydration appears to occur with the observed changes in color. These results agree with the literature that DPK coordinates initially through the nitrogen atoms and then hydration is facilitated across the carbonyl.⁵

Although both N,N-coordination followed by hydration appears to occur immediately, the reverse shift was only observed after a period of time. Hence, this would lead to the following: upon addition of DPK to the transition metal cation, the ligand coordinates via N,N-coordination. Since the nitrogen donor orbitals are not directed favorably for chelation, overlap is enhanced by the ligand breaking planarity forming the boat configuration of the six-membered ring where the metal cation and the carbonyl carbon atom are above the ring determined by the two pyridyl nitrogen atoms and #1 and #4 carbon atoms. By breaking the planarity of the DPK ligand, hydration is facilitated across the carbonyl. This ends the rapid part of the reaction. Following this, one of the hydroxyl groups from the newly formed diol displaces the water in the axial position. This final product then forms the insoluble crystals which is the solid product we have analyzed.

If this is the path followed by the reaction it also answers the question of whether the hydration reaction is intermolecular or intramolecular for in this scenario the water would have to come from the surrounding solution if the hydroxyl group slowly replaces the axial water molecule.

References

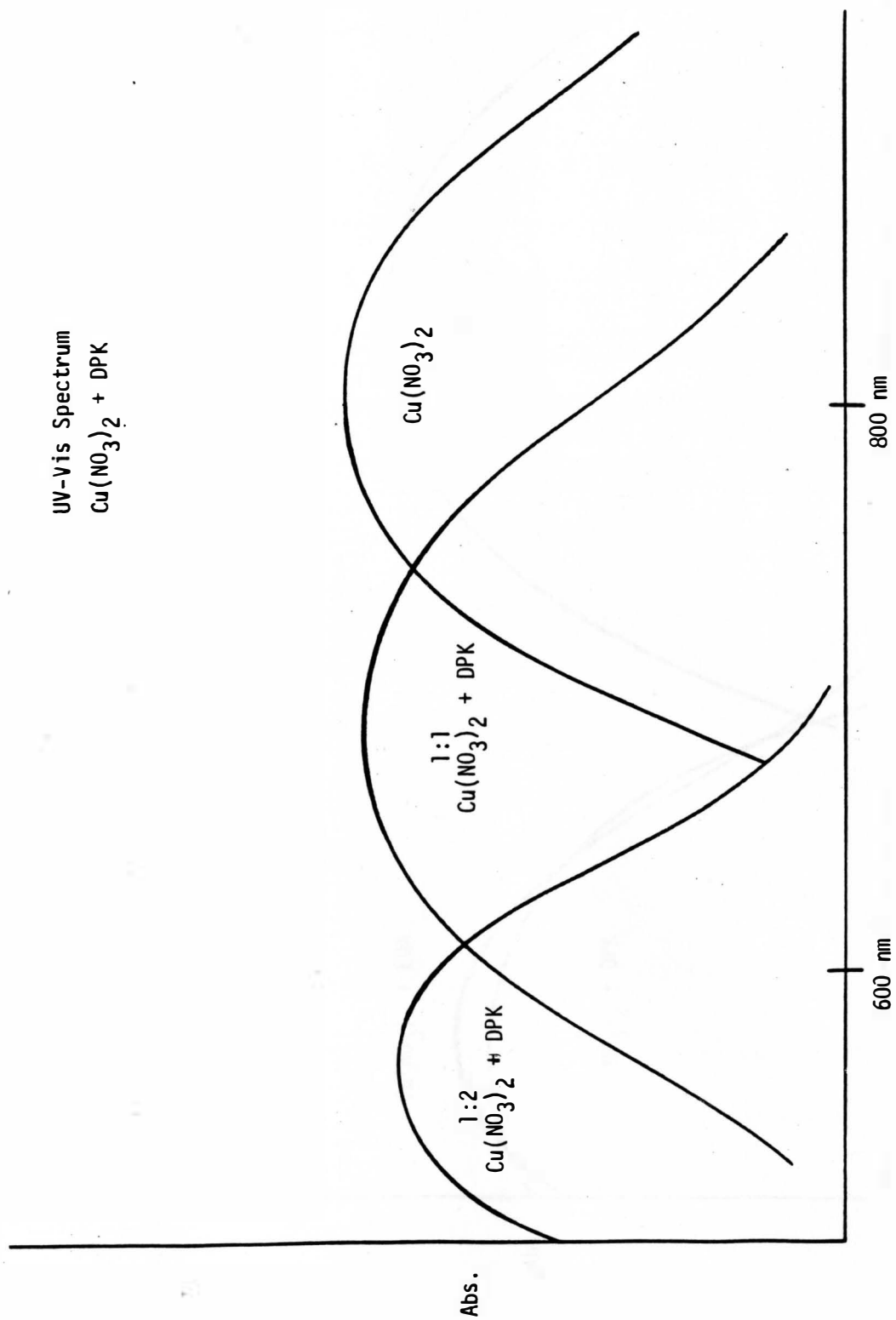
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Appendix 1: UV-Visible Spectra

