

## Coordination Chemistry of a Copper(II) Tetraimine Macrocyclic: Four-, Five-, and Six-Coordinate Derivatives and Reduction Transmetalation to the Zinc(II) Complex

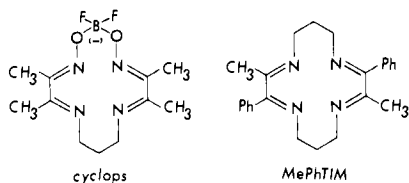
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The template condensation of 1-phenyl-1,2-propanedione and 1,3-diaminopropane in the presence of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol yields the Cu(II) complex of the macrocyclic ligand 2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (MePhTIM). Addition of excess potential ligands in methanol/water affords the five-coordinate complexes  $[\text{Cu}(\text{MePhTIM})\text{X}]\text{PF}_6$ , where  $\text{X} = \text{NCS}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , and  $[\text{Cu}(\text{MePhTIM})\text{L}](\text{PF}_6)_2$ , where  $\text{L} = \text{pyridine}$ , 4-methylpyridine, or *N*-methylimidazole. From acetone solutions containing excess potential ligand salts the following six-coordinate derivatives are isolated:  $[\text{Cu}(\text{MePhTIM})\text{X}_2]$ , where  $\text{X} = \text{NCS}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ . The formulations of the complexes are supported by elemental analyses, conductivity measurements, magnetic moments (solid state and solution), and spectroscopic measurements (solid-state and solution electronic spectra and infrared spectra). Data for the monothiocyanate derivative are consistent with a linkage isomerism in which thiocyanate is S-bonded in solution and N-bonded in solid state. The spectrochemical series for the five-coordinate derivatives is very similar to that observed for analogous  $[\text{Cu}(\text{cyclops})\text{L}]^{2+}$  complexes ( $\text{L} = \text{ligand}$ ), thus indicating that the complexes have rectangular-pyramidal geometry with the metal ion displaced out of the  $\text{N}_4$  plane. A qualitative molecular orbital treatment is offered to explain the apparent reversal of neutral ligands and anionic ligands in the spectrochemical series. The reduction of  $[\text{Cu}(\text{MePhTIM})]^{2+}$  by various chemical reducing agents is discussed. Reduction by zinc metal gives metallic copper and results in isolation of  $[\text{Zn}(\text{MePhTIM})\text{Cl}]\text{PF}_6$ . The proton and carbon-13 NMR spectra of the zinc complex are used to confirm the ligand structure. Finally,  $[\text{Zn}(\text{MePhTIM})\text{Cl}]^+$  is found to undergo transmetalation to the copper, nickel, or cobalt MePhTIM complex in the presence of acid and metal salt in methanol.

### Introduction

A number of recent studies involving copper(II) complexes of the macrocycle "cyclops" have demonstrated quite unusual



structural, spectroscopic, and chemical properties. X-ray structural investigations by Anderson and co-workers<sup>1-4</sup> of five-coordinate rectangular-pyramidal derivatives,  $[\text{Cu}(\text{cyclops})\text{L}]^{2+}$ , where  $\text{L} = \text{CN}^-$ ,  $\text{NCO}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{O}$ , or pyridine, have revealed a large apical displacement of the metal ion from the  $\text{N}_4$  plane, varying from 0.32 for  $\text{H}_2\text{O}$  to 0.58 Å for  $\text{NCO}^-$ . Also, a range of metal-apical ligand bond distances was found, varying from very short for  $\text{I}^-$  and  $\text{NCO}^-$  to normal for py and  $\text{H}_2\text{O}$ . Spectroscopic studies by Addison et al.<sup>5</sup> of the d-d maxima for a number of five-coordinate derivatives have resulted in the spectrochemical series  $\text{H}_2\text{O} \ll \text{C}(\text{CN})_3^- < \text{py} < \text{NMI} < \text{I}^- < \text{Br}^- < \text{N}(\text{CN})_2^- < \text{Cl}^- < \text{NCS}^- \ll \text{CN}^- < \text{NCO}^-$ . This series is atypical in the relative placement of the neutral nitrogen donor ligands and the halide ligands which are reversed in apparent ligand field strength compared to the classical spectrochemical series. Addison et al.<sup>5</sup> proposed an explanation for the series in terms of unusually strong interaction of anionic apical ligands with the metal ion and variability of apical displacement of the metal ion from the  $\text{N}_4$  plane. Their prediction is verified by the structural studies;<sup>4</sup> however, the two structural parameters are not found to vary systematically with respect to each other. This can be seen by comparing the  $\text{I}^-$  and py derivatives which have the same apical displacement but short and normal metal-apical ligand distances, respectively.

