

Coordination Chemistry of Copper Macrocyclic Complexes: Synthesis and Characterization of Copper Complexes of TIM¹

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A rigorously four-coordinate planar complex, [Cu(TIM)](BPh₄)₂, and several five-coordinate pyramidal complexes, [Cu(TIM)L](PF₆)₂ (L = 1-MeIm, Im, py, and NH₃) and [Cu(TIM)X]PF₆ (X = Cl⁻, Br⁻, I⁻, and NCS⁻); have been synthesized. The complexes were characterized in the solid state and in solution with use of a combination of elemental analysis, infrared, electronic, and EPR spectroscopy, and magnetic, conductivity, and molecular weight measurements. The position of the PF₆⁻ anion in the solid-state structures of [Cu(TIM)X]PF₆ (X = Cl⁻, Br⁻) is such that the displacement of Cu from the basal ligand plane in these pyramidal structures is smaller than might be expected. In acetone solution, [Cu(TIM)](BPh₄)₂ undergoes a reduction to the intensely blue Cu(TIM)⁺ cation ($E_{\text{max}} = 1.34 \mu\text{m}^{-1}$). In the presence of excess NCS⁻, [Cu(TIM)NCS]⁺ in acetone solution exists in equilibrium with the six-coordinate complex [Cu(TIM)(NCS)₂].

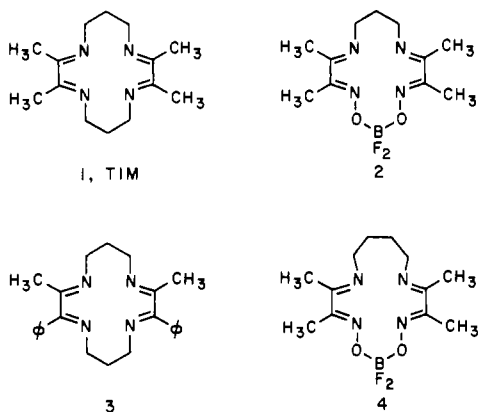
Introduction

The synthesis and study of Cu complexes of TIM, a neutral, 14-membered, tetraimine macrocycle (1) was motivated by three factors:

(1) The study of copper macrocyclic complexes containing imine nitrogen donor atoms contributes to *that bank* of definitive physical and chemical data which, in turn, will be of ultimate use in advancing the detailed understanding of relevant biological systems. Bovine erythrocyte superoxide dismutase³⁻⁷ is an example of such a biological system given that the copper complex contained therein features a "planar" array of four imine nitrogen atoms provided by imidazole groups of histidines.

(2) An interest in the redox properties of Cu(TIM) complexes was stimulated by the redox activity that has been demonstrated for Fe(TIM) complexes.⁸⁻¹⁰

(3) The Cu(TIM)L complexes provide another vehicle to examine the intriguing relationship that exists between structure, axial ligation, and spectral properties displayed by several related systems (2-4).¹¹⁻¹³



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This paper details the synthesis of several pyramidal Cu(TIM)L²⁺ and Cu(TIM)X⁺ complexes (where L is a neutral ligand and X has a charge of 1-) and a rare example of a rigorously four-coordinate planar Cu complex, [Cu(TIM)](BPh₄)₂. Important structural factors and their effect on the electronic and EPR spectra of the compounds are discussed. A theoretical study of the electronic structure of these compounds employing SCF-X α -SW theory appears in the following paper.¹⁴ The synthesis and spectral properties of the Cu^I species Cu(TIM)⁺ are also reported.

Experimental Section

The reagents and solvents used as starting materials were obtained commercially and used without further purification except where noted in the following descriptions of syntheses. For preparations employing Cu(TIM)(PF₆)₂·xH₂O as starting material, a molecular weight of 620 (x = 1) has been assumed in estimating yields.

Preparation of Cu^{II}(TIM) Compounds. Cu(TIM)(PF₆)₂·xH₂O. A solution of Cu(OAc)₂·2H₂O in methanol was prepared by stirring Cu(OAc)₂·2H₂O (16 g, 0.08 mol) in 125 mL of methanol for at least 1 h. The mixture was then filtered, and the undissolved Cu(OAc)₂·2H₂O was retained. Nitrogen was then bubbled through this methanol solution for ~45 min prior to its further use as described below.

Methanol (100 mL) was placed in a three-neck, 500-mL flask, cooled to -10 °C under nitrogen flow, and maintained at temperatures between -5 and +5 °C during sequential additions of 1,3-diaminopropane (13.4 mL, 0.16 mol), trifluoroacetic acid (12 mL, 0.16 mol), and a solution of 2,3-butanedione (14 mL, 0.16 mol) in 14 mL of methanol. This solution was stirred for 20 min.

The Cu(OAc)₂·2H₂O solution was then added slowly, over a period of 30-45 min, to the cooled ligand solution while the flow of nitrogen was maintained through the flask. When the addition was complete, the undissolved Cu(OAc)₂·2H₂O was added as a solid. The resulting purple solution was removed from the cooling bath and stirred for 1.5 h, during which time it warmed to room temperature. The solution was then warmed to about 40 °C over 2 h with a water bath and held at that temperature for 2 h, at which point metallic Cu was present in the mixture. The reaction mixture was removed from the water bath and stirred under a nitrogen atmosphere for 20 h at room temperature.

The flask was then opened to the air, and 1-methylimidazole (20 mL, 0.25 mol) and glacial acetic acid (25 mL, 0.44 mol) were added. The mixture was filtered to remove metallic Cu. A solution of NH₄PF₆ (10 g, 0.061 mol) in 80 mL of water was added slowly, dropwise to the rapidly stirring filtrate, causing the precipitation of a blue solid.

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The product was collected by filtration, washed sequentially with absolute ethanol (until the filtrate became colorless) and diethyl ether, and then air-dried; yield (of crude $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$) 8.8 g, 16%.

The crude product (4.0 g, 5.8 mmol) was suspended in 30 mL of H_2O , and 1 mL of 48% aqueous HBF_4 was added, with stirring. The resulting slurry was stirred for several minutes, during which time the color of the solid changed from blue to red-violet. The red-violet product was collected by filtration, washed sequentially with portions of absolute ethanol and diethyl ether, and then air-dried; yield 2.9 g, 80%. The crude product (2.00 g) may be crystallized from acetone (15 mL) and diethyl ether (15 mL) but powders upon drying.

$[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$. Analytically pure crystalline samples of $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$ deposited from a stirred solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (0.5 g, 0.8 mmol) in water (100 mL), upon addition of 7 drops of 1-methylimidazole. The blue product was collected by filtration, washed sequentially with absolute ethanol and diethyl ether, and then air-dried; yield 320 mg, 60%. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the filtrate.

$[\text{Cu}(\text{TIM})\text{Cl}](\text{PF}_6)_2$. A saturated solution of LiCl in acetone was prepared by stirring an excess amount of LiCl (1.5 g) in 100 mL of acetone for several minutes and then filtering the solution. A filtered solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (1.0 g, 1.6 mmol) in acetone (20 mL) was added slowly, dropwise to the rapidly stirring LiCl solution. The blue oil that formed initially was stirred for ~ 30 min, eventually forming a red-violet dequescent solid. The product was collected by suction filtration, washed several times with acetone, and dried by passing a stream of dry air through the sample. The product was dried further by vacuum desiccation over P_4O_{10} for 22 h, whereupon the sample becomes blue; yield 550 mg, 81% (assuming the product is $\text{Cu}(\text{TIM})\text{Cl}_2$).

The dried sample (260 mg, 0.68 mmol) and LiCl (120 mg, 2.8 mmol) were dissolved in 10.0 mL of absolute ethanol, and the mixture filtered. The resulting blue solution was combined with a filtered solution of NH_4PF_6 (120 mg, 0.74 mmol) in absolute ethanol (10.0 mL). Absolute ethanol (5.0 mL) was added after being used to rinse the filters. The solution was then swirled briefly and set aside for 3 h. The blue crystalline product that volunteered was collected by filtration, washed sequentially with portions of absolute ethanol and diethyl ether, and then dried with a stream of dry air; yield 160 mg, 48%. A second crop of crystals formed overnight upon cooling the filtrate to 4 °C. The total yield is 205 mg (62%). Crystals suitable for X-ray diffraction studies were obtained from the first crop.

$[\text{Cu}(\text{TIM})\text{Br}](\text{PF}_6)_2$. A filtered solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (1.0 g, 1.6 mmol) was added slowly, dropwise, to a vigorously stirred solution of LiBr (3.0 g, 35 mmol) in acetone (50 mL). The violet solid that formed was collected by suction filtration, washed several times with acetone, and dried with a stream of dry air.

The sample was dried by vacuum desiccation over P_4O_{10} for 22 h, whereupon the sample becomes forest green; yield 680 mg, 87% (assuming the product is $\text{Cu}(\text{TIM})\text{Br}_2$). A filtered solution of this product (200 mg, 0.41 mmol) and LiBr (140 mg, 1.6 mmol) in absolute ethanol (10.0 mL) was combined with a solution of NH_4PF_6 (70 mg, 4.5 mmol) in absolute ethanol (7.0 mL). Absolute ethanol (3 mL) was added after being used to rinse the filters. The solution was then swirled briefly and set aside for 4 h. The blue crystalline product that volunteered was collected by filtration, washed several times with absolute ethanol, and dried with a stream of dry air; yield 130 mg, 59%. A second crop was obtained by slowly cooling the filtrate to -20 to -25 °C.

