

second molecule of methylamine then enters the coordination sphere of the tungsten atom in order to preserve its 18-electron configuration.

Complex II contains both type 2 and type 3 carbonyl functions. The reactions of II with primary amines invariably proceed to give $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$ and amide. Unlike the reactions of I, the site of attack in II appears to have shifted from the carbon monoxide ligands to the carbon atom of the acetyl group. Subsequent proton transfer to the tungsten atom and cleavage of the metal acyl carbon bond result in formation of the tungsten hydride and the amide.

The reactions of I demonstrate the known reactivity of carbon monoxide ligands toward amines² but also indicate that they are more reactive than the organic carbonyl function, 1, also present in this complex. The reactions of II indicate an even higher reactivity of the tungsten-acetyl group. While all the reactions evidently proceed via amine attack on the carbon atoms of the carbonyl functions, it is also clear that bond-making and -breaking processes about the tungsten atom must also play a key role in defining the ultimate reaction path. Presently, however, we are unable to ascertain the relative importance of these latter processes in determining the course of the reactions.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. I, 60911-81-1; II, 64666-36-0; III, 64666-37-1; $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)(\text{CONHCH}_3)$, 64666-38-2; $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{CNCH}_3)(\text{CONHCH}_3)$, 64666-39-3; $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$, 12128-26-6; NH_2CH_3 , 74-89-5.

Supplementary Material Available: Observed and calculated structure factor amplitudes, selected intermolecular bond distances, molecular diagram of molecule 2, a crystal-packing diagram, and least-squares planes (18 pages). Ordering information is given on any current masthead page.

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Bidentate Chelate Compounds. 1. Pseudotetrahedral Copper(II) Complexes of Heterocyclic Secondary Amines

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Received May 16, 1977

Bis(heterocyclic secondary amine)copper(II) complexes of general formula $\text{Cu}(\text{HL})_2(\text{ClO}_4)_2$, where HL = 2-pyridyl-2'-pyrimidylamine (HPPA), 2-pyridyl-2'-thiazolylamine (HPTA), 2-pyridyl-2'-(4'-methylthiazolyl)amine (HMPTA), and 2-(6-methylpyridyl)-2'-(4'-methylthiazolyl)amine (HDMPTA), have been prepared and characterized. Some of the complexes can be deprotonated to neutral complexes of general formula $\text{M}(\text{L})_2$.² Spectral and magnetic data indicate a pseudotetrahedral geometry in the solid state for the copper(II) complexes; solution data indicate solvation of the protonated copper(II) complexes to species with coordination number six while the deprotonated complexes retain their coordination number of four. The d-d transitions in the solid-state spectra have been interpreted with the aid of an energy level diagram constructed for distortion of a tetrahedral CuN_4 chromophore and calibrated using the known spectrum of $\text{Cu}(\text{HDP A})_2(\text{ClO}_4)_2$.

Introduction

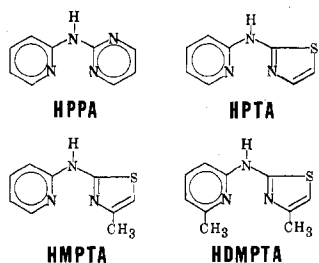
The ability of 2,2'-dipyridylamine (HDP A) to coordinate as a bidentate ligand to transition metal cations, particularly to copper(II), has been extensively investigated.³⁻⁶ The two

nitrogen atoms act as the electron-pair donors in the majority of the compounds, although in some instances the bridging amine nitrogen appears to have donor properties.⁷ A coordination number of four can be established when the ligand

to metal ratio is 2:1. These compounds are interesting not only because the hydrogen atoms of the bridging amino groups can be removed, rendering the complex ions neutral, but also because steric interactions prevent the ligands from being coplanar. This results in a pseudotetrahedral geometry for the CuN_4 chromophore of $\text{Cu}(\text{HDP A})_2^{2+8}$ and in a square-planar geometry for the PdN_4 chromophore in $\text{Pd}(\text{DPA})_2$, but with buckling of the ligands such that the interaction between adjacent pyridine rings is alleviated.⁹

In conjunction with our interest in the circular dichroism of chiral molecules of various geometries, we prepared several bidentate chelating agents that are related to HDP A by the replacement of one of the pyridine rings by another nitrogen heterocycle. In addition, methyl groups have been substituted for certain hydrogen atoms to increase steric interactions between contiguous rings.

Specifically, in this paper we report the preparation and properties of some copper(II) complexes of the bidentate ligands 2-pyridyl-2'-pyrimidylamine (HPPA), 2-pyridyl-2'-



thiazolylamine (HPTA), 2-pyridyl-2'-(4'-methylthiazolyl)amine (HMPTA), and 2-(6-methylpyridyl)-2'-(4'-methylthiazolyl)amine (HDMPTA).

Experimental Section

Analytical and Physical Measurements. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Oxygen percentages were obtained by difference.

A Cary 14 recording spectrophotometer was used to record the electronic spectra of all solutions with three exceptions. The spectra of HPPA in tetrachloromethane, dichloromethane, and methanol were taken on a GCA McPherson single beam spectrophotometer with digital output. Solid-state spectra were obtained from the Cary 14 modified with a Varian Model 1411 diffuse reflectance accessory.

Magnetic susceptibilities were obtained by the Faraday method in a helium atmosphere at room temperature.

The mass spectra of the ligands were measured on a DuPont 21-490 instrument. The derived experimental values of the molecular weights are followed by the theoretical value in parentheses.

Conductivities were measured in dimethylformamide at 0 °C using a YSI Model 31 conductivity bridge.

Molar conductivities and magnetic moments of the metal complexes are given in Table I.