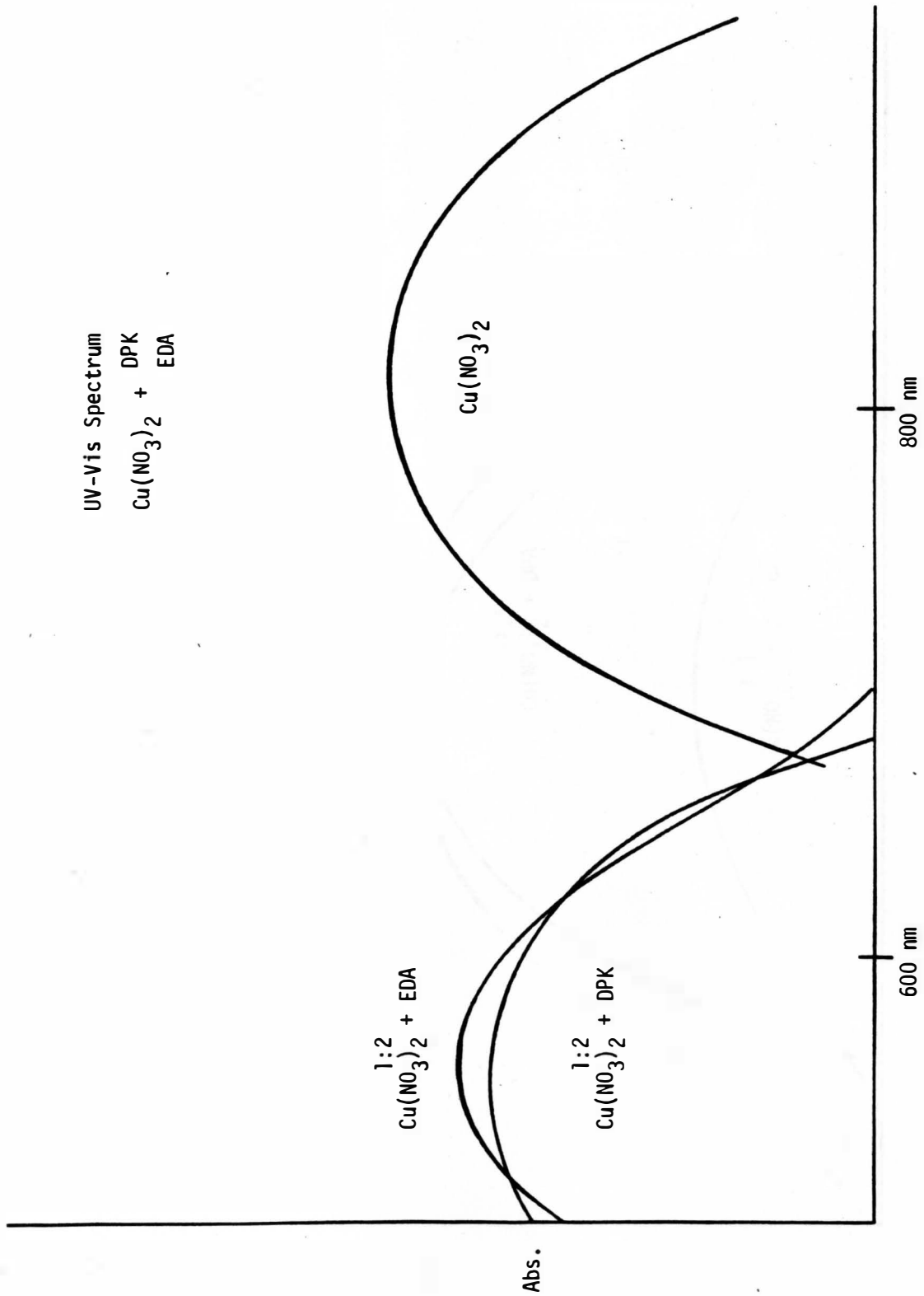
Spectra 1

UV-Vis Spectrum
 $\text{Cu}(\text{NO}_3)_2 + \text{DPK}$

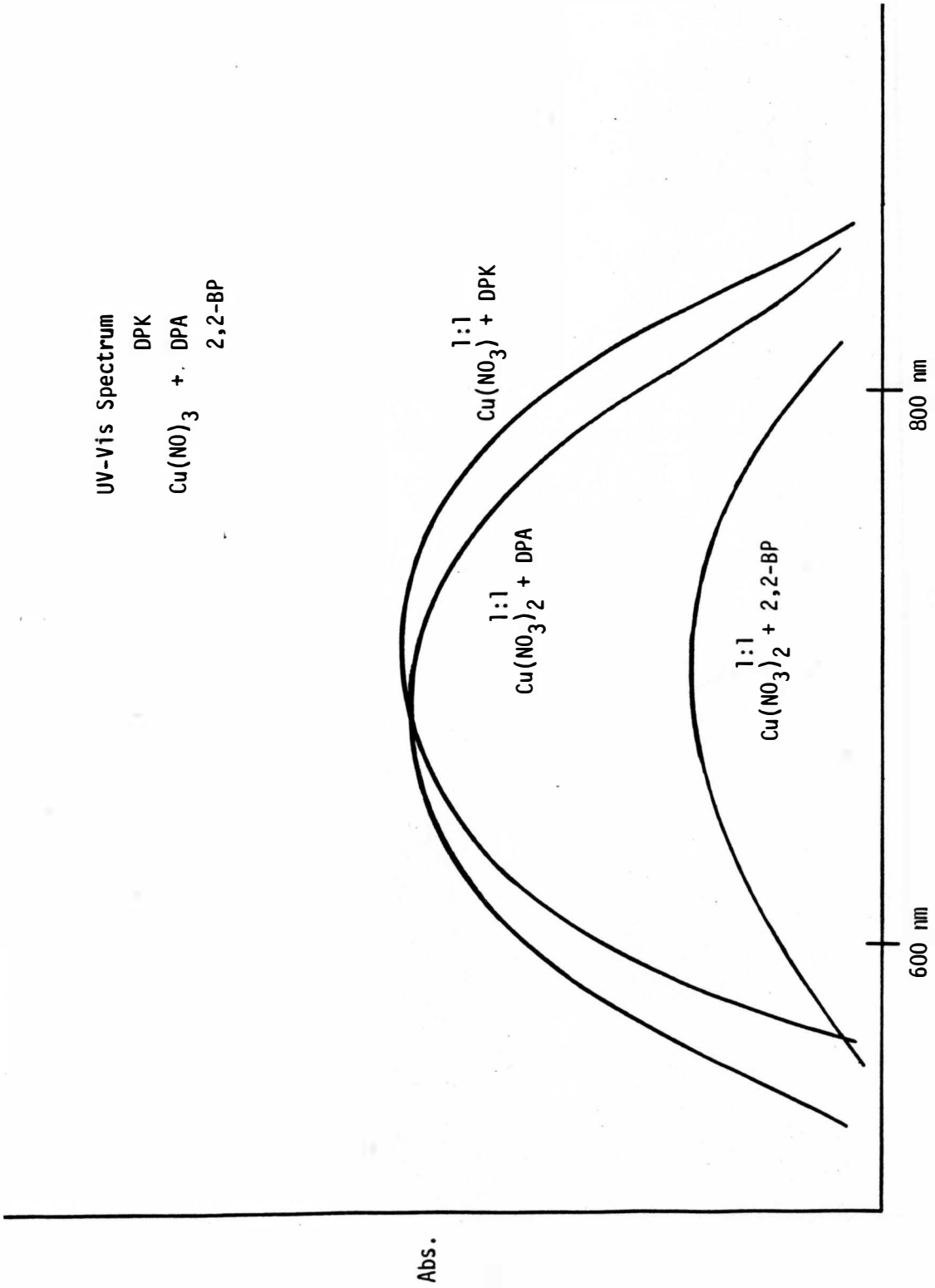