$\text{Cu}(\text{TIM})\text{I}_2$. A filtered solution of NaI (690 mg, 4.60 mmol) in a minimum amount of acetone (< 5 mL) was added dropwise to a vigorously stirred and filtered solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (1.46 g, 2.4 mmol) in acetone (10 mL). The dark green solid that formed was collected by filtration, washed sequentially with small amounts of acetone and diethyl ether, and then dried with air; yield 960 mg, 44%. The product was recrystallized from CH_2Cl_2 (50 mL) upon the slow addition of diethyl ether (16 mL). The sample was vacuum desiccated over P_4O_{10} for 17 h.

$[\text{Cu}(\text{TIM})\text{I}](\text{PF}_6)_2$. A solution of $[\text{Cu}(\text{TIM})\text{I}]\text{PF}_6$ was prepared by dissolving $\text{Cu}(\text{TIM})\text{I}_2$ (100 mg, 0.18 mmol) and $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (120 mg, 0.2 mmol) in acetone (5 mL). The product crystallized upon slow addition of *n*-hexane. The dark green product was collected by suction filtration, washed several times with absolute ethanol, and then dried with a stream of dry air; yield 150 mg, 75%. The product

may be recrystallized from dichloromethane and hexane.

$[\text{Cu}(\text{TIM})\text{NCS}](\text{PF}_6)_2$. A solution of sodium thiocyanate (70 mg, 0.86 mmol) in 1.0 mL of H_2O was added to a solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (500 mg, 0.79 mmol) in boiling methanol (50 mL). The resulting blue solution was cooled to room temperature and then to -20 °C overnight. The red-violet, crystalline solid that volunteered was collected by filtration, washed several times with absolute ethanol, and dried with air; yield 370 mg, 90%. The entire product was recrystallized from boiling methanol (25 mL) that was filtered hot and cooled slowly to room temperature.

$\text{Cu}(\text{TIM})(\text{NCS})_2$. The starting material (which is assumed to be $\text{Cu}(\text{TIM})\text{Cl}_2$, as described in the $[\text{Cu}(\text{TIM})\text{Cl}](\text{PF}_6)_2$ preparation) (300 mg, 0.8 mmol) and sodium thiocyanate (1.3 g, 16 mmol) were dissolved in H_2O (5 mL) to give a red-violet solution. This solution was filtered and then extracted with 160 mL of CH_2Cl_2 (approximately 10 mL at a time). The green CH_2Cl_2 solution was dried over anhydrous magnesium sulfate and filtered. An additional 25 mL of CH_2Cl_2 was used to wash the filter and drying agent. Violet crystals were obtained from this solution upon addition of hexane (150–175 mL). The product was collected by filtration, washed with a small amount of hexane, and dried with a stream of dry air; yield 140 mg, 12%. A second crop was obtained by adding an additional 100 mL of hexane to the filtrate.

$[\text{Cu}(\text{TIM})\text{Im}](\text{PF}_6)_2$. To a filtered solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (500 mg, 0.8 mmol) in H_2O (45 mL) was added dropwise, with stirring, a solution of imidazole (300 mg, 4.4 mmol) in H_2O (5 mL). The blue crystalline product that formed was collected by filtration, washed sequentially with water, ethanol, and diethyl ether, and then air-dried; yield 290 mg, 55%.

$[\text{Cu}(\text{TIM})\text{py}](\text{PF}_6)_2$. A relatively concentrated solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ was prepared by stirring a mixture of the complex (500 mg, 0.08 mmol) and H_2O (50 mL) at 40–45 °C, filtering it, and then allowing it to cool to room temperature. The desired blue crystalline product, which formed upon addition of 10 drops of pyridine to the solution, was collected by filtration, washed sequentially with absolute ethanol and diethyl ether, and then dried with air; yield 330 mg, 62%.

$[\text{Cu}(\text{TIM})\text{NH}_3](\text{PF}_6)_2$. A solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (500 mg, 0.8 mmol) in water (75 mL) was prepared and filtered. To this solution was added dropwise 1.0 mL of concentrated ammonium hydroxide, causing the precipitation of a blue microcrystalline solid. The product was collected by filtration, washed sequentially with several portions of absolute ethanol and diethyl ether, and then dried with air; yield 330 mg, 68%.

$[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$. To a filtered solution of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ (500 mg, 0.8 mmol) in H_2O (50 mL) was added a filtered solution of NaBPh_4 (560 mg, 1.6 mmol). A beige precipitate formed immediately. The solid was stirred for 20 min, during which time its color changed from beige to yellow-orange. The yellow-orange product was isolated by filtration and washed sequentially with water, several portions of absolute ethanol, and diethyl ether. The sample was dried with air; yield 700 mg, 95%. The product was recrystallized to obtain either an analytical sample or crystals suitable for X-ray diffraction studies by the following procedure. A solution of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ (100 mg, 0.010 mmol) in acetone (10 mL) was filtered, and 5.0 mL of diethyl ether was added. The solution was swirled and set aside for 10 min, during which time crystals began to form. Then, 5 drops of diethyl ether was added so as to cause minimum mixing of the solution. This was followed by seven more ether additions at 5-min intervals. During this time the crystals grew. The product was collected by filtration. It is important that the recrystallization be carried out in a minimum amount of time (~ 1 h) because the acetone solutions change color after ~ 1 h, and the desired product is no longer obtainable.

Preparation of $\text{Cu}(\text{TIM})^+$ in Acetone. The reduction of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ in acetone was studied at EPR concentrations (~ 5 mM), with use of the following procedure. Acetone (50 mL) was taken through three freeze-thaw cycles under vacuum to remove air dissolved in the solvent. The vacuum was then broken with Ar, and $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ (230 mg, 0.24 mmol) was added to the acetone from a side arm. The resulting red solution gradually becomes dark blue over a period of a few hours. The EPR spectrum of the solution was monitored at several-hour intervals for a period of 48 h.

An alternative procedure (illustrated for a preparation of $[\text{Cu}(\text{TIM})\text{HOBPh}_3]\text{BPh}_4$ under more concentrated conditions) is as follows. A flask containing a sample of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ (500 mg, 0.52 mmol) was evacuated and then purged with Ar. This process

Table I. Elemental Analyses and Molar Susceptibilities

Formula	calcd					found					$10^{-3} \times \chi_m^T$, cgsu	T, K
	% C	% H	% N	% Cu	% other	% C	% H	% N	% Cu	% other		
[Cu(TIM)](BPh ₄) ₂	78.36	6.79	5.90	6.69		79.20	6.78	6.00	6.62		0.743	296.0
Cu(TIM)(PF ₆) ₂ ^a	27.94	4.02	9.31	10.56		28.00	4.15	9.14	10.37			
[Cu(TIM)(1-MeIm)](PF ₆) ₂	31.61	4.42	12.29	9.29		31.61	4.34	12.27	9.45		1.18	291.7
[Cu(TIM)py](PF ₆) ₂	33.51	4.29	10.28	9.33		33.68	4.24	10.33	9.57		1.11	297.3
[Cu(TIM)(NH ₃)](PF ₆) ₂	27.17	4.40	11.32	10.27		27.41	4.34	11.41	10.39		1.16	296.6
[Cu(TIM)Cl]PF ₆	34.15	4.91	11.38	12.91	7.20 (Cl)	34.18	4.92	11.32	12.85	7.29 (Cl)	1.19	297.4
[Cu(TIM)Br]PF ₆	31.33	4.51	10.44	11.84	14.89 (Br)	31.30	4.47	10.29	11.84	14.59 (Br)	1.16	296.7
[Cu(TIM)I]PF ₆	28.80	4.14	9.60	10.89	21.74 (I)	28.70	4.19	9.46	10.61	21.68 (I)		
[Cu(TIM)NCS](PF ₆)	34.99	4.70	13.60	12.34		34.98	4.65	13.68	12.37		1.16	297.4
Cu(TIM)(NCS) ₂	44.89	5.65	19.63	14.84		44.78	5.78	19.48	14.65		1.21	297.1
Cu(TIM)I ₂	29.72	4.28	9.90		44.86 (I)	29.56	4.26	9.90		43.8 (I)	1.05	294.1

^a This hygroscopic yellowish solid is prepared from the pink Cu(TIM)(PF₆)₂·xH₂O by heating at 100 °C at ~1 torr for ~12 h. The value for x in the preheated sample is approximately 1. The preparation of the ClO₄⁻ salt is reported by: Fabbri, L.; Lari, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* 1982, 21, 2083.