Reagents and Syntheses. Copper(II) perchlorate hexahydrate was purchased from G. Fredric Smith Chemical Co. The compounds 2-amino-6-methylpyridine, 2-aminopyridine, 2-aminopyrimidine, chloroacetone, and 2-bromopyridine were purchased from Eastman Kodak Co., and 2,2'-dipyridylamine was purchased from Aldrich Chemical Co. The compound 2-chloro-4-methylthiazole was prepared by the method of Tcherniac.¹⁰

$\text{Cu}(\text{HDP A})_2(\text{ClO}_4)_2$ was prepared by Black's method¹¹ and deprotonated to $\text{Cu}(\text{DPA})_2$ by the technique of Hurley and Robinson.⁷

HPPA, HPTA, and the sodium salts of the various heterocyclic amines were prepared according to the methods of Detweiler and Amstutz¹² in their reported yields.

Preparation of HMPTA. Anhydrous xylene (50 mL) was added to the dried crude sodium salt of 2-aminopyridine (0.11 mol, theoretical yield) in a 1-L, three-necked round-bottom flask. The mixture was refluxed for 1 h at 140 to 150 °C with a calcium chloride drying tube fitted on the condenser. The flask was cooled to room temperature, and a mixture of 2-chloro-4-methylthiazole in anhydrous xylene (0.1

Table I. Physical Data for Coordination Compounds

Compound	Color	Molar conductivity, ^a $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$	$\mu_{\text{eff}},^b$ μ_{B}
$\text{Cu}(\text{HDP A})_2(\text{ClO}_4)_2$	Purple	104.0	2.06
$\text{Cu}(\text{HPP A})_2(\text{ClO}_4)_2$	Purple	105.0	1.82
$\text{Cu}(\text{HPT A})_2(\text{ClO}_4)_2$	Purple	101.0	1.96
$\text{Cu}(\text{HMPT A})_2 \cdot (\text{ClO}_4)_2$	Royal blue	97.5	1.86
$\text{Cu}(\text{HDMPT A})_2 \cdot (\text{ClO}_4)_2$	Purple ^c	90.9	1.61
$\text{Cu}(\text{DPA})_2$	Blue-green	3.13	1.70
$\text{Cu}(\text{PTA})_2$	Blue	1.81	1.76
$\text{Cu}(\text{MPTA})_2$	Green	1.06	2.68
1:1 electrolyte		37.4	
1:2 electrolyte		76.6	

^a Measured in DMF at 0 °C. ^b Measured at room temperature. ^c Freshly precipitated.

mol in 50 mL) was slowly added with thorough stirring. The reaction mixture was refluxed for 18 h, cooled, and thoroughly extracted with several portions of 1:1 concentrated hydrochloric acid-water solution. The dark brown extract was chilled and made slightly basic with aqueous sodium hydroxide solution (48% by weight). The resulting tan precipitate (6.08 g, 31.8% yield) was dissolved in hot 95% ethanol and treated with activated charcoal. The mixture was filtered and cooled, precipitating tan crystals. Purification by vacuum sublimation resulted in a white product (mp 159–161 °C). Anal. Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{S}$: C, 56.5; H, 4.7; N, 22.0; S, 16.8; mol wt, 191.25. Found: C, 56.6; H, 4.7; N, 21.9; S, 16.8; mol wt, 191.

Preparation of HDMPTA. The sodium salt of 2-amino-6-methylpyridine (0.3 mol) was prepared and treated as above using 50 mL of anhydrous xylene. Then 2-chloro-4-methylthiazole (0.3 mol) in anhydrous xylene (20 mL) was slowly added, more anhydrous xylene was added (30 mL), and the flask was placed in an oil bath (140–150 °C). An exothermic reaction was observed, and the dark gray color of the reaction mixture turned red-brown. After refluxing the reaction mixture for 20 h and cooling, it was extracted thoroughly with a 1:1 concentrated hydrochloric acid-water solution. The chilled extract was made strongly basic with aqueous sodium hydroxide solution. The resulting brown solid was treated with activated charcoal in a 95% ethanolic solution. The mixture was filtered, and the volume of the filtrate was reduced to one-half. After cooling and adding water, a tan solid (23.1 g, 37.5% yield) precipitated. The solid was collected and air-dried. Vacuum sublimation was used to obtain a pure white sample (mp 135–137 °C). Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}$: C, 58.5; H, 5.4; N, 20.5; S, 15.6; mol wt, 205.28. Found: C, 58.3; H, 5.3; N, 20.3; S, 15.7; mol wt, 205.

$\text{Cu}(\text{HPP A})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{HPT A})_2(\text{ClO}_4)_2$. Hot ethanolic solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the respective ligand (1 mol of metal salt:2 mol of ligand) were mixed, resulting in the precipitation of a purple solid. The solid was filtered and air-dried. Recrystallization from hot water gave purple twinned blades of the pure compounds. Anal. Calcd for $\text{CuC}_{18}\text{H}_{16}\text{N}_8\text{Cl}_2\text{O}_8$: Cu, 10.47; C, 35.62; H, 2.66; N, 18.47; Cl, 11.69. Found: Cu, 10.48; C, 35.67; H, 2.40; N, 18.25; Cl, 11.87. Calcd for $\text{CuC}_{16}\text{H}_{14}\text{N}_6\text{S}_2\text{Cl}_2\text{O}_8$: Cu, 10.30; C, 31.15; H, 2.29; N, 13.63; S, 10.39; Cl, 11.49. Found: Cu, 10.60; C, 30.90; H, 2.20; N, 13.85; S, 10.08; Cl, 11.23.