The unusual chemical reactivity of  $\text{Cu}^{\text{II}}(\text{cyclops})$  includes the ability to form adducts<sup>5</sup> with  $\text{I}^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$ . These

ligands normally cause reduction or disproportionation of  $\text{Cu}(\text{II})$ .<sup>6</sup> Upon chemical reduction the cyclops complexes do disproportionate,<sup>7,8</sup> but, interestingly, when the reducing agent is Zn metal,  $\text{Zn}^{\text{II}}(\text{cyclops})$  is isolated as a product.<sup>9</sup> Gagné and co-workers<sup>10</sup> used electrochemical methods to prepare and study  $\text{Cu}^{\text{I}}(\text{cyclops})$  and found stable five-coordinate adducts with  $\pi$ -accepting ligands such as CO and phosphines. An X-ray structural study<sup>9</sup> of  $[\text{Cu}(\text{cyclops})\text{CO}]$  revealed that the copper atom is situated 0.96 Å out of the  $\text{N}_4$  plane. A final aspect of  $\text{Cu}(\text{cyclops})$  chemistry is the facile formation of monoligand-bridged dimers,  $[\text{Cu}_2(\text{cyclops})_2\text{X}]^{2+}$ , where X is an anion or pyrazine.<sup>11</sup> The copper(II) ions in these complexes were found to be very weakly antiferromagnetically coupled ( $J < 1 \text{ cm}^{-1}$ ) because the unpaired electron on each copper ion is in a  $d_{x^2-y^2}$  orbital which is orthogonal to the bridging ligand orbitals.

Our interest in these complexes stems from our recent studies<sup>12</sup> of a similar ligand, 2,9-dimethyl-3,10-diphenyl-14]-1,3,8,10-tetraene $\text{N}_4$ , hereafter denoted MePhTIM.  $\text{Cu}(\text{MePhTIM})$  complexes are of interest for comparison with  $\text{Cu}(\text{cyclops})$  in order to ascertain to what degree the unusual properties of the cyclops complexes are determined by ligand character. MePhTIM has the same bis- $\alpha$ -diimine structure and ring size as cyclops but differs in charge due to replacement of the difluoroborate group by methylene groups. MePhTIM might be expected to provide a slightly weaker ligand field than cyclops, and thus the copper ion would be expected to interact more strongly with axial ligands. In the work described herein we used a template synthesis<sup>12</sup> to prepare  $\text{Cu}^{\text{II}}(\text{MePhTIM})$  and then prepared a series of axial ligand derivatives. The complexes were found to be quite versatile in forming four-, five-, and six-coordinate derivatives. The  $\text{Zn}^{\text{II}}(\text{MePhTIM})$  complex was inaccessible via the template synthesis but could be isolated upon reduction of  $[\text{Cu}$

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(MePhTIM)]<sup>2+</sup> with zinc metal. Characterization data for both the Cu and Zn complexes are interpreted with a view toward further understanding the unusual properties found for both Cu(cyclops) and Cu(MePhTIM).

### Experimental Section

**Materials.** The reagents and solvents used in the following preparations were commercially obtained as reagent grade unless otherwise noted and were used without further purification. The 1,3-diaminopropane (Eastman, practical) showed a trace water impurity by NMR and was used as obtained. Solvents used for electronic spectra, conductivities, and magnetic moments were of spectral analytical quality. Deuterated solvents were obtained from Norell Chemical Co.

**Preparations.** Unless otherwise stated the following compounds were collected by suction filtration, washed with ethanol or 1:1 methanol/water, and then dried in a vacuum over activated alumina for at least 12 h.