Table II. Selected Structural Data for Cu^{II}(TIM) Complexes

compd	dist, Å			angles, deg		δ, Å ^b	ref
	av Cu-N _{TIM}	Cu-L _s	Cu-L _e (L ₆)	N-M-N	L _s -M-L _e		
[Cu(TIM)](BPh ₄) ₂	1.945 (7)			81.31 (32) 98.69 (32)	180.0	0.00	17
[Cu(TIM)(1-MeIm)](PF ₆) ₂	1.988 (3)	2.139 (3)	3.55 (F-PF ₆) ^a	80.46 (15) 94.00 (14)	162 ^a	0.44	17, 32
[Cu(TIM)Cl]PF ₆	1.955 (9)	2.404 (3)	3.38 (1) (F-PF ₆)	79.60 (40) 97.01 (38)	163.9	0.34	17
[Cu(TIM)NCS]PF ₆	1.987 (10)	2.385 (10)	3.337 (8) (-SCN)	84.79 (44) 94.09 (42)	180.0	0.07	17, 33
[Cu(TIM)Br]PF ₆	1.947 (16)	2.549 (11)	3.41 (2) (F-PF ₆)	79.67 (69) 98.29 (68)	165.0	0.30	17
[Cu(TIM)(H ₂ O) ₂](NO ₃) ₂	1.969 (2)	2.556 (5)	2.556 (5)	81.1 (1) 98.9 (1)	180.0	0.00	50

^a Result represents a weighted average for axial fluorine contacts calculated from models for a badly disordered PF₆⁻ anion. ^b Displacement of the Cu atom from the N₄ plane of the macrocycle.

was repeated two more times. Then acetone (20–25 mL), which had been freeze-thaw degassed under vacuum and stored under Ar, was added via syringe. The resulting red solution begins to turn blue in ~10 min. After 20 min, a light blue crystalline product volunteers from the now blue-violet solution. This solid was isolated (after ~2 h) by filtration under Ar in a Schlenk filter. This procedure was used until the air stability of the solid was known. Subsequent preparations involved rapidly filtering the mixture in air; yield ~200 mg.

Physical Measurements. Infrared Spectra. Infrared spectra were recorded in the 4000–600-cm⁻¹ region as Nujol mulls between potassium bromide plates or as acetone or dichloromethane solutions in potassium bromide cells, with a Perkin-Elmer 727B infrared spectrophotometer. The spectra were calibrated with polystyrene bands at 3028, 1601, and 1208 cm⁻¹, and the values reported are ±2 cm⁻¹ in the region of 2000–600 cm⁻¹ and ±5 cm⁻¹ in the 4000–2000-cm⁻¹ region.

Electronic Spectra. Electronic spectra were recorded on solid-state samples as Nujol mulls between quartz plates, with a Cary 219 spectrophotometer in the visible region at ambient temperature. Spectra on solutions in quartz or Pyrex cells were recorded in the visible and near-UV regions with a Cary 219 and in the near-IR with a Cary 14. Low-temperature spectra were recorded at 77 K on Nujol mulls between microscope cover slips, with a Cary 219. The photoacoustic spectrum of [Cu(TIM)](BPh₄)₂ was recorded with a Princeton Applied Research 6001 spectrometer and was kindly provided by Professor R. A. Palmer of Duke University.

EPR Spectra. EPR spectra were recorded on 5 mM solutions of complexes both at ambient temperature and at 77 K, with a Varian E-3 X-band spectrometer. The spectrum of [Cu(TIM)](BPh₄)₂ in the solid state was obtained from a powdered sample of [Ni(TIM)](BPh₄)₂ doped with 0.1% [Cu(TIM)](BPh₄)₂ obtained by precipitating the mixture from nitromethane solution with diethyl ether. The spectra were calibrated vs. a radical present in the quartz EPR tubes, whose g value was determined to be 2.001 by calibration with DPPH (g = 2.0037). The accuracy of the g values estimated from the spectra is ±0.001. The error in the ^{Cu}A_{||} values estimated from the spectra is largely due to the accuracy of determining the center

of the features and is <3 × 10⁻⁴ cm⁻¹ in any case.

Conductivity Measurements. Conductivity measurements were made on acetone solutions of the complexes thermostated to 25.00 ± 0.05 °C with a Lauda bath. Conductivities were measured with a 1-cm cell (cell constant 0.3273 ± 0.5%) and a Beckman RC-18A conductivity bridge.

Molecular Weight Determinations. Molecular weights of non-electrolytes were determined in CHCl₃ solutions at 37 °C with a Mechrolab Model 301-A vapor pressure osmometer. A working curve was constructed from data obtained on standard solutions of benzil that had been recrystallized from ethanol and dried in vacuo.

Magnetic Data. Magnetic susceptibilities were determined by the Faraday technique at ambient temperature, with Hg[Co(SCN)₄] as a standard.

Elemental Analysis. Elemental analysis on all compounds was obtained commercially from either Spang Microanalytical Laboratory, Box 142, Eagle Harbor, MI 49951, or Canadian Microanalytical Service Ltd., Vancouver, British Columbia V6T 1K6, Canada. The only exception was the I⁻ analysis on Cu(TIM)I₂, which was determined gravimetrically with use of a method involving the precipitation of AgI.

Results and Discussion

Analytical data and molar magnetic susceptibilities for several complexes are collected in Table I. The magnetic susceptibilities were measured in the solid state at room temperature, are uncorrected for Pascal's constants, and fall in the range of 1.5–1.8 μ_B (with the exception of [Cu(TIM)](BPh₄)₂, which is low due to a large diamagnetic contribution from the anions). In all cases the susceptibilities are typical of noninteracting Cu^{II} centers. Structural data pertinent to the following discussions may be found in Table II. Information regarding the electronic and EPR spectra of the complexes are collected in Tables III and IV. The results of SCF-Xα calculations are of great help in interpreting the spectra of Cu(TIM) complexes and are discussed in detail in the fol-

Table III. Electronic Transitions for Cu(TIM) Complexes

compd	medium	$E, \mu\text{m}^{-1} (\epsilon, \text{M}^{-1} \text{cm}^{-1})$	
[Cu(TIM)](BPh ₄) ₂	solid powder	2.3	
	acetone	1.90 (127)	
	CH ₃ CN	1.85 (121)	
Cu(TIM)(PF ₆) ₂ ·xH ₂ O	Nujol	1.96	
	TFAA	1.92	
	H ₂ O	1.88	
	CH ₃ CN	1.86	
	acetone	1.89	
	MeOH	1.86	2.81, 2.90
[Cu(TIM)(NH ₃)](PF ₆) ₂	Nujol	1.67	
	acetone	1.77 (149)	
[Cu(TIM)py](PF ₆) ₂	Nujol	1.67	
	py	1.72 (200)	
	acetone	1.88 (121)	
[Cu(TIM)Im](PF ₆) ₂	Nujol	1.61	
	acetone	1.66 (152)	
[Cu(TIM)(1-MeIm)]-(PF ₆) ₂	Nujol (77 K)	1.67	
	Nujol	1.64	
	acetone	1.64 (161)	
	MeOH	1.86 (150)	2.81, 2.90
	TFAA	1.92 (184)	
[Cu(TIM)I]PF ₆	acetone	1.63 (sh)	2.50 (3203)
	MeOH/0.1 M NaI	1.79 (sh) (161)	
	MeOH		2.66 (3710)
[Cu(TIM)Br]PF ₆	Nujol	1.74	
	acetone	1.55 (186)	
	CH ₂ Cl ₂	1.55 (182)	
[Cu(TIM)Cl]PF ₆	Nujol (77 K)	1.68	
	Nujol	1.66	
	acetone	1.53 (156)	
	CH ₂ Cl ₂	1.53 (163)	
	CHCl ₃	1.55 (167)	3.08
[Cu(TIM)NCS]PF ₆	Nujol	~1.8	
	acetone	1.61 (157)	2.79 (2354)
	CH ₂ Cl ₂	1.59 (149)	2.75 (2480)
	acetone + 10 equiv of NaSCN	1.62 (143)	2.75 (2584)
Cu(TIM)(NCS) ₂	acetone	1.61 (131)	2.79 (2458)
	CH ₂ Cl ₂	1.65 (100)	2.60 (3390)
	CHCl ₃	1.73 (sh)	2.60 (3830)
Cu(TIM)Cl ₂	Nujol	~1.9	
	CH ₂ Cl ₂	1.54	3.03
	CH ₂ Cl ₂ /Ph ₄ AsCl added	1.56	
	CHCl ₃	1.61 (124)	3.04

lowing paper.¹⁴ Conductivity data for several of the complexes and representative PF₆⁻ salts in acetone solution at 25.0 °C are contained in Table V.

With the exception of the complexes discussed below, the infrared spectra of Cu^{II}(TIM) complexes are unremarkable. In addition to bands associated with the axial ligand(s) and counterion(s), the complexes display several bands characteristic of TIM,^{15,16} including a strong ν_{CN} absorption at 1600–1620 cm⁻¹ (which is remarkably insensitive to Cu displacement in pyramidal complexes) and a band diagnostic for the macrocycle at approximately 1210 cm⁻¹. A representative spectrum is shown in Figure 1A.