$\text{Cu}(\text{HMPT A})_2(\text{ClO}_4)_2$. Hot ethanolic solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (one molar proportion) and HMPTA (two molar proportions) were prepared and mixed. The deep red solution that formed quickly turned green. After chilling the solution in an ice-water bath, it was filtered into an equivalent volume of ethyl ether, also chilled to 0 °C. A deep blue solid formed upon standing. The pure compound was collected, washed with several portions of cold ethyl ether, and air-dried. Anal. Calcd for $\text{CuC}_{18}\text{H}_{18}\text{N}_8\text{S}_2\text{Cl}_2\text{O}_8$: Cu, 9.85; C, 33.52; H, 2.81; N, 13.03; S, 9.94; Cl, 10.99. Found: Cu, 9.71; C, 33.49; H, 2.70; N, 13.12; S, 10.00; Cl, 10.81.

$\text{Cu}(\text{HDMPT A})_2(\text{ClO}_4)_2$. Solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and HDMPTA were prepared by dissolving each in a minimum amount of ethyl ether (1:2 molar proportions, respectively). The ligand solution was filtered into a conical flask and chilled in an ice-water bath. The

Table II. Electronic Spectra of the Ligands

Ligand	Solvent (dielectric constant)			
	CCl ₄ (2.23)	CHCl ₃ (4.70)	CH ₂ Cl ₂ (8.9)	CH ₃ OH (32.6)
HPPA	34.6 ^a (11 200) ^b	27.2 ^a (609)	35.2 (13 500)	34.8 (13 900)
	37.0 (14 900)	31.7 (7480)	37.7 (20 200)	38.1 (20 200)
HPTA	32.5 ^a (8960)	32.5 (12 000)	32.6 (9680)	32.6 (8810)
	35.5 (11 200)	36.3 (11 900)	36.2 (13 300)	36.2 (11 900)
HMPTA	32.1 (9480)	32.3 (8210)	32.4 (9090)	32.4 (9120)
	34.9 (11 100)	35.6 (9360)	35.9 (10 600)	35.9 (10 600)
HDMPTA	31.9 (9880)	32.0 (10 200)	32.2 (10 800)	32.0 (10 100)
	35.2 (10 400)	35.5 (10 700)	35.5 (11 300)	35.9 (10 500)
HDPA	32.2 (13 600) ^c			31.8 (16 000) ^d
	36.4 (16 900)			37.7 (25 000)

^a Shoulder. ^b Band maxima or shoulders in units of 10^3 cm^{-1} , followed by the molar extinction coefficient in parentheses. ^c In heptane. ^d In ethanol.

Cu(ClO₄)₂·6H₂O solution was then filtered into the cold ligand solution, precipitating a purple solid. The mixture was stirred for another 5 min while being chilled. The complex salt was filtered, washed with several portions of ethyl ether, and dried in a vacuum desiccator. This compound was observed to decompose upon exposure to the atmosphere. Anal. Calcd for CuC₂₀H₁₂N₆S₂Cl₂O₈: Cu, 9.44; C, 35.69; H, 3.29; N, 12.49; S, 9.53; Cl, 10.54. Found: Cu, 9.33; C, 35.74; H, 3.31; N, 12.52; S, 9.55; Cl, 10.44.

Cu(PTA)₂. To a warm aqueous solution of Cu(HPTA)₂(ClO₄)₂ was added 10% KOH solution (1:2 molar proportions, respectively). A blue-green solid immediately precipitated. The mixture was filtered, and the compound was recrystallized from benzene. Anal. Calcd for CuC₁₆H₁₂N₆S₂: Cu, 15.27; C, 46.19; H, 2.91; N, 20.21; S, 15.41. Found: Cu, 15.47; C, 46.24; H, 2.70; N, 20.02; S, 15.24.

Cu(MPTA)₂. Solid Cu(HMPTA)₂(ClO₄)₂ was suspended in water, and the mixture was chilled in an ice-water bath. Ethanol was added to dissolve the perchlorate salt. A 0.5 molar NaOH solution (2 mol of NaOH:1 mol of salt) was added to the cold red solution. The mixture was stirred and filtered. The deep green solid was thoroughly washed with several portions of cold water and air-dried. The residue was extracted with several volumes of ethyl ether, and the extracts were combined and concentrated. While being chilled in a dry ice-acetone bath, small green crystals of the pure compound formed. These crystals were filtered and dried under vacuum. Anal. Calcd for CuC₁₈H₁₆N₆S₂: Cu, 14.31; C, 48.69; H, 3.63; N, 18.93; S, 14.44. Found: Cu, 14.08; C, 48.56; H, 3.70; N, 18.74; S, 14.34.

Results and Discussion

1. Ligands. The four ligands used in this study are white sublimable solids. All are generally insoluble in water, but they dissolve with ease in organic solvents. Table II shows the band maxima and molar extinction coefficients for all four ligands in four organic solvents of different polarity. The spectrum of HDPA^{4,13} is included for comparison. With one exception, each spectrum consists of two bands. In the spectra of HPPA, there are low energy bands at $35 \times 10^3 \text{ cm}^{-1}$ with more intense bands generally at $38 \times 10^3 \text{ cm}^{-1}$. The low energy bands of HPTA, HMPTA, and HDMPTA occur at approximately $32 \times 10^3 \text{ cm}^{-1}$, the other bands ranging from 35 to $36 \times 10^3 \text{ cm}^{-1}$. The spectra are very similar to the spectrum of HDPA measured in heptane.

A spectral feature common to the four ligands is a blue shift for the two bands as the dipole moment of the solvent increases. This shift can be attributed to better stabilization of the ground states than the excited states by electrostatic interaction with the solvent and is characteristic of $n-\pi^*$ transitions. The band intensities, however, are much greater than are usually observed in such transitions and can be rationalized as follows.