**[Cu(MePhTIM)]ZnCl<sub>4</sub>.** 1-Phenyl-1,2-propanedione (5.92 mL, 0.04 mol) was added dropwise to a stirred solution of 1,3-diaminopropane (3.36 mL, 0.04 mol) in methanol (65 mL). After 15 min a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (2.72 g, 0.016 mol) in 30 mL methanol was added in bulk, resulting in a deep blue solution. After the mixture was stirred for 40 min, a solution of ZnCl<sub>2</sub> (8.00 g, 0.06 mol) in methanol/ethanol (10 mL/30 mL) was added to give a purple solution. After 3–5 h absolute ethanol (20 mL) was added, and the solution was refrigerated for 24 h to yield the purple crystalline product (3.4 g, 33%). The yield of this reaction is quite sensitive to variations in mixing times and amount of CuCl<sub>2</sub>·2H<sub>2</sub>O.

**[Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub>.** A solution of KPF<sub>6</sub> (1.72 g, 0.009 mol) in 1:1 methanol/water (70 mL) was added slowly to a stirred solution of [Cu(MePhTIM)]ZnCl<sub>4</sub> (2.0 g, 0.003 mol) in warm (50 °C) 1:1 methanol/water (60 mL), yielding the red-purple microcrystalline product (1.6 g (71%)).

**[Cu(MePhTIM)NMI](PF<sub>6</sub>)<sub>2</sub>.** *N*-Methylimidazole (1.5 mL, 0.02 mol) was added to a suspension of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> (0.60 g, 8.3 × 10<sup>-4</sup> mol) in water (50 mL). After 30 min the purple starting material was replaced by the blue solid product which was collected and washed with water (yield 0.60 g (90%)).

**[Cu(MePhTIM)py](PF<sub>6</sub>)<sub>2</sub>.** Pyridine (3 mL, 0.04 mol) was added dropwise to a solution of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> (0.60 g, 8.3 × 10<sup>-4</sup> mol) in hot 1:1 methanol/water (100 mL). The solution was cooled and refrigerated for 18 h, yielding the blue crystalline product (0.47 g (70%)).

**[Cu(MePhTIM)(4-Mepy)](PF<sub>6</sub>)<sub>2</sub>.** This compound was prepared analogously to the py derivative by adding 4-Mepy (0.7 mL, 0.007 mol) and omitting refrigeration, yielding pale blue microcrystals (0.40 g (59%)).

**[Cu(MePhTIM)X]PF<sub>6</sub>,** X = NCS<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>. These compounds were prepared analogously to the py derivative by adding a 1:1 methanol/water solution of axial ligand salt (0.2 g of NaSCN in 10 mL, 3.5 g of LiBr in 10 mL, or 0.25 g of NaI in 15 mL) and allowing the solution to cool and stand 18 h. The colors and yields of crystalline products, respectively, were as follows: turquoise, 0.48 g (90%); dark blue, 0.42 g (75%); dark green, 0.37 g (64%). The bromide derivative contained one water of crystallization which could be partially removed by vacuum desiccation.

**[Cu(MePhTIM)(aniline)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** This compound was prepared analogously to the py derivative by adding aniline (0.75 mL, 8.3 × 10<sup>-3</sup> mol) and allowing the solution to cool and stand for 18 h, yielding the golden-brown product (0.53 g (70%)).

**[Cu(MePhTIM)X<sub>2</sub>],** X = NCS<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>. These compounds were all prepared analogously by adding an acetone solution of axial ligand salt (0.32 g of KSCN/60 mL, 0.13 g of LiCl/30 mL, 1.07 g of Bu<sub>4</sub>NBr/10 mL, or 1.22 g of Bu<sub>4</sub>NI/10 mL) to a warm acetone solution of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> (0.6 g/60 mL in all cases except LiCl for which the volume was 25 mL). The products crystallized upon cooling and refrigeration of the solutions. The colors and yields of products, respectively, were as follows: brown, 0.21 g (48%); blue, 0.24 g (53%); green, 0.40 g (80%); orange, 0.33 g (58%).