Four-Coordination: [Cu(TIM)](BPh₄)₂. The structure¹⁷ of [Cu(TIM)](BPh₄)₂ is shown in Figure 2. The copper atom resides at a center of symmetry with phenyl groups from the BPh₄⁻ counterions centered above and below the planar CuN₄ unit. Carbon atoms of these phenyl groups are the nearest potential axial ligands, and they are over 4.25 Å from the

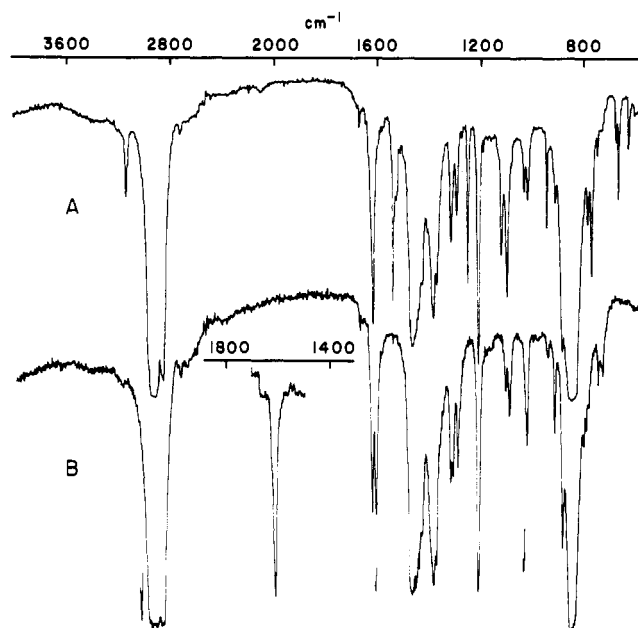


Figure 1. Infrared spectra of (A) [Cu(TIM)(1-MeIm)](PF₆)₂ and (B) [Cu(TIM)Cl]PF₆. Insert is ν_{CN} of a CH₂Cl₂ solution.

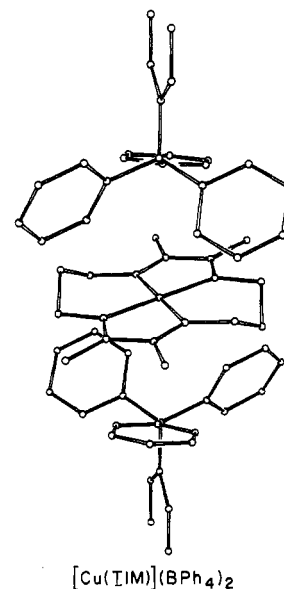


Figure 2. Structure of [Cu(TIM)](BPh₄)₂ showing relationship of Cu to BPh₄⁻.

copper atom. Thus, the [Cu(TIM)]²⁺ cation in this structure is appropriately considered as a member of the relatively rare class of rigorously four-coordinate planar Cu^{II} complexes.

The electronic spectrum of [Cu(TIM)](BPh₄)₂ was obtained in the solid state with use of photoacoustic spectroscopy. The spectrum consists of two intense absorptions at 3.85 and 2.94 μm^{-1} and a lower energy shoulder at 2.3 μm^{-1} . All Cu^{II} complexes of [14]-4,11-diene-N₄ macrocycles exhibit an intense absorption at approximately 3.85 μm^{-1} .¹⁸ This absorption is also observed for Cu^{II} complexes of [14]ane-N₄ macrocycles and may therefore be assigned to a L_{N σ} → M _{σ} charge-transfer transition.^{19–22} The observation of two intense near-UV transitions for [Cu(TIM)](BPh₄)₂ is characteristic

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Table IV. EPR Spectra^a

compd	medium	g_{\parallel}	g_{\perp}	g_{iso}	$10^4 \times A_{\parallel}$, cm ⁻¹	$10^4 \times A_{\perp}$, ^b cm ⁻¹	$10^4 \times A_{iso}$, cm ⁻¹	$10^4 \times {}^N A_{\parallel}$, cm ⁻¹	$10^4 \times {}^N A_{\perp}$, cm ⁻¹
Cu(TIM)(BPh ₄) ₂	Ni(TIM)(BPh ₄) ₂	2.141	2.037	2.072 ^c	216	40	99 ^d	13	15
Cu(TIM)(PF ₆) ₂ ·xH ₂ O	acetone	2.158	2.054	2.083	203	30	86		
Cu(TIM)Cl ₂	CHCl ₃	2.165	2.051	2.099	204	20	71		
Cu(TIM)(NCS) ₂	CH ₂ Cl ₂	2.171	2.054	2.107	199	30	84	12 ^g	13 ^g
[Cu(TIM)]PF ₆	acetone	2.158	2.060	2.093	197	30	72		
[Cu(TIM)Br]PF ₆	CH ₂ Cl ₂	2.174	2.060	2.102	196	30	69		
[Cu(TIM)Cl]PF ₆	CH ₂ Cl ₂ ^e	2.165	2.060	2.100	195	20	65		
	acetone	2.159	2.055	2.098	190	20	65		
[Cu(TIM)NCS]PF ₆	acetone	2.161	2.060	2.093	191	20	70		
	CH ₂ Cl ₂	2.165	2.070	2.098	195	20	69	11	15
	acetone + NaNCS ^f	2.156	2.053	2.096	206	35	72		
[Cu(TIM)(1-MeIm)](PF ₆) ₂	acetone	2.155	2.051	2.096	183	20	67		

^a Via first-order spectral analysis: g_{\parallel} , g_{\perp} , and A_{\parallel} determined at 77 K; A_{iso} and g_{iso} determined at ambient temperature for 5×10^{-3} M solutions. ^b Maximum values estimated from spectra taken at 77 K. ^c Calculated using $g_{\perp} = 1/2(3g_{iso} - g_{\parallel})$. ^d Estimated using $A_{iso} = 1/3(A_{\parallel} + 2A_{\perp})$, given that A_{\parallel} and A_{\perp} have the same sign. ^e Spectrum was taken at ~100 K. ^f $[NCS^-]/[Cu] = 3.5$. ^g Superhyperfine due to TIM nitrogen atoms.

Table V. Conductivity Data in Acetone

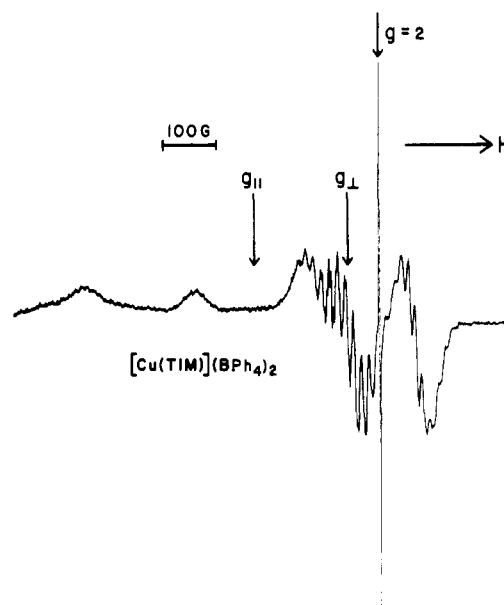
compd	slope of $c^{1/2}$ vs. λ_e	λ_0	type	ref
[Cu(terpy) ₂](PF ₆) ₂	-2360	211	2:1	this work
[Cu(TIM)(1-MeIm)](PF ₆) ₂ ^a	-2695	217	2:1	this work
[Cu(TIM)Cl]PF ₆	-844	166	1:1	this work
[Cu(TIM)NCS]PF ₆	-1130	184	1:1	this work
[Ni[16]dieneN ₄](PF ₆) ₂	-3180	214	2:1	23
[Ni[16]dieneN ₄] ₂ Ox](PF ₆) ₂	-2240	195	2:1	23
[Ni(AT)]PF ₆	-900	188	1:1	23
[Ni(CHOAT)]PF ₆	-800	182	1:1	23
[Cu(terpy)OAc]PF ₆	-790	167	1:1	58

^a Data for this complex represent the best straight-line fit to a smooth curve.

of other TIM complexes as well. For example, the spectra of Ni(TIM) complexes generally feature intense absorptions at approximately 2.5 and 3.4 μm^{-1} .²³ In light of the foregoing discussion, and given the X α calculations,¹⁴ the absorption at 3.85 μm^{-1} is assigned to a LMCT transition where the orbitals involved are essentially N lone pair and Cu d_{xy} in character, respectively. The 2.94- μm^{-1} band is assigned to a LMCT transition originating in an orbital with C-N π character.¹⁴ The assignment of the transition giving rise to the 2.3- μm^{-1} shoulder is consistently less straightforward. Such a band might be assigned to an envelope of d-d transitions (as is the commonly accepted practice).²⁰ However, the observed shoulder has tentatively been assigned to a transition best described as having a character intermediate between those of LMCT and d-d transitions.¹⁴

The color of [Cu(TIM)](BPh₄)₂ dissolved in acetone and acetonitrile is pink and clearly different from the yellow-orange of the solid. This qualitative observation, coupled with several systematic studies of Cu(TIM)²⁺ complexes in solution, lead us to the following conclusions and observations: (1) Cu(TIM)²⁺ ions in solvents with even very modest donor abilities (e.g., trifluoroacetic acid) are most probably five- or six-coordinate. (2) [Cu(TIM)](BPh₄)₂ undergoes reaction in solution with the formation of at least two new copper complexes (vide infra).