As a result of the pyramidal nature of the amine nitrogen, the lone pair is able to interact with the heterocyclic ring π orbitals through its p-orbital component. There are no pure $n-\pi^*$ transitions for this lone pair. The transitions have some $\pi-\pi^*$ character and probably correspond to charge transfer from the amino nitrogen into the rings. Transitions corre-

sponding to the $n-\pi^*$ transitions involving the heterocyclic ring nitrogens were not observed.

The one exception to the general features of these spectra is observed in the spectrum of HPPA in chloroform. A shoulder at $27.2 \times 10^3 \text{ cm}^{-1}$ (ϵ 609) and a maximum at $31.7 \times 10^3 \text{ cm}^{-1}$ (ϵ 7480) are observed in addition to the other bands. Examination of all the spectra indicates unresolved components. These components are probably due both to vibrational progressions and to overlapping transitions. At present, we can offer no explanation for the origin of the bands at 27.2 and $31.7 \times 10^3 \text{ cm}^{-1}$ except to say that they are not vibrational progressions since the splittings are on the order of $4 \times 10^3 \text{ cm}^{-1}$.

It has been reported¹³ that the spectrum of HDPA in heptane does not obey Beer's law, although a more recent study¹⁴ shows that it is obeyed in *N,N*-dimethylformamide over the concentration range 10^{-5} – 10^{-6} M. This same study also showed that the molecular weight of HDPA in 10^{-2} M methanol, benzene, and carbon tetrachloride solutions corresponds to the monomer, despite the evidence for hydrogen-bonded dimers in both solution¹⁵ and the solid state.¹⁶ Beer's law plots for the two highest energy bands of HPPA, HPTA, HMPTA, and HDMPTA in carbon tetrachloride or CCl₄ show strict linearity in the range 10^{-5} – 10^{-4} M.

2. Copper Complexes. General Data. The copper(II) complexes of general formula Cu(HL)₂(ClO₄)₂ may be prepared by the reaction of two molar proportions of ligand to one of copper(II) perchlorate. The complexes of HDPA, HPPA, and HPTA are quite similar; all three precipitate from green ethanolic solutions as purple solids with a metallic lustre, and all three dissolve with difficulty in hot water, giving green solutions from which the complexes recrystallize on cooling. The complexes detonate rather than melt. Cu(HMPTA)₂(ClO₄)₂ is very soluble in ethanol but can be precipitated from the green solution as a royal blue microcrystalline powder by the addition of cold ether. Cu(HDMPTA)₂(ClO₄)₂ is prepared in and precipitates from ether solution. The initially purple solid turns brown on exposure to the atmosphere, the metamorphosis not affecting the elemental analysis. The brown material is hygroscopic.

The deprotonated complexes Cu(PTA)₂ and Cu(MPTA)₂ are formed from the ionic complexes by treatment with hydroxide ion; a butanol slurry of Cu(HDPA)₂Cl₂ requires sodium butoxide for neutralization. Cu(HPPA)₂(ClO₄)₂ could not be deprotonated.

Diffuse Reflectance Spectra and Structure. The features of the diffuse reflectance spectra of the charged and neutral copper compounds are given in Table III. We assign a pseudotetrahedral structure to both the charged and uncharged copper complexes in the solid state, based on the following considerations: Cu(HDPA)₂(ClO₄)₂ was originally assigned

Table III. Diffuse Reflectance Spectra of the Copper(II) Complexes

Complex	$\bar{\nu}_{\max} \times 10^3 \text{ cm}^{-1}$ and band assignments ^a					
	1	2	3	4	5	6
Cu(HDPA) ₂ (ClO ₄) ₂	7.5 ^b	10.1		16.0 ^b	18.3	26.7
Cu(HPPA) ₂ (ClO ₄) ₂	7.5	10.3		15.9 ^b	19.4	27.4 ^b
Cu(HPTA) ₂ (ClO ₄) ₂	7.6	10.3		16.0 ^b	19.0	27.4 ^b
Cu(HMPTA) ₂ (ClO ₄) ₂		9.0 ^c	11.2	14.5		26.0 ^b
Cu(HDMPTA) ₂ (ClO ₄) ₂		10.8 ^b	11.8 ^d			
Cu(DPA) ₂		9.9 ^b		15.6 ^c		22.0 ^b
Cu(PTA) ₂	8.7	16.9 ^c				22.0 ^b
Cu(MPTA) ₂	6.1		10.9 ^b	13.7 ^c		21.3 ^b

^a Bands 1–4 are assigned to transitions from $\Gamma_1(T_2)$ to $\Gamma_2(T_2)$, $\Gamma_1(E)$, $\Gamma_3(T_2)$, and $\Gamma_2(E)$, respectively. Bands 5 and 6 are assigned to ligand transitions. ^b Shoulder. ^c Broad absorption. ^d Featureless absorption persists from 11.8 to $28.6 \times 10^3 \text{ cm}^{-1}$.

a square-planar configuration⁴ but later was shown to have a pseudotetrahedral configuration⁸, the dihedral angle between the N–Cu–N planes of the two ligands being 55.6° instead of 90° , as required in a tetrahedral one. Subsequently, the single-crystal electronic and ESR spectra of the complex were measured.¹⁷ Despite a problem of misalignment of the in-plane axes of the electronic and ESR spectra, these authors gave the following preferred assignment for the visible spectrum: $d_{xy} \leftarrow d_{x^2-y^2}$, $10.4 \times 10^3 \text{ cm}^{-1}$; $d_{xz} \leftarrow d_{x^2-y^2}$, $13.5 \times 10^3 \text{ cm}^{-1}$; $d_z^2 \leftarrow d_{x^2-y^2}$, $15.7 \times 10^3 \text{ cm}^{-1}$; $d_{yz} \leftarrow d_{x^2-y^2}$, $18.5 \times 10^3 \text{ cm}^{-1}$.