Spectra 2

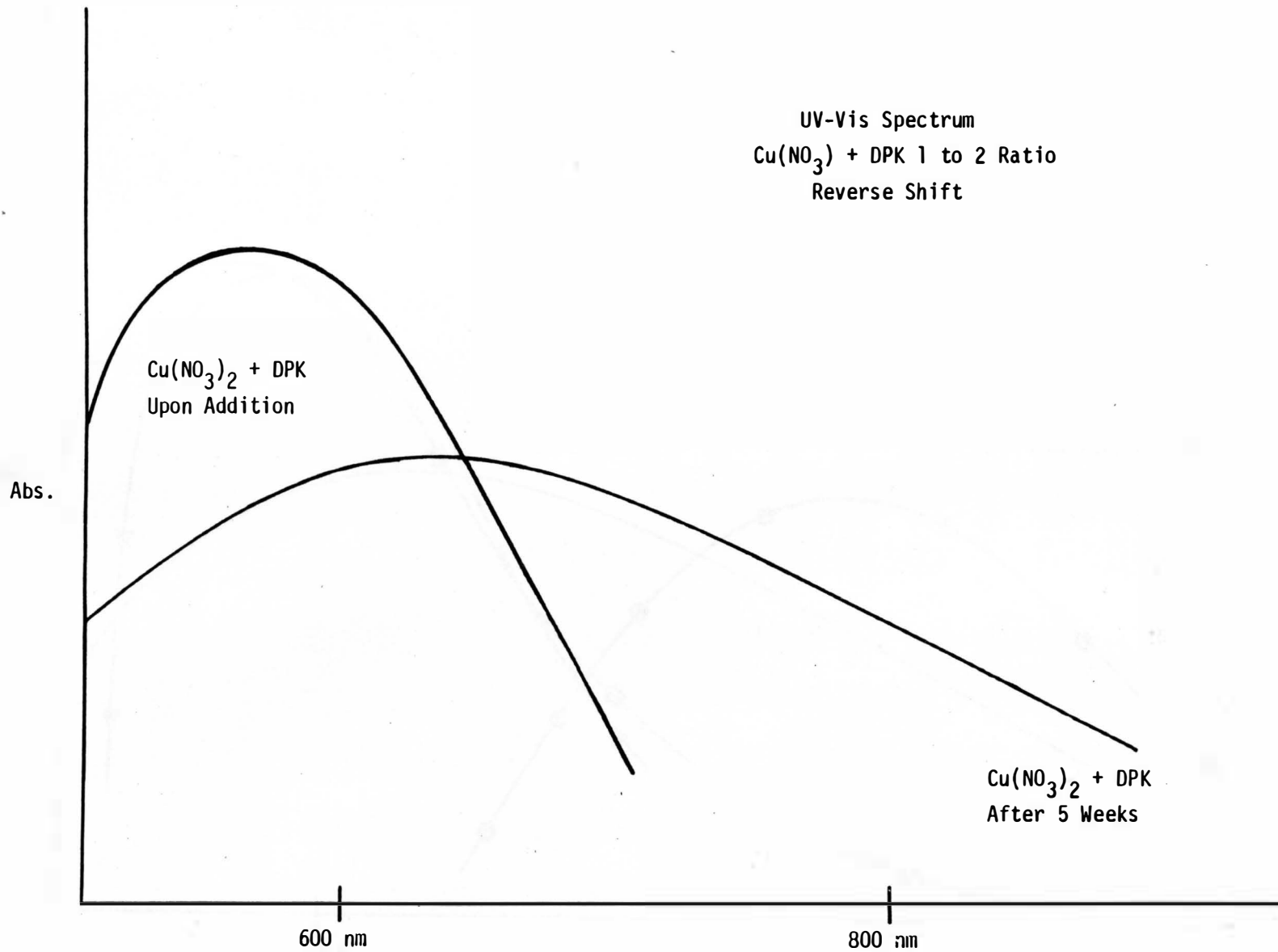
UV-Vis Spectrum
 $\text{Cu}(\text{NO}_3)_2$ + DPK
 $\text{Cu}(\text{NO}_3)_2$ + EDA