The EPR powder spectrum of the complex obtained from a sample diluted by and coprecipitated with [Ni(TIM)](BPh₄)₂ is shown in Figure 3. With an X-band spectrometer, the nonaxial character of the molecule is not resolved and an axial spectrum with overlap of parallel and perpendicular features is observed. In addition to hyperfine splitting arising from the

Figure 3. EPR spectrum of [Cu(TIM)](BPh₄)₂.

interaction of the unpaired spin with the copper nucleus, superhyperfine splitting from interaction with four equivalent nitrogen atoms is observed. Values for the hyperfine coupling constants and g values obtained from this spectrum may be found in Table IV. The value of ${}^{\text{Cu}}A_{\parallel}$ (216×10^{-4} cm⁻¹) is large, as expected for four-coordinate planar Cu^{II} complexes, and comparable with values that have been obtained for copper phthalocyanine (217×10^{-4} cm⁻¹),²⁴ copper tetraphenylporphyrin (206×10^{-4} cm⁻¹),²⁵ and other 14-membered tetraazamacrocycles ($(199-222) \times 10^{-4}$ cm⁻¹).²⁶ The values of g_{\parallel} obtained for tetraaza macrocycles have been correlated with the σ -donor ability of the macrocycle and show the expected increase in value with increasing macrocycle ring size.²⁶ Values of g_{\parallel} from 2.13 to 2.15 are characteristic of 14-membered tetraaza macrocycles and comparable with the value of 2.141 obtained for [Cu(TIM)](BPh₄)₂. The g_{\perp} values for the Cu^{II} complexes of the phthalocyanine and tetraphenylporphyrin macrocycles are 2.160²⁴ and 2.19,²⁵ respectively. The EPR spectra of frozen acetone solutions of [Cu(TIM)](BPh₄)₂ are

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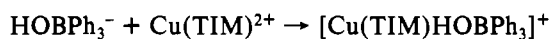
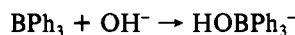
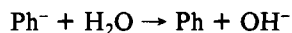
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indistinguishable from those obtained for $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ and are most consistent with a five- or six-coordinate structure in solution from comparison with the EPR spectra of $\text{Cu}(\text{TIM})$ complexes of known structure (see Table IV).

When acetone solutions of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ are prepared anaerobically, the color changes from pink to an intense blue ($E_{\text{max}} = 1.34 \mu\text{m}^{-1}$) over a period of hours. The EPR spectra of these solutions diminishes over time and is nearly absent after 19 h. Upon exposure of the solutions to air, the intense absorption at $1.34 \mu\text{m}^{-1}$ disappears and the solution becomes yellow-brown. When the reaction of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ in acetone was scaled up to concentrations suitable for isolation of $\text{Cu}(\text{TIM})^+$ salts, light blue crystals formed in 25 min. These crystals were not air sensitive and are characterized as the five-coordinate Cu^{II} complex $[\text{Cu}(\text{TIM})\text{HOBPh}_3](\text{BPh}_4)$. The light blue crystals redissolve in acetone to give a solution that under anaerobic conditions also loses its EPR spectrum upon standing. The EPR spectrum of the light blue crystals (freshly dissolved in acetone and then studied in frozen solution) is similar to the EPR spectra of the other five-coordinate $\text{Cu}^{\text{II}}(\text{TIM})$ complexes (Table IV) with $A_{\parallel} = 195 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} \leq 23 \times 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 2.168$, and $g_{\perp} = 2.059$. The infrared spectrum of the crystals contains bands characteristic of TIM ($\nu_{\text{CN}} = 1602 \text{ cm}^{-1}$, a band at 1203 cm^{-1}), BPh_4^- ($\nu_{\text{CH}} = 3060 \text{ cm}^{-1}$, $\nu_{\text{C=C}} = 1580 \text{ cm}^{-1}$, several strong bands in the $700\text{--}800\text{-cm}^{-1}$ region), and a new Ph-containing species which features absorptions in the $3000\text{--}3850\text{-}$, $1540\text{--}1580\text{-}$, and $850\text{--}900\text{-cm}^{-1}$ regions. When the compound is dissolved in acetone, the axial ligand can be removed with acid. The resulting spectrum has a broad absorption maximum at $1.87 \mu\text{m}^{-1}$ and is identical with that obtained for solutions of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$ ($E_{\text{max}} = 1.87 \mu\text{m}^{-1}$, $\epsilon = 96.6 \text{ M}^{-1} \text{ cm}^{-1}$) under the same acidic conditions. With use of the above extinction coefficient, the molecular weight of the unknown compound was calculated to be 862, corresponding to a loss of 78 molecular weight units from $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$. This molecular weight is in excellent agreement with the value obtained from the nitrogen analysis (865) discussed below and corresponds to the loss of approximately one phenyl group from the starting material. These data suggest that the compound contains $\text{Cu}(\text{TIM})$, BPh_4^- , and a ligand containing the BPh_3 group. A possible scheme for deriving a uninegative ligand containing BPh_3 is



The suggestion that the product is $[\text{Cu}(\text{TIM})\text{HOBPh}_3](\text{BPh}_4)$ is supported by its infrared spectrum. A sharp absorption at 3590 cm^{-1} is attributable to ν_{OH} , and the bands at 844 and 862 cm^{-1} are split by an amount consistent with B–O bonds involving ^{10}B and ^{11}B isotopes. The conclusion is also supported by the elemental analysis of the compound. (Anal. Calcd for $[\text{Cu}(\text{TIM})\text{HOBPh}_3](\text{BPh}_4)$: C, 75.55; H, 6.68; N, 6.29; Cu, 7.14. Found: C, 75.45; H, 6.82; N, 6.28; Cu, 7.09.)

The apparent reduction of the $\text{Cu}^{\text{II}}(\text{TIM})$ species in acetone is presumably due to the BPh_4^- anion, given that other salts of $\text{Cu}(\text{TIM})$ were not observed to undergo the same reaction. Since BPh_4^- is known to be a source of Ph^- anions^{27–29} and a reducing agent,³⁰ and given that the similar copper complex

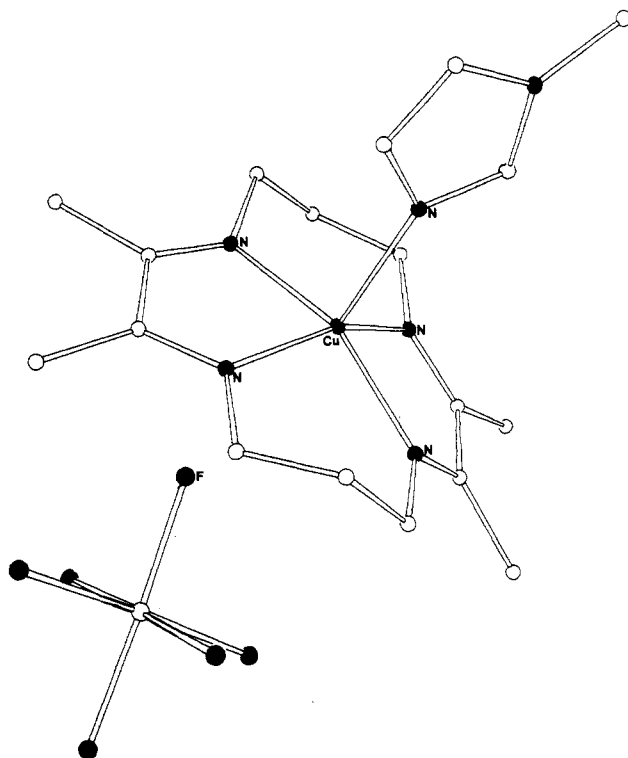


Figure 4. Structure of $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$.

of **2** undergoes reduction to give an intensely blue species ($E_{\text{max}} = 1.48 \mu\text{m}^{-1}$),^{11,31} there is ample precedence for the proposed reduction of $\text{Cu}(\text{TIM})^{2+}$ to $\text{Cu}(\text{TIM})^+$ in our system, where $\text{Cu}(\text{TIM})^+$ is the complex giving rise to the $1.34\text{-}\mu\text{m}^{-1}$ absorption. The results of $X\alpha$ calculations of models for $\text{Cu}(\text{TIM})^+$ suggest that such a complex is a Cu^{I} species, with the intense $1.34\text{-}\mu\text{m}^{-1}$ band being assigned to a MLCT transition.¹⁴

Five-Coordination. The crystal structures of the following five-coordinate complexes of $\text{Cu}(\text{TIM})$ have been determined:¹⁷ $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$,³² $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$, $[\text{Cu}(\text{TIM})\text{Br}]\text{PF}_6$, and $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$.³³ The structure of the first compound is shown in Figure 4. It features pyramidal coordination of the copper atom, with the four TIM nitrogen atoms forming a rectangular base. The copper atom is displaced 0.44 \AA from the plane of the TIM nitrogen atoms. This displacement is significantly greater than the $0.2\text{--}0.3 \text{ \AA}$ typically observed for pyramidal copper complexes³⁴ but appears to be characteristic of pyramidal copper complexes of both TIM¹⁷ and **2**.^{35–38} Displacements ranging from 0.32 ³⁶ to 0.58 \AA ³⁵ have been observed for $\text{Cu}(\text{2})\text{L}$ complexes, with the pyridine adduct exhibiting a displacement of 0.48 \AA .³⁸ In the pyramidal copper complexes of TIM and **2**, the macrocycle is not flat but is bowed.^{17,35–38} Figure 4 also shows the position of one of the PF_6^- anions, which is situated such that a fluorine atom is in an axial position to the copper, although at a distance quite long to be considered a sixth ligand (3.55 \AA). (It is to be noted that axially coordinated PF_6^- has been observed in the structures of two macrocyclic complexes, $[\text{Co}([14]\text{-dieneN}_4)(\text{H}_2\text{O})(\text{PF}_6)]\text{PF}_6$ ³⁹ and $[\text{Cu}([14]\text{-dieneN}_4)(\text{H}_2\text{O})$

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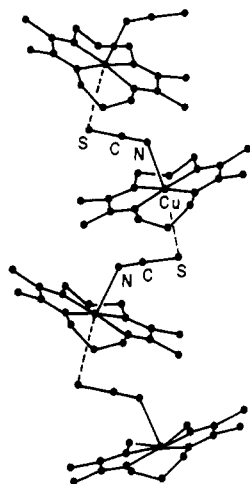


Figure 5. Structure of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$.