**[Zn(MePhTIM)Cl]PF<sub>6</sub>.** [Cu(MePhTIM)]ZnCl<sub>4</sub> (1.0 g) was suspended in methanol (60 mL) under a blanket of N<sub>2</sub>. Granulated zinc metal (1.0 g, 20 mesh) was added, and the mixture was stirred for 2 h, resulting in a nearly colorless solution with suspended metallic copper. The solution was removed from the N<sub>2</sub> blanket and filtered, and a solution of NH<sub>4</sub>PF<sub>6</sub> (0.67 g) in ethanol (30 mL) was added

slowly, yielding the white microcrystalline product (0.37 g (39%)). Anal. Calcd for ZnC<sub>24</sub>H<sub>28</sub>N<sub>4</sub>ClPF<sub>6</sub>: C, 46.62; H, 4.56; N, 9.06; Zn, 10.57. Found: C, 46.15; H, 4.40; N, 9.15; Zn, 10.78.

**Physical Measurements.** Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Conductivity measurements were made with an Industrial Instruments Model RCM-15BI conductivity bridge and an immersion-type cell at room temperature. Infrared spectra were recorded with use of a Perkin-Elmer 621 spectrophotometer and were calibrated with use of polystyrene film. Spectra in the range of 800–200 nm were recorded with use of a Cary 219 spectrophotometer and 1-cm quartz cells. Solid-state spectra (300–1500 nm) were obtained either as mineral oil mulls on quartz plates accompanied by a dispersion filter in the reference beam of the Cary 219 spectrophotometer or as mulls with magnesium oxide with use of a Princeton Applied Research 6001 photoacoustic spectrometer at Duke University. Proton NMR spectra were recorded with a Perkin-Elmer R32 spectrometer (90 MHz) at 35 °C. Solid-state magnetic moments were measured at room temperature (26–28 °C) by the Faraday method with a Cahn 7600 magnetic susceptibility apparatus and Ni(en)<sub>3</sub>S<sub>2</sub>O<sub>3</sub> as standard. The solution magnetic moments were determined with use of the Evans NMR method<sup>13</sup> with 0.1 M solutions in CH<sub>2</sub>Cl<sub>2</sub> at 21 °C and are density corrected. Diamagnetic contributions from the ligands and anions were estimated with use of Pascal's constants.<sup>14</sup> The effective moment of copper was evaluated with the equation  $\mu_{\text{eff}} = 2.84(\chi_{\text{m}}T)^{1/2}$ . The carbon-13 NMR spectrum was recorded by Dr. David Harris using a Varian XL-100 spectrometer at the University of North Carolina, Chapel Hill, N.C.

### Results and Discussion

**Synthesis and Characterization of Derivatives.** Complexes of tetraimine macrocycles are traditionally prepared by template syntheses involving diketones and diamines. Iron, cobalt, and nickel complexes of MePhTIM have been prepared by a template reaction employing 1-phenyl-1,2-propanedione, 1,3-diaminopropane, and metal halide salt in methanol.<sup>12</sup> The analogous reaction was used previously to prepare complexes of the tetramethyl-substituted analogue TIM,<sup>15,16</sup> and Gagné used a similar reaction to prepare Cu<sup>II</sup>(TIM).<sup>10</sup> Cu<sup>II</sup>-(MePhTIM) was isolated in about 30% yield from the template reaction as [Cu(MePhTIM)]ZnCl<sub>4</sub>. Metathesis with KPF<sub>6</sub> in methanol/water gave [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> which served as the starting material for the preparation of derivatives. Five-coordinate derivatives were prepared by adding excess potential axial ligand to warm methanol/water solutions of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub>, giving complexes formulated as [Cu(MePhTIM)X]PF<sub>6</sub>, where X is NCS<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, and as [Cu(MePhTIM)L](PF<sub>6</sub>)<sub>2</sub>, where L is *N*-methylimidazole, pyridine, or 4-methylpyridine. With aniline as the potential ligand, [Cu(MePhTIM)(aniline)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was isolated. In contrast, when acetone solutions containing excess thiocyanate or halide salts were added to acetone solutions of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub>, the color changes differed from those in methanol/water, and compounds formulated as [Cu(MePhTIM)X<sub>2</sub>] were isolated. Table I lists the derivatives prepared and their elemental analyses.