We now report an additional weak transition at $7.5 \times 10^3 \text{ cm}^{-1}$ in the spectrum of $\text{Cu}(\text{HDPA})_2(\text{ClO}_4)_2$. A band in this general position is also present in the diffuse reflectance spectra of all the ionic and neutral complexes reported here. As a result, one of the transitions in the range 14 – $18 \times 10^3 \text{ cm}^{-1}$ must be reassigned; its origin is probably a combination of an $n-\pi^*$ and a ligand–copper charge-transfer transition. The observation of this new band now brings the electronic properties more into line with the known geometric properties. The dihedral angle of 55.6° indicates that the complex is more tetrahedral than square planar, and the spectra of the complexes should reflect this fact.

The energies of d–d transitions decrease progressively as the dihedral angle between the two N–Cu–N planes varies from 0° (square planar) to 90° (tetrahedral). This effect has been observed in the spectra of a series of *N*-substituted bis(salicylideneamino)- and bis(diketiminato)copper(II) complexes^{18,19} and in a series of 5,5'-disubstituted bis(dipyrromethene)copper(II) complexes.²⁰ A similar trend is observed in the present compounds. The copper complexes of HPPA and HPTA have spectra very similar to $\text{Cu}(\text{HDPA})_2^{2+}$: a band at $27 \times 10^3 \text{ cm}^{-1}$, broad absorption in the region from 19 to about $12 \times 10^3 \text{ cm}^{-1}$, and a band at $10.2 \times 10^3 \text{ cm}^{-1}$ with a shoulder at $7.5 \times 10^3 \text{ cm}^{-1}$. Substitution of one methyl group into the ligand (HMPTA) causes the transitions to shift to lower energies by approximately $2 \times 10^3 \text{ cm}^{-1}$, except for the lowest energy one which shifts $1 \times 10^3 \text{ cm}^{-1}$ lower. Models indicate that the methyl groups increase interactions between ligands; the shift of the transitions to lower energies probably means that in $\text{Cu}(\text{HMPTA})_2^{2+}$ the dihedral angle between N–Cu–N planes is even larger than the 55.6° found in $\text{Cu}(\text{HDPA})_2^{2+}$. This shift should be even greater in the spectrum of $\text{Cu}(\text{HDMPTA})_2(\text{ClO}_4)_2$, but the compound's instability prevents any accurate or meaningful measurement of the spectrum.

The values of Dq for $\text{Ni}(\text{HDPA})_3^{2+}$ and $\text{Ni}(\text{en})_3^{2+}$ (en = ethylenediamine) are 1.126 and $1.16 \times 10^3 \text{ cm}^{-1}$,²¹ respectively; for $\text{Cu}(\text{en})_3^{2+}$ the value is $1.64 \times 10^3 \text{ cm}^{-1}$.²¹ By proportion, the value of Dq expected for the unknown $\text{Cu}(\text{HDPA})_3^{2+}$ ion would be $1.58 \times 10^3 \text{ cm}^{-1}$, making the value for a tetrahedral complex $0.7 \times 10^3 \text{ cm}^{-1}$. We assign the bands at 7.5 , 10.4 , 13.5 , and $15.7 \times 10^3 \text{ cm}^{-1}$ to the copper(II) d–d transition in

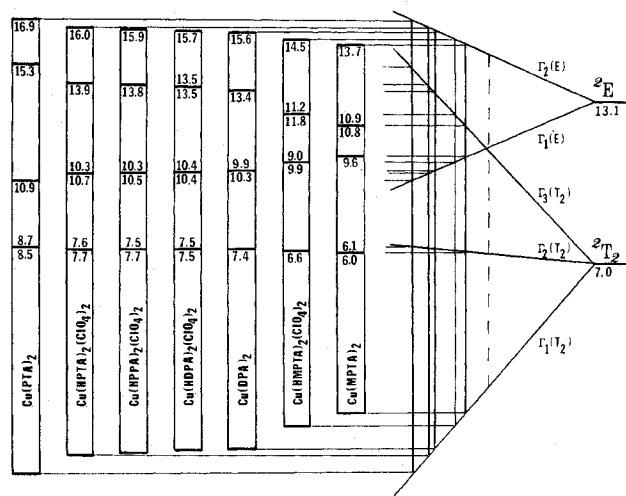


Figure 1. Predicted and observed transition energies in $10^3 \times \text{cm}^{-1}$ for pseudotetrahedral copper(II) complexes. See the text under "Diffuse Reflectance Spectra and Structure" for an explanation.

the complex $\text{Cu}(\text{HDPA})_2(\text{ClO}_4)_2$ and rationalize the spectra of the other complexes as follows.

The terms of a d^9 configuration in a tetrahedral field are a 2T_2 ground state and a 2E excited state. In the C_2 point symmetry group of these complexes, the degeneracy of each term is lifted completely. We assume that the two energy levels at 10.4 and $15.7 \times 10^3 \text{ cm}^{-1}$ arise from the 2E term, and that the ground state and the two levels at 7.5 and $13.5 \times 10^3 \text{ cm}^{-1}$ arise from the 2T_2 term, such that the energies of the original terms lie at the mean energy of each set, or at $13.1 \times 10^3 \text{ cm}^{-1}$ for the 2E term and at $7.0 \times 10^3 \text{ cm}^{-1}$ for the 2T_2 term. This gives a value of $0.61 \times 10^3 \text{ cm}^{-1}$ for Dq , comparable to the estimated $0.7 \times 10^3 \text{ cm}^{-1}$.