$(\text{PF}_6)\text{PF}_6$,⁴⁰ where the M–F distances are 2.559 and 2.652 Å, respectively.)

The complexes $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$ and $[\text{Cu}(\text{TIM})\text{Br}]\text{PF}_6$ have been shown by X-ray diffraction studies to be isomorphous.¹⁷ The structure of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$ is similar to that of $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$. The copper atom is displaced 0.34 Å from the N_4 plane. The Cu–Cl bond length of 2.404 Å is similar to that observed for other pyramidal complexes with axial Cl^{41,42} and intermediate between the distances expected for ionic (2.62 Å) and covalent (2.27 Å) Cu–Cl bonds.⁴¹ The PF_6^- anion is again located in the vacant axial site with a Cu–F distance of 3.38 Å. One of the six-membered rings is situated such that the middle methylene carbon is “up” (on the same side of the copper atom as the chlorine atom). The other six-membered ring is disordered and exists in both “up” and “down” positions. Thus, both boat and chair conformations of TIM exist in the solid state of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$. The infrared spectra of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$ (see Figure 1B) and $[\text{Cu}(\text{TIM})\text{Br}]\text{PF}_6$ are atypical in that these compounds feature two ν_{CN} bands near 1600 cm^{-1} separated by 15 cm^{-1} . The hypothesis is that the splitting of the single ν_{CN} band arises from the presence of both chair and boat conformations of the macrocycle in the solid state and is supported by the observation of only one strong ν_{CN} band at 1605 cm^{-1} in the CH_2Cl_2 solution spectrum, where the lattice forces that might cause the disorder are removed.

The structure of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ is shown in Figure 5.^{17,33} The structure has been described as consisting of $\text{Cu}(\text{TIM})\text{NCS}$ units, each copper atom having a long axial interaction with a sulfur atom from an NCS^- ligand of a neighboring molecule (see Table II).¹⁷ This structure is similar to that observed for *catena*-(μ -isothiocyanato)-*N'*-(pyridylmethylene)-*N'*-salicyloylhydrazinato-*N,N',O*copper(II).⁴³ Generally, covalent M–NCS interactions lead to linear M–NCS bonds.⁴⁴ Bent M–NCS interactions like those in $[\text{Cu}(\text{en})_2\text{NCS}]\text{ClO}_4$ (M–N–C angle 97°) have been described as involving ionic interactions.⁴⁵ The M–NCS bond length is 2.73 Å in $[\text{Cu}(\text{en})_2\text{NCS}]\text{ClO}_4$. A Cu–N bond length that

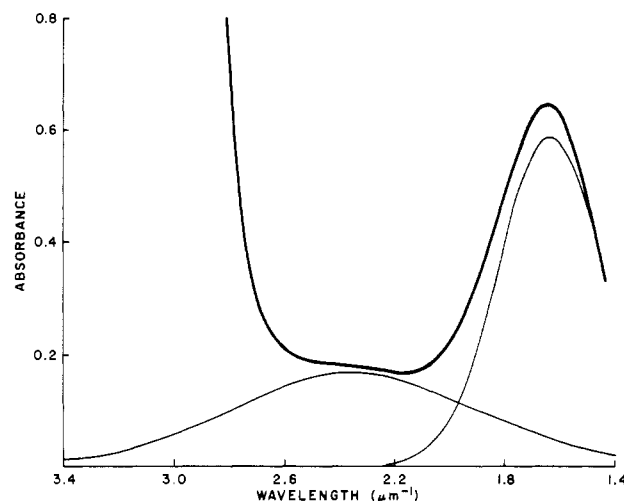


Figure 6. Electronic spectrum of $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$ in acetone.

might be considered typical for $\text{Cu}(\text{TIM})$ would be about 2.15 Å (Cu– $\text{N}_{\text{ax}} = 2.139$ Å in $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$;¹⁷ Cu– $\text{N}_{\text{ax}} = 2.17$ Å in $[\text{Cu}(2\text{py})\text{ClO}_4]$.³⁸ The Cu–NCS bond length in $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ (2.39 Å) thus may be intermediate between an ionic and a covalent Cu–N interaction. It is interesting to note that the Cu–NCS angle in the complex is also intermediate between those observed for the covalent and the ionic NCS^- interactions described above. Alternatively, the complex may be described as having a tetragonal six-coordinate (4+2) structure with a sulfur atom in the sixth position. The Cu–S distance (3.34 Å) is only 0.07 Å longer than that observed for tetragonal-octahedral $\text{Cu}(\text{en})_2(\text{SCN})_2$,⁴⁶ although it is 0.73 Å longer than that observed for the axial Cu–SCN bond in square-pyramidal $[\text{Cu}(\text{trien})\text{SCN}]\text{SCN}$ ⁴⁷ and 1.0 Å longer than found for an equatorial Cu–SCN bond in another square-pyramidal complex.⁴⁸

The question of the coordination number of the copper in $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ may be an open one. The chief piece of data supporting a five-coordinate description is the “long” Cu–S distance. Those data favoring a tetragonal six-coordinate (4+2) description are as follows: (1) the small displacement of the copper from the N_4 plane (0.07 Å), (2) the “intermediate” Cu–NCS distance, and (3) the dramatic change in electronic spectrum of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ on going from the solid state to solution (vide infra).

Electronic Spectra. In keeping with the characteristics of other $\text{Cu}(\text{II})$ tetraimine macrocyclic complexes, 2–4,^{11–13} the electronic spectra of pyramidal $\text{Cu}(\text{TIM})\text{L}$ complexes exhibit a broad, low-energy absorption in the visible region of the spectrum (2.0–1.5 μm^{-1}). For $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2(\text{s})$ and for $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6(\text{s})$ this band sharpens upon cooling to 77 K but does not display any multiplicity and shifts only slightly in energy from the value observed at room temperature (see Table III). In solution the dominant features of the spectra of the pyramidal complexes are an intense absorption in the near-UV, which trails into the visible region, and the broad absorption previously mentioned. (However, evidence of an absorption of low intensity between these two features is usually observed as illustrated in Figure 6). The energies (Δ) of the maximum of this broad absorption have been used to generate spectrochemical series for various axial ligands in complexes of 2–4.^{11–13} For TIM, the series obtained is dependent on the physical state. The series consists in part of the sequence $\text{Im} < 1\text{-MeIm} < \text{Cl}^- \approx \text{py} \approx \text{NH}_3 < \text{Br} \leq \text{NCS}^-$

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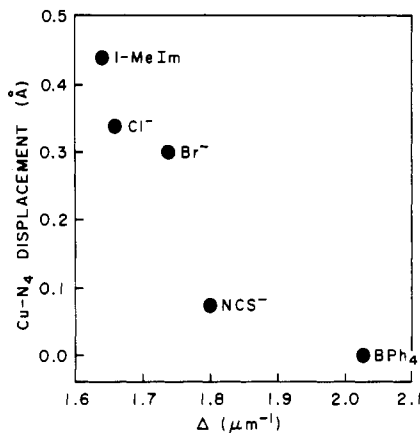


Figure 7. Relationship between copper displacement (δ) and the energy of the lowest energy electronic transition (Δ).

in the solid state and $\text{Cl}^- < \text{Br}^- < \text{NCS}^- < 1\text{-MeIm} \approx \text{Im} < \text{py}$ in acetone solution, when written in the usual convention of increasing Δ . With respect to their usual positions in the standard spectrochemical series,⁴⁹ it is noted that the halides are in an inverted order and are positioned significantly higher in the solid series than expected.

Addison, Wicholas, and co-workers have discussed the observed spectrochemical series in terms of a crystal field model wherein the lowest energy absorption is described as an envelope of d-d transitions, the energy of which, Δ , is representative of the $d_{z^2} \rightarrow d_{xy}$ transition (or the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition depending upon the orientation of the macrocyclic ligand with respect to the x and y axes).¹¹ They have proposed that Δ is determined primarily by two factors: (1) the strength of the axial donor (the stronger this donor, the higher in energy the d_{z^2} orbital will be and the smaller Δ will be) and (2) the displacement of the copper from the N_4 plane (the larger the displacement, the lower in energy the d_{xy} (or $d_{x^2-y^2}$) orbital will be and the smaller Δ will be). Coltrain and Jackels¹² have suggested that the π -donating or -accepting properties of the axial ligand must also be considered. Specifically, they suggest that the π -donor capability of the anionic axial ligands may raise the energy of the d_{xz} and d_{xy} orbitals above that of the d_{z^2} orbital and thereby contribute to the red shift observed in the spectra of complexes containing these ligands.