Spectra 3

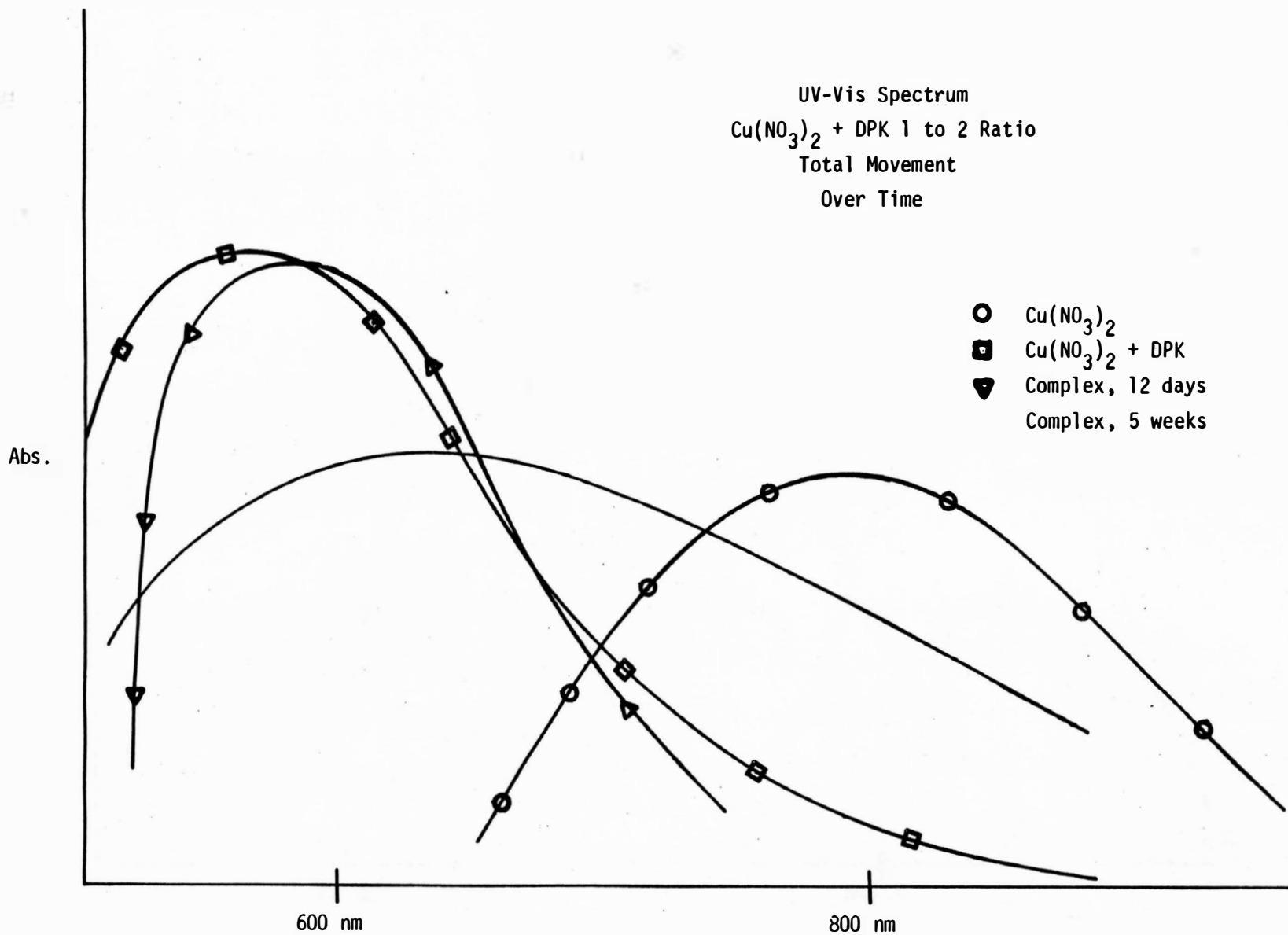


Spectra 4

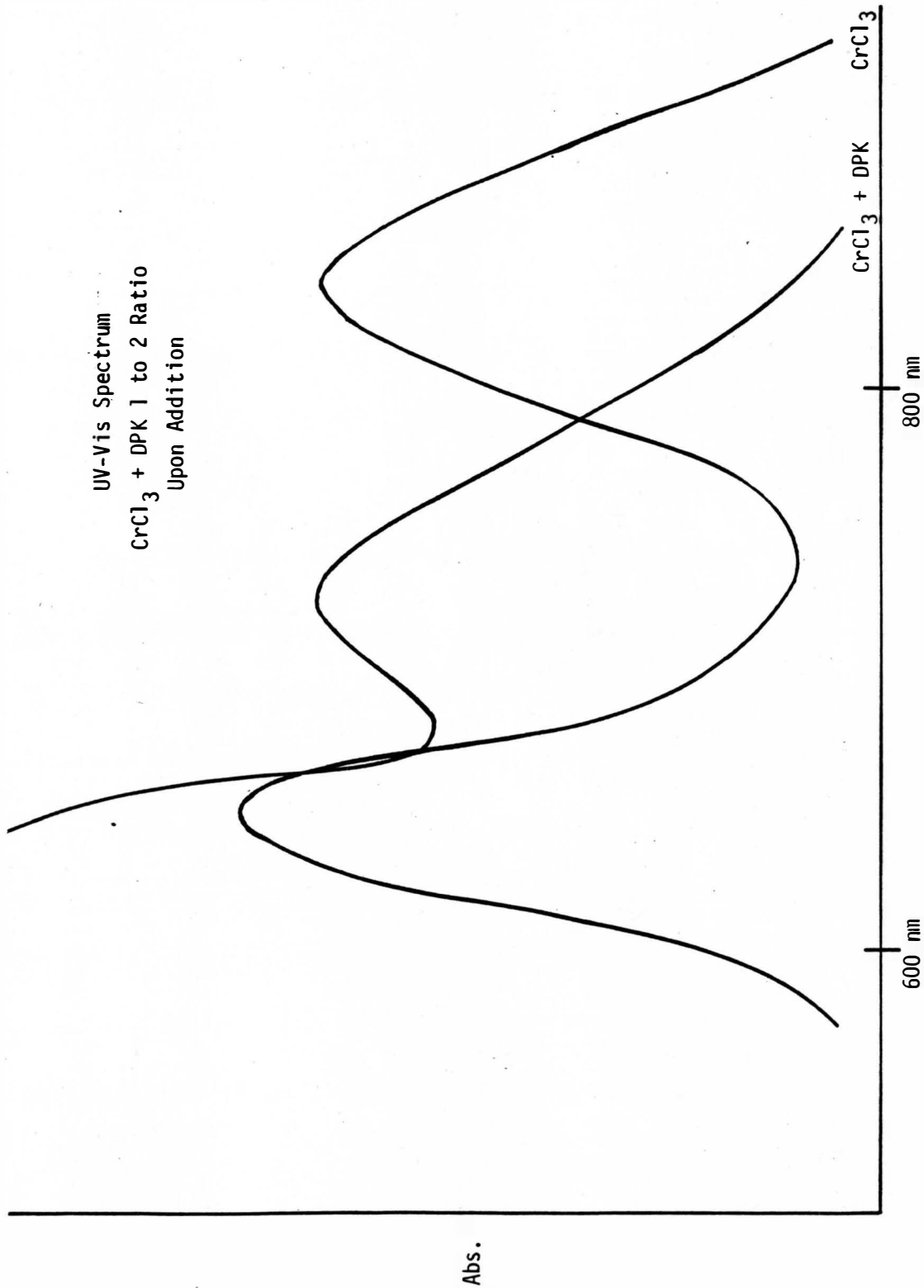


Spectra 5