An energy level diagram has been constructed using the spectrum of $\text{Cu}(\text{HDPA})_2(\text{ClO}_4)_2$ to calibrate the term energies (see Figure 1). The term energies can be considered as functions of the variation in the dihedral angle subtended by the ligands at copper, with a tetrahedral CuN_4 chromophore at a dihedral angle of 90° . The terms are designated $\Gamma_1(T_2)$ and so on. The spectra of the other copper complexes have been fitted to the diagram by assigning a band near $15 \times 10^3 \text{ cm}^{-1}$ to the transition $\Gamma_2(E) \leftarrow \Gamma_1(T_2)$. Three other transitions are then predicted; their values are shown below the energy levels on the left of the figure. Observed values are shown above the energy levels for comparison, except for the value used to fix the $\Gamma_2(E) \leftarrow \Gamma_1(T_2)$ transition energy. The terms $\Gamma_1(E)$ and $\Gamma_2(E)$ each span the A representation, and $\Gamma_3(T_2)$ spans the B if indeed $\Gamma_3(T_2)$ crosses $\Gamma_1(E)$ as the dihedral angle is varied. The symmetries of $\Gamma_1(T_2)$ and $\Gamma_2(T_2)$ cannot be assigned from the data presented here.

Three comments need to be made concerning Figure 1. Firstly, the other possible assignments for the terms lead either to unacceptable values for Dq or to predicted spectra that do not satisfactorily agree with the observed spectra. Secondly, the values of Dq for the ligands and their deprotonated forms would be expected to vary slightly, but any error arising from the fitting of the other spectra to the diagram should be small. Thirdly, the positions of the shoulders and maxima reported for the complexes usually do not coincide with the true transition energies because of the overlap of adjacent bands. Furthermore, a transition may show up as a broad absorption rather than a definite shoulder or maximum. An example is the transition at $13.5 \times 10^3 \text{ cm}^{-1}$ in the spectrum of $\text{Cu}(\text{HDPA})_2(\text{ClO}_4)_2$. Although the band is quite distinct in the polarized single-crystal spectrum, there is no well-defined shoulder in the diffuse reflectance spectrum, just broad ab-

Table IV. Electronic Spectra of the Copper(II) Complexes in Solution

Ligand ^a	Solvent ^b	$\bar{\nu} \times 10^3 \text{ cm}^{-1}$ (molar extinction coefficient, $\text{L cm}^{-1} \text{ mol}^{-1}$)							
HPPA	1	10.0 (22)	15.0 (40)	25.4 (140)	33.6 (24 800)	40.2 (33 800)			
	2	10.4 (32)	15.6 (54)	24.4 (164)	35.1 ^d (32 300)	38.5 (52 200)	45.4 (25 600)		
	3	10.0 (19)	14.6 (61)	23.0 ^d (146)	34.8 (23 000)	37.7 (33 200)			
	4	10.5 (18)	14.4 (52)		34.5 (28 900)	38.1 (36 200)			
HPTA	1	10.8 (55)	15.1 (91)	23.0 ^d (215)		32.0 (32 000)	37.0 (28 000)		
	2	10.3 (65)	15.5 (109)	21.8 ^d (260)		32.5 (18 700)	36.0 (27 100)		
	3	10.7 ^d (28)	14.6 (70)	21.5 ^d (178)	26.8 (15 400)	32.0 (20 500)	35.7 (20 800)		
	4	10.5 ^d (26)	13.8 (53)	23.0 ^d (190)		32.0 (23 400)	35.4 (30 600)		
HMPTA	5		14.2 (83)	21.0 ^d (223)	27.2 (13 300)	32.2 (20 600)	36.0 (19 600)		
	2		18.0 (60)	21.5 ^d (222)		32.0 (19 600)	36.5 (17 200)		
	3		17.0 (136)		26.7 (11 300)	32.0 (17 700)			
	4		12.3 (38)		26.3 (12 600)	32.0 (23 000)	35.2 (29 000)		
HDMPTA	5		13.5 (15)		26.3 (30 700)	32.8 (30 200)	36.4 (20 400)		
	2					32.2 (21 900)	36.0 (24 200)		
	3		13.2 (22)		26.0 (21 800)	31.8 (23 900)	35.5 (26 500)		
	4		12.1 (22)		25.3 (11 500)	31.7 (25 800)	35.2 (28 900)		
HDPA ^c	1	10.0 (22)	14.5 (33)	15.0 (43)	16.7 (40)	23.4 (157)			
	6	12.0 (71)	15.5 (173)	19.0 (215)	25.0 (315)	26.3 (411)			
PTA ⁻	5	8.9 (53)	14.5 ^d (334)	17.5 (622)	23.0 ^d (292)	26.5 ^d (15 200)	27.6 (19 100)	32.8 (20 300)	36.0 (15 500)
	2	8.9 (87)	14.5 ^d (453)	17.4 (826)	23.0 ^d (887)	25.8 (23 100)	26.8 (27 900)	32.0 (20 200)	
	3	8.9 (69)	14.5 ^d (364)	17.4 (615)	21.3 ^d (158)	26.0 ^d (14 000)	26.8 (15 500)	32.1 (20 100)	35.7 (19 300)
	4	8.9 (68)	14.5 ^d (368)	17.4 (602)	22.5 ^d (356)	26.0 ^d (17 000)	26.8 (18 800)	32.0 (22 300)	35.4 (20 700)
MPTA ⁻	5		12.0 ^d (683)	14.3 (950)	22.5 ^d (537)	26.1 ^d (16 300)	27.2 (20 200)	32.5 (21 100)	35.7 ^d (13 600)
	2	6.7 (193)	12.0 ^d (818)	13.9 (1160)	22.0 ^d (547)	25.5 ^d (19 300)	26.5 (24 800)	32.0 (21 900)	
	3	6.6 (143)	11.5 ^d (397)	14.0 (650)	21.5 ^d (459)	26.7 (25 800)		32.2 (20 000)	35.7 (26 700)
	4	6.6 (124)	11.5 ^d (560)	13.9 (870)	21.5 ^d (568)	25.5 ^d (13 000)	26.3 (15 600)	31.7 (20 900)	35.1 (19 500)