The results of the SCF- $X\alpha$ -SW calculations on models of pyramidal $[\text{Cu}(\text{TIM})\text{Cl}]^+$ indicate the following:¹⁴ (1) The Cu-Cl π interaction is essentially zero. (2) The lowest energy transition is analogous to those involved in the lowest energy transition predicted for the four-coordinate complex. Thus this transition cannot be simply described as either a d-d transition or a LMCT transition. (3) The dominant structural feature influencing the lowest energy transition is not the Cu-Cl distance but the degree of copper displacement from the N_4 plane.

Given these results, it seems appropriate to focus attention on the out-of-plane distance. For Cu(TIM) complexes, there currently are available six single-crystal structures.^{17,32,33,50} The out-of-plane distances for five of these complexes are plotted against the values for Δ in the solid state (see Figure 7). As can be seen, the plot is certainly consistent with the notion that displacement dominates the value of Δ . However, structures are needed with displacements in the 0.1–0.3- \AA range in order to more clearly define the relationship between Δ and displacement.

One of the interesting aspects of the spectra of the five-coordinate complexes is the variable sensitivity to change as a function of physical state. For $\text{Cu}(\text{TIM})\text{L}$ complexes where L is a neutral ligand, there is a relatively small variation in Δ from the solid state to solution. However, when L is NCS^- or a halide, there is a significant red shift from solid to solution (Table III). With use of the concepts developed in conjunction with Figure 7 it is as though the Cu- N_4 displacement increases for anionic ligands as the state changes from solid to solution. In fact, we propose that this increase in displacement has occurred. For $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ this is easily rationalized in terms of the dissociation of the "polymeric" solid-state structure into discrete five-coordinate cations through the loss of the weak Cu-S interaction. The loss of this axial interaction would then allow the Cu to move farther out of the equatorial plane toward the remaining NCS^- ligand. Evidence supporting this dissociation includes the following: (1) Conductivity data are consistent with $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ being a 1:1 electrolyte in acetone solution (Table V). (2) The observed red shift in the lowest energy absorption places the band maximum at a value consistent with those of other $\text{Cu}(\text{TIM})\text{L}$ complexes where L is a nitrogen donor ligand (Table III). (3) Frozen CH_2Cl_2 solutions exhibit EPR spectra with ¹⁴N superhyperfine splittings arising from four equivalent nitrogen atoms and one unique nitrogen atom.

Similar arguments can be advanced to explain the red shifts observed for the halide complexes. Hathaway has suggested that potential ligands (particularly charged ones) that are located in axial positions at rather large distances from the copper affect the physical properties of the complex because of their electrostatic interaction with the copper center.^{34,51} It has already been pointed out that the known structures of PF_6^- salts of $\text{Cu}(\text{TIM})$ complexes feature an F atom of a PF_6^- anion in the "vacant" axial position. If, due to solvation, this PF_6^- anion were further separated from the cation, then the electrostatic interaction between them would be diminished or removed. This electrostatic or ionic interaction between the PF_6^- and the copper center can be thought of in terms of moderating or lessening the displacement of the copper out of the TIM N_4 plane toward the fifth ligand. In solution, therefore, the copper atom would be displaced even further from the N_4 plane in the direction of the fifth ligand. If the presence of PF_6^- in the solid state of the $[\text{Cu}(\text{TIM})\text{X}]\text{PF}_6$ complexes ($\text{X} = \text{Cl}^-, \text{Br}^-$) were responsible for the difference in the solid-state and solution-state spectra, then the red shift observed for these complexes should not be observed for $\text{Cu}(\text{2})\text{X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) since the latter complexes are neutral, and therefore no counterion is present. In fact, the spectra of the $\text{Cu}(\text{2})\text{X}$ complexes show little dependency on physical state.¹¹ This fact, coupled with the observation of similar Δ values for $\text{Cu}(\text{TIM})\text{X}^+$ and $\text{Cu}(\text{2})\text{X}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) in solution, suggests that there is significant interaction between copper and PF_6^- in the solid state of $[\text{Cu}(\text{TIM})\text{X}]\text{PF}_6$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) salts. Conductivity studies of acetone solutions of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$ have yielded data consistent with other PF_6^- salts of univalent cations (Table V), indicating that no special association between the cation and the PF_6^- anion exists in solution. The question of why the spectra of $[\text{Cu}(\text{TIM})\text{L}](\text{PF}_6)_2$ ($\text{L} =$ neutral nitrogen donor) complexes do not show a similar tendency to be red shifted may be answered in part by noting that they are uni-divalent electrolytes. One would expect much more extensive and stronger ion pairing between divalent cations and PF_6^- than between univalent cations and PF_6^- . Thus, it can be argued that the change in the copper center's environment from the solid state to solution is much less for the PF_6^- salts of the divalent cations.

(49) When only the strength of the ligand-metal interaction is of importance, the spectrochemical series expected is $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NCS}^- < \text{py} \approx \text{NH}_3$.

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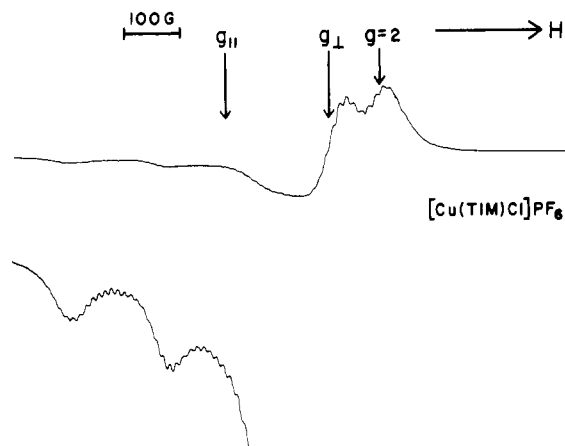


Figure 8. EPR spectrum of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$. The lower curve is an enlargement of the two low-field features.

EPR. The EPR spectra obtained from frozen solutions of $\text{Cu}(\text{TIM})\text{L}$ complexes are similar to the powder spectrum of $[\text{Cu}(\text{TIM})](\text{BPh}_4)_2$. Examination of the data in Table IV indicates that the addition of a fifth ligand has the effect of decreasing A_{\parallel} and A_{iso} while increasing g_{\parallel} and g_{\perp} . The changes in g values can be understood qualitatively from the expressions

$$g_{\parallel} = 2.0023 - \frac{8\lambda\alpha^2\beta^2}{\Delta_{\parallel}} \quad g_{\perp} = 2.0023 - \frac{2\lambda\alpha^2\delta^2}{\Delta_{\perp}}$$

which assume C_{4v} symmetry (axial symmetry) for the complexes. These expressions are identical with those employed for interpreting square-planar Cu^{II} EPR spectra.^{34,52} The values of λ (the spin-orbit coupling constant) and α^2 , β^2 , and δ^2 (the coefficients of the Cu d_{xy} , $d_{x^2-y^2}$, and e_g orbitals in their respective molecular orbitals) are assumed to be relatively constant. Thus only Δ_{\parallel} and Δ_{\perp} (the energies of the $d_{x^2-y^2} \rightarrow d_{xy}$ and $e_g \rightarrow d_{xy}$ transitions) are variables. Larger g values are expected to accompany the pyramidalization of the Cu site, since the electronic transitions Δ_{\parallel} and Δ_{\perp} would shift to lower energies upon addition of a fifth ligand, and displacement of the Cu from the N_4 plane.^{34,53} The lowering of the absolute value of the Cu hyperfine coupling constants from the value obtained for the planar complex is expected to occur along with the positive shift of the g values. An expression for A_{\parallel} may be written as⁵⁴

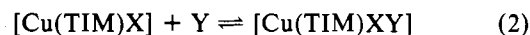
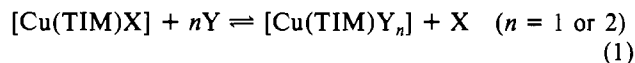
$$A_{\parallel} = P[-\alpha^2(\frac{4}{7} + K) + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0.04]$$

The parameters P ($P = \beta_e g_e \beta_n g_n \langle r^{-3} \rangle_{3d} = 0.0388 \text{ cm}^{-1}$ for a free Cu^{2+} ion), and K (a Fermi hyperfine coupling term) are relatively constant.⁵⁵ Assuming that A_{\parallel} is negative (as is usually the case⁵⁶), then as g_{\parallel} and g_{\perp} increase, the absolute value of A_{\parallel} decreases.

The EPR spectrum of $[\text{Cu}(\text{TIM})\text{Cl}]\text{PF}_6$ (Figure 8), like that of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$, shows evidence of hyperfine interaction of the unpaired spin with the nucleus of the axially ligating atom. Spectral simulation⁵⁷ and theoretical predictions based on SCF- $X\alpha$ -SW calculations¹⁴ both indicate that this interaction is small. A detailed analysis of the factors determining

the EPR spectrum of $\text{Cu}(\text{TIM})\text{Cl}^+$ in light of the results of $X\alpha$ calculations is presented in the following paper.¹⁴

Variable Axial Ligation. Two general equations can be used to represent axial ligation in the $\text{Cu}(\text{TIM})^{2+}$ system (eq 1 and 2).