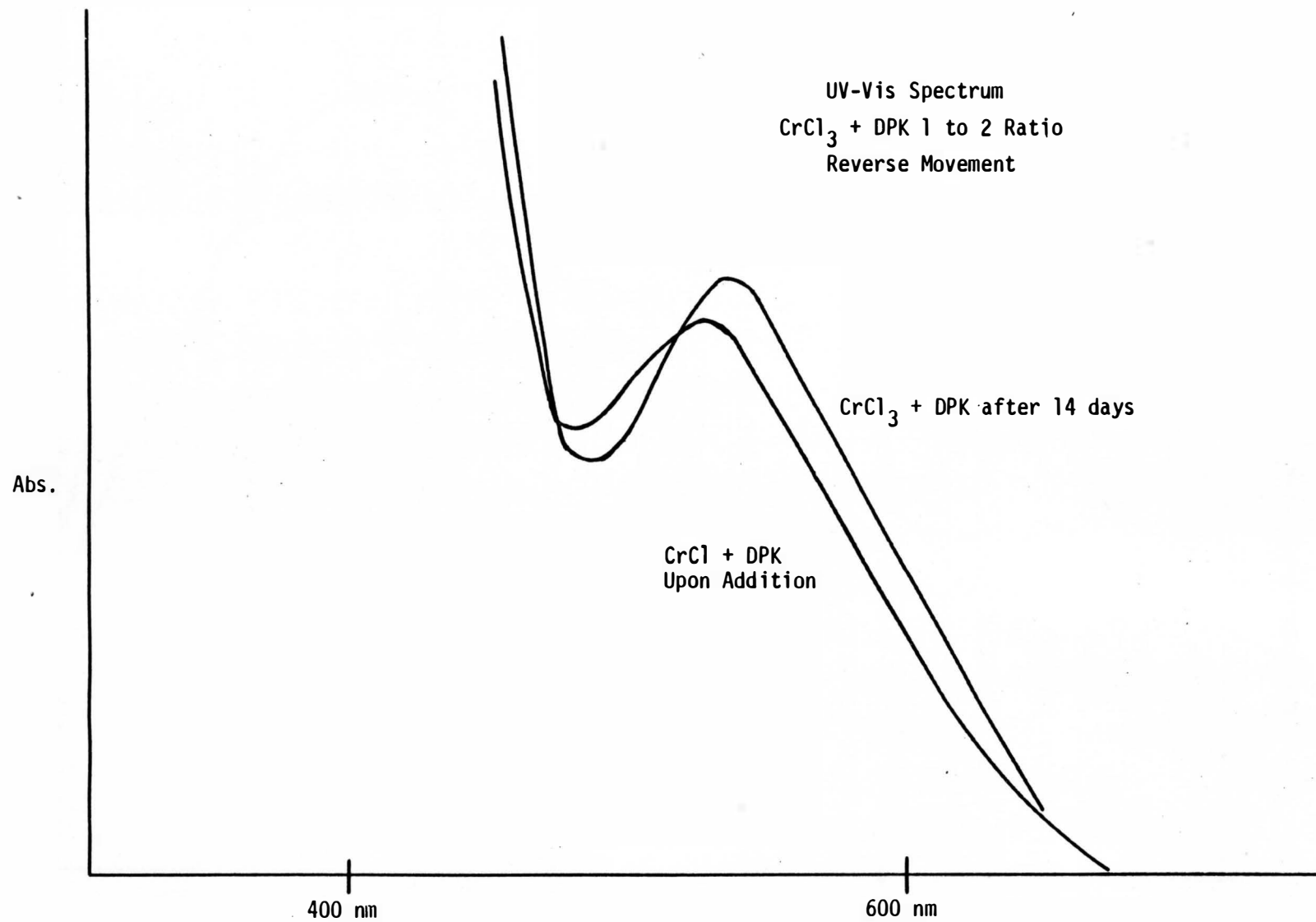
UV-Vis Spectrum
 $\text{Cu}(\text{NO}_3)_2$ + DPK 1 to 2 Ratio
Total Movement
Over Time