^a The specific HL in the complexes $\text{Cu}(\text{HL})_2(\text{ClO}_4)_2$ or the specific L^- in the complexes $\text{Cu}(\text{L})_2$. ^b Solvents are designated as follows: 1, water; 2, acetonitrile; 3, dimethylformamide; 4, dimethyl sulfoxide; 5, methyl alcohol; 6, nitromethane. ^c From ref 4. ^d Shoulder.

sorption. This broad absorption is characteristic of the spectra of the rest of the copper complexes, suggesting that a band corresponding to the transition $\Gamma_3(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$ is indeed present.

Despite these provisos, the agreement between the predicted and observed transition energies is quite good. Of the protonated complexes, only $\text{Cu}(\text{HMPTA})_2(\text{ClO}_4)_2$ shows some disagreement in that the band predicted at $6.6 \times 10^3 \text{ cm}^{-1}$ for the transition $\Gamma_2(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$ is not clearly observed, although there is definitely absorption in this region. The deprotonated complexes need more comment. A band is predicted at $7.4 \times 10^3 \text{ cm}^{-1}$ for the same transition in $\text{Cu}(\text{DPA})_2$ and at $9.6 \times 10^3 \text{ cm}^{-1}$ for the transition $\Gamma_1(\text{E}) \leftarrow \Gamma_1(\text{T}_2)$ in $\text{Cu}(\text{MPTA})_2$. Our measured spectra show definite absorption in these areas for both complexes but no well-defined shoulders or peaks. Only the spectrum of $\text{Cu}(\text{PTA})_2$ presents a real problem in interpretation. If the assignment is made as shown in Figure 1, then there is good agreement between the observed and predicted energy of the $\Gamma_2(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$ transition, but the predicted value of $10.9 \times 10^3 \text{ cm}^{-1}$ for the energy of the $\Gamma_1(\text{E}) \leftarrow \Gamma_1(\text{T}_2)$ transition falls where there is no absorption in the spectrum—at a minimum in fact. An alternative assignment can be made by assuming that the transition at $8.7 \times 10^3 \text{ cm}^{-1}$ corresponds to the transition $\Gamma_3(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$. This assignment is shown in Figure 1 by the dashed line to the right side of the diagram, and it predicts an energy of $4.9 \times 10^3 \text{ cm}^{-1}$ for the transition $\Gamma_2(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$. The transition $\Gamma_1(\text{E}) \leftarrow \Gamma_1(\text{T}_2)$ is almost degenerate with the $\Gamma_3(\text{T}_2) \leftarrow \Gamma_1(\text{T}_2)$ transition. The transition $\Gamma_2(\text{E}) \leftarrow \Gamma_1(\text{T}_2)$ has an energy of $12.3 \times 10^3 \text{ cm}^{-1}$. There is absorption in the spectrum at this region, but none in the region from 4 to $8 \times 10^3 \text{ cm}^{-1}$.

We reject this latter assignment in favor of the former. Because of the increased steric interaction of the methyl group, $\text{Cu}(\text{MPTA})_2$ should be more tetrahedral than $\text{Cu}(\text{PTA})_2$, not the reverse. $\text{Cu}(\text{PTA})_2$ might reasonably be supposed to be less tetrahedral than $\text{Cu}(\text{DPA})_2$ because the steric interaction between ligands should be decreased when a five-membered ring replaces a six-membered one. In support of a decreased

dihedral angle in $\text{Cu}(\text{PTA})_2$ is the fact that the absorption intensities in the solution spectra are much weaker than the more tetrahedral counterparts (see Table IV).

We conclude this discussion of the diffuse reflectance spectra by pointing out that, so far, a meaningful spectrum of $\text{Cu}(\text{HDMPTA})_2(\text{ClO}_4)_2$ has not been obtained and that $\text{Cu}(\text{DMPTA})_2$ has not been prepared. The significance of Figure 1 would be enhanced if it also rationalized the spectra of these two compounds.

Solution Spectra. The relevant features of the solution spectra of the ionic and neutral copper complexes are given in Table IV. Also included in the table are the reported solution spectra for $\text{Cu}(\text{HDPA})_2(\text{ClO}_4)_2$. The ionic complexes are solvated to six-coordinate species; the neutral ones are not.

When the purple $\text{Cu}(\text{HDPA})_2^{2+}$ salts are dissolved in water, water-dioxane mixtures, or nitromethane, green solutions are obtained, suggesting that the coordination number of the copper(II) ion has increased from four to six. In fact, the chloride and nitrate salts are green in the solid state,⁴ indicating presumably that these anions are in the coordination sphere of the copper.

The spectral features of $\text{Cu}(\text{HPPA})_2^{2+}$ in solution are similar to those of $\text{Cu}(\text{HDPA})_2^{2+}$, with the exception that the transitions at 14.4 and $16.7 \times 10^3 \text{ cm}^{-1}$ are not seen. There is, however, broad absorption in the region at $14 \times 10^3 \text{ cm}^{-1}$ and a distinct high-energy distortion of the peak at $15 \times 10^3 \text{ cm}^{-1}$, suggesting another band in the proximity of $16.5 \times 10^3 \text{ cm}^{-1}$. We presume that the two extra bands, whatever their origin, are present in these new spectra.