A case pertaining to eq 1 involves $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$. The coordination polyhedron of the copper persists on going from the solid state to acetone solution (as indicated by its electronic spectrum) but clearly changes when either MeOH or trifluoroacetic acid is used as the solvent. Given that the electronic spectra of $\text{Cu}(\text{TIM})(\text{PF}_6)_2 \cdot x\text{H}_2\text{O}$ and $[\text{Cu}(\text{TIM})(1\text{-MeIm})](\text{PF}_6)_2$ are identical in MeOH (Table III), it is assumed that eq 1 represents the process when $\text{X} = 1\text{-MeIm}$ and $\text{Y} = \text{MeOH}$. The two complexes also give the same spectrum in trifluoroacetic acid (Table III). Once again the 1-MeIm has clearly dissociated from the coordination polyhedron, the dissociation being enhanced by protonation of 1-MeIm.

Equation 2 unambiguously represents the formation of six-coordinated complexes. Although the only unmistakable example of six-coordination known to us is $[\text{Cu}(\text{TIM})(\text{H}_2\text{O})_2]^{2+}$ in the nitrate salt (Table II), studies of the $\text{Cu}(\text{TIM})^{2+}\text{-NCS}^-$ system in solution suggest that the bis-(thiocyanate) complex is present under certain circumstances. However, in the solid state, the readily prepared crystalline $\text{Cu}(\text{TIM})(\text{NCS})_2$ (see Experimental Section) is probably best described as $[\text{Cu}(\text{TIM})\text{NCS}]\text{NCS}$, a direct analogue of the crystalline $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ previously discussed. We conclude this because of the similarity of the electronic spectra of the two solids (Table III) and because $\text{Cu}(\text{TIM})(\text{NCS})_2$ exhibits two ν_{CN} bands (2060 and 2045 cm^{-1}), the latter of which is at the same position as the band for $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ (2045 cm^{-1}). (Note: TIM restricts the coordination polyhedron to the trans isomers only.)

The electronic spectra of $\text{Cu}(\text{TIM})(\text{NCS})_2$ and $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ dissolved in CH_2Cl_2 differ in that the lowest energy transition of the all-thiocyanate derivative is at higher energy with a lower extinction coefficient than the PF_6^- salt (Table III). This is consistent with the formation of $[\text{Cu}(\text{TIM})(\text{NCS})_2]$, where the copper would be expected to reside in the TIM nitrogen atom plane at a center of symmetry¹⁷ (vide infra). With use of benzil as a standard the experimentally determined molecular weight for $\text{Cu}(\text{TIM})(\text{NCS})_2$ in CHCl_3 is 495; the infrared spectrum of a CHCl_3 solution exhibits one ν_{CN} band (2070 cm^{-1}). The experimentally determined molecular weight, although high by 16%, taken with the infrared spectrum supports the notion that $[\text{Cu}(\text{TIM})(\text{NCS})_2]$ is present in CHCl_3 .

The conductivity of acetone solutions of $\text{Cu}(\text{TIM})(\text{NCS})_2$ as a function of concentration and the electronic spectra of acetone solutions of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ containing variable amounts of NCS^- suggest that $[\text{Cu}(\text{TIM})\text{NCS}]^+$ and $[\text{Cu}(\text{TIM})(\text{NCS})_2]^0$ are in equilibrium in that solvent (eq 2, where $\text{X} = \text{Y} = \text{NCS}^-$). The equilibrium constant corresponding to eq 2 determined conductometrically at 25 °C⁵⁸ is $7.7 \times 10^2 \text{ M}^{-1}$. The value of the association constant was also estimated spectrophotometrically at ambient temperatures with use of standard solutions of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ with varying concentrations of NaNCS . The spectra obtained from solutions containing added NCS^- exhibit an isosbestic point at 1.93 μm^{-1} and give a value for the association constant of $4.5 \times 10^2 \text{ M}^{-1}$. The spectrum containing no added NaNCS does not pass

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through the isosbestic point, and we propose that the reaction represented by eq 1 may also be important for solutions with low concentrations of free NCS^- (where $\text{X} = \text{NCS}^-$ and $\text{Y} = \text{acetone}$ or impurities in the solvent, such as water). This postulate is consistent with the fact that the solution with the lowest concentration of $[\text{Cu}(\text{TIM})\text{NCS}]\text{PF}_6$ in the Onsager study gives an equivalent conductance higher than that predicted from the straight line described by the other four points.

The picture for the $\text{Cu}(\text{TIM})^{2+}-\text{Cl}^-$ system is considerably less well developed than that for the NCS^- system just described. A deliquescent solid, tentatively formulated as $\text{Cu}(\text{TIM})\text{Cl}_2$, forms from a blue oil, which in turn separates from acetone solutions of $\text{Cu}(\text{TIM})(\text{PF}_6) \cdot x\text{H}_2\text{O}$ and excess LiCl . The solid is soluble in CH_2Cl_2 and CHCl_3 . In the latter the molecular weight is found to be 440 (calculated for $[\text{Cu}(\text{TIM})\text{Cl}_2]$, 383) with benzil as a standard. Given that this experimental value is 15% high and that for the NCS^- derivative is 16% high, it would seem that the two complexes exhibit similar states of aggregation in CHCl_3 .

Specifying the exact nature of the copper-axial ligand interaction for some complexes of the $\text{Cu}(\text{TIM})$ class clearly is not trivial and must be approached with great care whether in the solid phase or in solution.

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Electronic Structure of Copper Complexes Containing α -Diimine Ligands¹

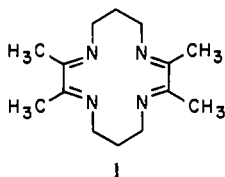
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SCF-X α -SW calculations have been carried out for $\text{Cu}(\text{N}_2\text{C}_2\text{H}_4)_2^{2+}$ and $\text{Cu}(\text{N}_2\text{C}_2\text{H}_4)_2\text{Cl}^+$, the simplest possible models for planar $\text{Cu}(\text{TIM})^{2+}$ and pyramidal $\text{Cu}(\text{TIM})\text{Cl}^+$, respectively, where TIM is a 14-membered macrocycle containing two α -diimine moieties. The electronic and EPR spectra of the complexes are interpreted with use of the results of the calculations. The electronic absorptions observed for $[\text{Cu}(\text{TIM})][\text{BPh}_4]_2$ at 2.94 and 3.85 μm^{-1} are confidently assigned to the LMCT transitions. The lowest energy absorptions observed for $[\text{Cu}(\text{TIM})][\text{BPh}_4]_2$ and $[\text{Cu}(\text{TIM})\text{Cl}][\text{PF}_6]$ are best described as intermediate in character between LMCT and d-d transitions. The largest factor influencing the energy of the lowest energy transition is shown to be the degree of copper atom displacement from the basal ligand plane. The effects of adding a fifth ligand to the planar complex to produce a pyramidal complex are discussed. Little covalency is predicted to result from the interaction of the $\text{Cu}(\text{II})$ and apical Cl^- centers in $\text{Cu}(\text{TIM})\text{Cl}^+$. The covalent bonding that is present appears to be almost entirely σ in character. The role of Cu 4s and 4p orbitals in the bonding scheme of $\text{Cu}(\text{TIM})\text{Cl}^+$ is predicted to be small. The ground state calculated for the reduced complex, $\text{Cu}(\text{TIM})^+$, contains a $\text{Cu}(\text{I})$ center obtained by addition of the electron acquired upon reduction to a molecular orbital that is largely $\text{Cu } d_{xy}$ in character. The intense absorption experimentally observed in the electronic spectrum of $\text{Cu}(\text{TIM})^+$ is assigned to a $d_{xy} \rightarrow \pi^*$ MLCT transition. No significant π interaction between Cu and ligand π^* orbitals is predicted to occur in the ground state of $\text{Cu}(\text{TIM})^+$, but a significant fraction of the electron added upon reduction does end up in the ligand σ -electron systems. This may explain the lowering of $\nu_{\text{C=N}}$ that has been observed upon reduction of $\text{Cu}(\text{II})$ α -diimine complexes.

Introduction

Complexes of the neutral, 14-membered, macrocyclic ligand TIM (1) have been synthesized and characterized for first-row



transition-metal ions of Fe ,²⁻⁵ Co ,^{6,7} Ni ,⁸ and Cu .⁹ In many cases the ligand possesses the ability to stabilize more than one oxidation state of a metal and is capable of allowing for facile interconversion of two oxidation states.⁴ Four-,¹⁰ five-,^{10,11} and six-coordinate^{2-5,8,12} complexes of TIM have been characterized via single-crystal X-ray diffraction techniques, and TIM invariably features a planar arrangement of its four N-donor atoms.

The coordination chemistry of copper complexes of TIM, discussed in the preceding paper, is extremely varied. Four-,

five-, and six-coordinate complexes have been characterized in the solid state,⁹⁻¹² and five- and six-coordinate complexes have been characterized in solution.⁹ Copper is the only metal explored to date that displays all three possible coordination numbers with TIM.

Both $\text{Cu}(\text{II})$ and formally $\text{Cu}(\text{I})$ complexes have been prepared.⁹ The latter have been characterized only in solutions that are not stable in air. The electronic structure of formally

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