Spectra 6

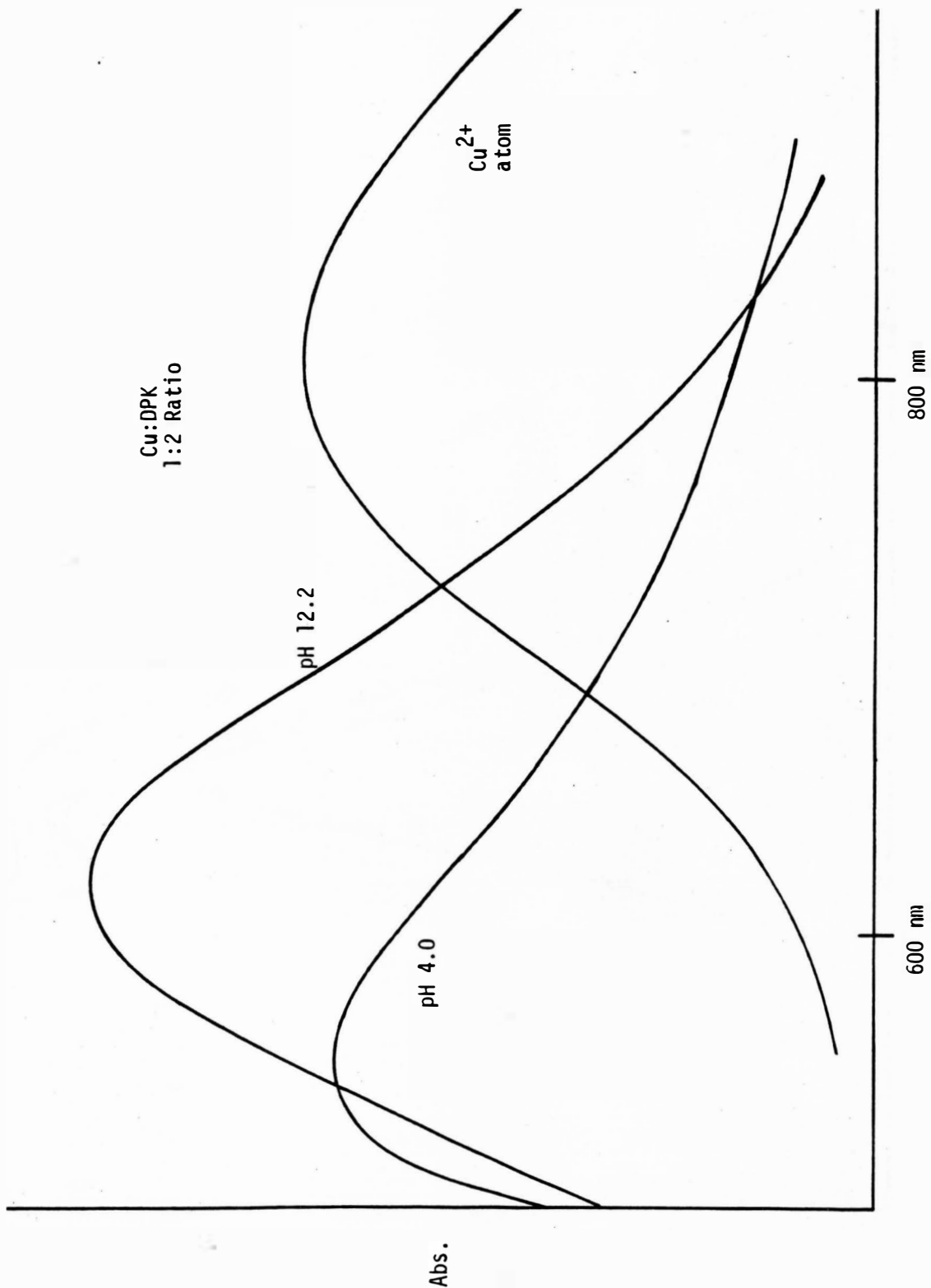


Spectra 7

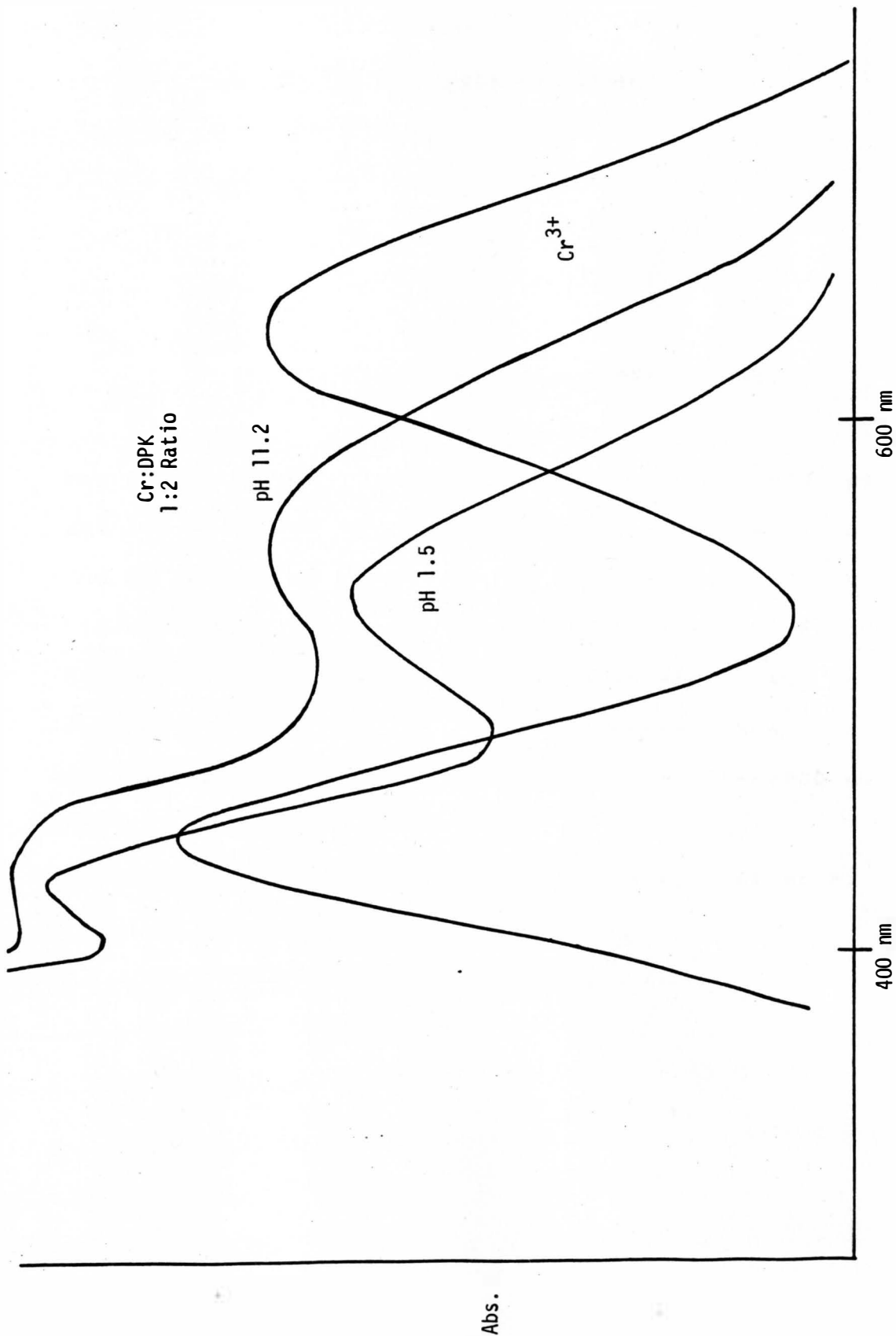


Appendix 2: UV-Visible Spectra (pH Study)

Spectra 8



Spectra 9



Appendix 3: Kodak d19-b Developer

Elon-Hydroquinone (Kodak D-19b)

Water (about 125°F) (52°C)-----	500	ml
Elon (p-Methylaminophenol Sulfate)-----	2.2	g
Sodium Sulfite,anh-----	72	g
Hydroquinone-----	8.8	g
Sodium Carbonate,anh-----	48	g
Potassium Bromide-----	4	g
Cold Water to make-----	1000	ml

Use without dilution. Develop for 5 min. at 65 F.