Beer's law plots of the spectra of $\text{Cu}(\text{HPPA})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{HPTA})_2(\text{ClO}_4)_2$ show distinct nonlinear behavior at concentrations of 10^{-5} M . This fact suggests the presence of more than one species in solution and is complemented by the observation that the specific conductance of DMF solutions of both compounds varies dramatically as a function of concentration. Various degrees of solvation and equilibria of the sort $\text{Cu}(\text{HL})_2^{2+} \rightleftharpoons \text{Cu}(\text{HL})\text{L}^+ + \text{H}^+$ are probably responsible for these observed spectra and the high conductivities shown in Table I.

Cu(HMPTA)₂(ClO₄)₂ and Cu(HDMPTA)₂(ClO₄)₂ dissolve in CH₃OH, CH₃CN, DMF, or Me₂SO to produce red solutions that turn pale yellow upon standing. It is the spectra of these pale yellow solutions that are reported in Table IV. Although transitions of typical d-d intensity can be seen in the spectra at 12-14 × 10³ cm⁻¹, most detail in the visible region is obscured by the very intense peaks near 26 × 10³ cm⁻¹. The complexes are irreversibly altered by the solution process and cannot be recovered upon evaporation of the solvent, as is the case with the complexes of HDPA, HPPA, and HPTA. Further examination of the phenomenon resulted in the observation that even the ionic complexes of HDPA, HPPA, and HPTA could be made to produce red solutions in acetonitrile by merely heating the solutions. The red color is not due to perchlorate ion coordination as has been suggested⁴ because the red solutions have 1:2 electrolytic character. We now report, without elaborating on the experimental details, that the color is due to the formation of appropriate analogues of diphenylbenzidine violet,²² a well-known indicator in analytical chemistry.

The solution spectra of the neutral complexes provide an interesting contrast to those of the ionic complexes—the neutral complexes retain their pseudotetrahedral configuration in solution. There is little difference between the positions of the various d-d bands in the various solution spectra and those in the solid-state spectra, suggesting that solvent interactions are not affecting the energies of the d-d transitions. This is not true for the charge-transfer transitions and the ligand π-π* transitions, which are affected both in position and intensity. The intensities of the d-d transitions are appropriate to tetrahedral CuN₄ chromophores.

Magnetic Moments. The values of the magnetic moments (μ_{eff}) of the various copper(II) complexes are given in Table I. Because of electron spin and orbital motion, the magnetic moment of copper(II) may range from a value of 1.73 μ_{B} (no orbital contribution) to a value of 3.00 μ_{B} (full orbital contribution). Experimental values range from 1.7 to 2.2 μ_{B} . Different degrees of an orbital contribution are predicted in square-planar and tetrahedral environments. In the former geometry, no orbital moment is expected by virtue of a nondegenerate ground state. In the latter geometry, however, an orbital contribution is expected because of the ²T₂ ground state. A full contribution is not expected because the Jahn-Teller effect prevents a rigorously degenerate ground state. Moments that contain large orbital contributions have been used as evidence for pseudotetrahedral fields in bis-

(bidentate)copper(II) compounds.²³

As shown in Table I, the moments reported here have essentially spin-only values that show some degree of an orbital contribution. The large moment of Cu(MPTA)₂ is field independent, as are the others, and cannot be attributed to ferromagnetism. Basically, the moments support a pseudotetrahedral geometry for these complexes.

Registry No. Cu(HDPA)₂(ClO₄)₂, 14128-78-0; Cu(HPPA)₂(ClO₄)₂, 64682-68-4; Cu(HPTA)₂(ClO₄)₂, 64726-47-2; Cu(HMPTA)₂(ClO₄)₂, 64682-70-8; Cu(HDMPTA)₂(ClO₄)₂, 64682-72-0; Cu(DPA)₂, 19358-74-8; Cu(PTA)₂, 64728-26-3; Cu(MPTA)₂, 64682-73-1; HPPA, 64682-29-7; HPTA, 54670-80-3; HMPTA, 64728-27-4; HDMPTA, 64682-30-0; HDPA, 1202-34-2; 2-aminopyridine, sodium salt, 40825-17-0; 2-chloro-4-methylthiazole, 26847-01-8; 2-amino-6-methylpyridine, sodium salt, 64682-28-6.

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Proton Nuclear Magnetic Resonance Spectra of n-Butylcopper(I)-n-Butyllithium and Related Complexes in Diethyl Ether and Pentane^{1a}

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Received March 8, 1977

Proton magnetic resonance spectra of ether and pentane solutions of lithium di-n-butylcuprate with n-butyllithium have been examined over a range of temperatures. In ether these spectra are consistent with species of the form (R₂CuLi)₂ and R₄CuLi₃, while in pentane 1:1 and 1:2 complexes of n-butylcopper(I) with n-butyllithium are proposed. The influence of tri-n-butylphosphine and lithium iodide on the solution structure of certain lithium organocuprates has also been studied. These results suggest that copper(I)-phosphine coordination serves only to complete the coordination shell of copper(I) which, in phosphine-free donor solvents, is probably occupied by a solvent molecule. Lithium iodide is readily incorporated by solutions of n-butyl(tri-n-butylphosphine)copper-n-butyllithium. Spectral evidence is reasonable for a 1:1:2 lithium iodide-n-butyl(tri-n-butylphosphine)copper(I)-n-butyllithium complex in ether and a 1:1:1 and a 1:1:4 species in pentane.

Lithium organocuprates, (R₂CuLi)_m, rank among the most important of organometallic reagents, and considerable effort

has been extended to the study of the mechanism of their reactions with a variety of substrates. All of these studies share