Appendix 4: d-Spacings of Isolated Solid State

DPK Compounds

Co-3+	Cd-2+	Ru-3+	Fe-3+	CuCl ₂
8.42 S	10.85W	9.07 S	8.89 S	7.89 W
7.56 M	7.63 W	8.67 S	8.50 S	7.25 S
6.53 S	7.08 S	8.19 S	7.86 W	6.14 W
6.0 M	6.56 M	6.76 S	6.66 S	5.70 S
5.56 M	6.22 M	6.22 M	6.15 W	0.12 S
4.97 M	4.90 W	5.83 M	5.80 S	4.48 W
4.42 W	4.36 W	5.54 M	5.49 S	4.26 S
4.25 W	3.98 W	5.10 W	5.07 W	3.98 M
4.07 W	3.80 S	4.49 S	4.46 S	3.77 S
3.79 S	3.46 M	4.09 M	4.11 S	3.60 S
3.55 M	3.35 M	3.97 W	3.92 W	3.37 S
3.19 M	3.13 W	3.53 W	3.52 S	3.12 W
	3.04 W	3.40 W	3.31 S	3.04 S
	2.92 W	2.61 W	2.62 W	2.89 M
	2.62 W		2.35 S	2.78 M
	2.50 W			2.64 M
	2.41 W			2.34 M
	2.32 W			
	2.26 W			
	2.21 W			
	2.12 W			

Ag-1+

8.14 W
7.55 S
6.03 M
5.45 M
4.68 M
4.40 M
4.09 S
3.72 S
3.60 M
3.49 M
3.33 M
3.14 M
2.91 M
2.80 M
2.60 M
2.52 M
2.47 M
2.43 M

CuNO ₄	Mn-2+	Al-3+	Cr-3+
8.93 S	9.61 W	11.33 S	9.46 S
8.50 W	7.76 S	10.59 S	8.80 S
7.97 W	7.28 S	9.88 S	8.27 S
7.28 S	6.92 M	9.36 W	6.73 S
6.89 M	6.56 S	8.76 M	6.30 S
6.44 W	5.77 S	8.04 M	5.72 S
6.17 S	5.22 W	7.40 S	5.45 M
5.96 W	4.97 S	6.61 W	5.20 W
4.69 S	4.80 S	6.09 W	4.91 M
4.51 W	4.32 S	5.70 W	4.77 M
4.19 W	4.17 M	5.40 W	4.60 W
3.98 W	3.96 S	5.16 W	4.22 S
3.88 S	3.86 S	4.96 W	8.00 S
3.75 S	3.73 S	4.77 M	3.99 S
3.61 S	3.61 M	4.50 S	3.87 W
3.59 M	3.53 S	4.32 S	3.58 W
3.54 M	3.46 S	4.06 S	3.48 W
3.49 M	3.33 M	3.95 S	3.31 W
3.32 M	3.01 M	3.90 W	3.20 S
3.24 W	2.90 W	3.82 M	3.11 S
3.09 W	2.84 S	3.72 M	2.87 S
2.99 W	2.77 W	3.55 M	2.73 M
2.89 W	2.63 W	3.45 W	2.65 M
2.82 W	2.57 W	3.36 W	2.58 S
2.73 W	2.43 W	3.22 W	2.49 S
2.61 W	2.34 W	2.97 W	2.30 M
2.40 W	2.29 W		2.24 W
2.21 W	2.26 W		

**Appendix 5: Basic Program for Determination of Bond Angles
and Bond Distances in Crystal Space**

```

10 'Program to calculate distance and angles between atoms in crystal space
20 PRINT"a =";A;"b =";B;"c =";C
30 PRINT"alpha =";AL;"beta =";BE;"gamma =";GA
40 INPUT "To Change Parameters Type y";Y$
50 IF LEFT$(Y$,1)="Y" OR LEFT$(Y$,1)="y" THEN GOTO 390
60 INPUT"Coordinates of Atom 1";X1,Y1,Z1
70 INPUT"Coordinates of Atom 2";X2,Y2,Z2
80 INPUT"Coordinates of Atom 3";X3,Y3,Z3
90 D12=(X2-X1)^2*A^2
100 D12=D12+(Y2-Y1)^2*B^2
110 D12=D12+(Z2-Z1)^2*C^2
120 D12=D12+2*(X2-X1)*(Y2-Y1)*A*B*(COS(GA/57.29578))
130 D12=D12+2*(Z2-Z1)*(X2-X1)*A*C*(COS(BE/57.29578))
140 D12=D12+2*(Y2-Y1)*(Z2-Z1)*B*C*(COS(AL/57.29578))
150 D12=D12^.5
160 D13=(X3-X1)^2*A^2
170 D13=D13+(Y3-Y1)^2*B^2
180 D13=D13+(Z3-Z1)^2*C^2
190 D13=D13+2*(X3-X1)*(Y3-Y1)*A*B*(COS(GA/57.29578))
200 D13=D13+2*(Z3-Z1)*(X3-X1)*A*C*(COS(BE/57.29578))
210 D13=D13+2*(Y3-Y1)*(Z3-Z1)*B*C*(COS(AL/57.29578))
220 D13=D13^.5
230 Q=(X2-X1)*(X3-X1)*A^2
240 Q=Q+(Y2-Y1)*(Y3-Y1)*B^2
250 Q=Q+(Z2-Z1)*(Z3-Z1)*C^2
260 Q=Q+(((X2-X1)*(Y3-Y1))+((Y2-Y1)*(X3-X1)))*A*B*(COS(GA/57.29578))
270 Q=Q+(((Z2-Z1)*(X3-X1))+((X2-X1)*(Z3-Z1)))*A*C*(COS(BE/57.29578))
280 Q=Q+(((Y2-Y1)*(Z3-Z1))+((Z2-Z1)*(Y3-Y1)))*B*C*(COS(AL/57.29578))
290 S=Q/(D12*D13)
300 SI=SQR(1-S^2)
310 T=SI/S
320 T=ATN(T)*57.29578
330 IF S<0 AND SI>0 THEN T=T+180
340 PRINT"Distance 1 to 2 =";D12
350 PRINT"Distance 1 to 3 =";D13
360 PRINT"Cos of the Angle =";S
370 PRINT"The Angle is = ";T
380 GOTO 60
390 INPUT"a = ";A
400 INPUT "b = ";B
410 INPUT "c = ";C
420 IF S<0 AND SI>0 THEN T = T +180
430 INPUT "alpha = ";AL
440 INPUT "beta = ";BE
450 INPUT "gamma = ";GA
460 CLS: PRINT A,B,C
470 PRINT AL,BE,GA
480 INPUT "to continue type y";Y$
490 IF LEFT$(Y$,1)="Y" OR LEFT$(Y$,1)="y" THEN 60 ELSE GOTO 390

```

Appendix 6: Basic Program for Calculating Aromatic Hydrogen

Positions in Crystal Space

```

10 ' PROGRAM TO CALC HYDROGEN ATOM POSITIONS FOR AROMATIC COMPOUNDS  AROH
20 CLS:INPUT "BOND LENGTH ";BOND
30 A = 8.084
40 B = 9.979
50 C = 20.696
60 AL = 90!
70 BE = 90.66001
80 GA = 90!
90 RAD = 57.2957795#
100 AL = AL/RAD
110 BE = BE/RAD
120 GA = GA/RAD
130 COSAL = COS(AL)
140 SINAL = SIN(AL)
150 COSBE = COS(BE)
160 SINBE = SIN(BE)
170 COSGA = COS(GA)
180 SINGA = SIN(GA)
190 ABCG = A*B*COSGA
200 ACCB = A*C*COSBE
210 BCCA = B*C*COSAL
220 V = 1!-COSAL*COSAL - COSBE*COSBE - COSGA*COSGA + 2!*COSAL*COSBE*COSGA
230 V = SQR(V)
240 V = A*B*C*V
250 AS = B*C*SINAL/V
260 BS = A*C*SINBE/V
270 CS = A*B*SINGA/V
280 CALS = (COSBE*COSGA-COSAL)/(SINBE*SINGA)
290 CBES = (COSAL*COSGA-COSBE)/(SINAL*SINGA)
300 CGAS = (COSAL*COSBE-COSGA)/(SINAL*SINBE)
310 PRINT "ENTER THE SIX CARBON ATOMS IN SEQUENCE (X,Y,Z) "
320 FOR I=1 TO 6
330 INPUT X(I),Y(I),Z(I)
340 NEXT I
350 CLS:PRINT "TO CHANGE AN ATOM TYPE ITS NUMBER ELSE TYPE 0"
360 FOR I=1 TO 6
370 PRINT I,X(I) TAB(25) Y(I) TAB(35) Z(I)
380 NEXT I
390 INPUT K
400 IF K = 0 THEN 450
410 INPUT "ENTER NEW COORDINATES (X,Y,Z ";X(K),Y(K),Z(K)
420 GOTO 350
450 A1(1)=0!:A1(2)=0:A1(3)=0
460 A2(1)=X(5)-X(2)+X(4)-X(3)+X(6)-X(1)
470 A2(2)=Y(5)-Y(2)+Y(4)-Y(3)+Y(6)-Y(1)
480 A2(3)=Z(5)-Z(2)+Z(4)-Z(3)+Z(6)-Z(1)
490 GOSUB 1200
500 RATIO=BOND/D
510 HX=X(2)-A2(1)*RATIO
520 HY=Y(2)-A2(2)*RATIO
530 HZ=Z(2)-A2(3)*RATIO
535 LPRINT "
540 LPRINT "FOR ";X(2);" ";Y(2);" ";Z(2);" "X" "Y" "Z"
";HX;" ";HY;" ";HZ
560 A2(1)=X(6)-X(3)+X(5)-X(4)+X(1)-X(2)
570 A2(2)=Y(6)-Y(3)+Y(5)-Y(4)+Y(1)-Y(2)
580 A2(3)=Z(6)-Z(3)+Z(5)-Z(4)+Z(1)-Z(2)

```

```

590 GOSUB 1200
600 RATIO=BOND/D
610 HX=X(3)-A2(1)*RATIO
620 HY=Y(3)-A2(2)*RATIO
630 HZ=Z(3)-A2(3)*RATIO
640 LPRINT "FOR ";X(3);" ";Y(3);" ";Z(3);" ";HX;" ";HY;" ";HZ
660 A2(1)=X(1)-X(4)+X(6)-X(5)+X(2)-X(3)
670 A2(2)=Y(1)-Y(4)+Y(6)-Y(5)+Y(2)-Y(3)
680 A2(3)=Z(1)-Z(4)+Z(6)-Z(5)+Z(2)-Z(3)
690 GOSUB 1200
700 RATIO=BOND/D
710 HX=X(4)-A2(1)*RATIO
720 HY=Y(4)-A2(2)*RATIO
730 HZ=Z(4)-A2(3)*RATIO
740 LPRINT "FOR ";X(4);" ";Y(4);" ";Z(4);" ";HX;" ";HY;" ";HZ
760 A2(1)=X(2)-X(5)+X(1)-X(6)+X(3)-X(4)
770 A2(2)=Y(2)-Y(5)+Y(1)-Y(6)+Y(3)-Y(4)
780 A2(3)=Z(2)-Z(5)+Z(1)-Z(6)+Z(3)-Z(4)
790 GOSUB 1200
800 RATIO=BOND/D
810 HX=X(5)-A2(1)*RATIO
820 HY=Y(5)-A2(2)*RATIO
830 HZ=Z(5)-A2(3)*RATIO
840 LPRINT "FOR ";X(5);" ";Y(5);" ";Z(5);" ";HX;" ";HY;" ";HZ
860 A2(1)=X(3)-X(6)+X(2)-X(1)+X(4)-X(5)
870 A2(2)=Y(3)-Y(6)+Y(2)-Y(1)+Y(4)-Y(5)
880 A2(3)=Z(3)-Z(6)+Z(2)-Z(1)+Z(4)-Z(5)
890 GOSUB 1200
900 RATIO=BOND/D
910 HX=X(6)-A2(1)*RATIO
920 HY=Y(6)-A2(2)*RATIO
930 HZ=Z(6)-A2(3)*RATIO
940 LPRINT "FOR ";X(6);" ";Y(6);" ";Z(6);" ";HX;" ";HY;" ";HZ
950 INPUT "FOR ADDITIONAL GROUPS TYPE Y ";Y$
960 IF LEFT$(Y$,1)="Y" OR LEFT$(Y$,1)="y" THEN 310 ELSE END
1200 DX=A1(1)-A2(1)
1210 DY=A1(2)-A2(2)
1220 DZ=A1(3)-A2(3)
1230 IF DX < -.5 THEN DX = DX +1!
1240 IF DX > .5 THEN DX = DX -1!
1250 IF DY < -.5 THEN DY = DY +1!
1260 IF DY > .5 THEN DY = DY -1!
1270 IF DZ < -.5 THEN DZ = DZ +1!
1280 IF DZ > .5 THEN DZ = DZ -1!
1290 D = DX*DX*A*A+DY*DY*B*B+DZ*DZ*C*C+2!*DX*DY*ABCG+2!*DX*DZ*ACCB+2!*DY*DZ*BCCA

1300 D = SQR(D)
1330 RETURN

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