Molar conductivities of 10<sup>-3</sup> M solutions in CH<sub>3</sub>NO<sub>2</sub> (Table II) for [Cu(MePhTIM)X]PF<sub>6</sub> derivatives are within the range accepted for 1:1 electrolytes.<sup>17</sup> The visible spectra of these compounds in CH<sub>3</sub>NO<sub>2</sub> are very similar to those in the solid state (Table III), indicating that the complexes are five-coordinate and that gross changes in coordination number and axial ligands do not occur in solution. However, conductivity studies on more dilute solutions (10<sup>-3</sup>–10<sup>-5</sup> M) do result in

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Table I. Elemental Analyses

compd	% calcd			% found		
	C	H	N	C	H	N
[Cu(MePhTIM)](ZnCl <sub>4</sub> )	44.81	4.39	8.70	44.64	4.50	8.49
[Cu(MePhTIM)](PF <sub>6</sub> ) <sub>2</sub>	39.71	3.89	7.72	39.83	3.80	7.90
[Cu(MePhTIM)NMI](PF <sub>6</sub> ) <sub>2</sub>	41.67	4.25	10.41	41.47	4.20	10.51
[Cu(MePhTIM)py](PF <sub>6</sub> ) <sub>2</sub>	43.26	4.13	8.70	43.27	4.31	8.53
[Cu(MePhTIM)(4-Mepy)](PF <sub>6</sub> ) <sub>2</sub>	43.99	4.31	8.55	43.79	4.27	8.90
[Cu(MePhTIM)(aniline) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	47.40	4.64	9.21	47.67	4.57	9.31
[Cu(MePhTIM)Br](PF <sub>6</sub> )·H <sub>2</sub> O	42.46	4.45	8.25	42.40	4.46	8.11
[Cu(MePhTIM)I](PF <sub>6</sub> )	40.72	3.99	7.91	40.59	3.89	7.87
[Cu(MePhTIM)NCS](PF <sub>6</sub> )	46.98	4.40	10.96	47.23	4.30	11.15
[Cu(MePhTIM)Br <sub>2</sub> ]	48.38	4.74	9.40	48.60	4.62	9.34
[Cu(MePhTIM)Cl <sub>2</sub> ]·2H <sub>2</sub> O	53.06	5.93	10.31	52.70	6.07	10.17
[Cu(MePhTIM)I <sub>2</sub> ]	41.78	4.09	8.12	41.79	4.06	8.16
[Cu(MePhTIM)(SCN) <sub>2</sub> ]	56.55	5.11	15.22	56.35	5.20	15.38

Table II. Molar Conductivities and Magnetic Moments

compd	$\Lambda_m^a$	$\mu_{\text{eff}}^b$ (solvent)	$\mu_{\text{eff}}^b$ (solid)
[Cu(MePhTIM)](PF <sub>6</sub> ) <sub>2</sub>	179	1.79 (CH <sub>3</sub> NO <sub>2</sub> )	1.89
[Cu(MePhTIM)NMI](PF <sub>6</sub> ) <sub>2</sub>	176	1.73 (CH <sub>3</sub> NO <sub>2</sub> )	1.89
[Cu(MePhTIM)py](PF <sub>6</sub> ) <sub>2</sub>	169	1.91 (CH <sub>3</sub> NO <sub>2</sub> ) <sup>d</sup>	1.86
[Cu(MePhTIM)(4-Mepy)](PF <sub>6</sub> ) <sub>2</sub>	170	1.85 (CH <sub>3</sub> NO <sub>2</sub> ) <sup>c</sup>	1.87
[Cu(MePhTIM)NCS]PF <sub>6</sub>	81		1.87
[Cu(MePhTIM)Br]PF <sub>6</sub> ·H <sub>2</sub> O	80	1.75 (CH <sub>2</sub> Cl <sub>2</sub> )	1.85
[Cu(MePhTIM)I]PF <sub>6</sub>	71	1.67 (CH <sub>2</sub> Cl <sub>2</sub> )	1.85
[Cu(MePhTIM)(aniline) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	178		1.84
[Cu(MePhTIM)Cl <sub>2</sub> ]·2H <sub>2</sub> O			1.81
[Cu(MePhTIM)Br <sub>2</sub> ]		1.73 (CH <sub>2</sub> Cl <sub>2</sub> ) <sup>d</sup>	1.81
[Cu(MePhTIM)I <sub>2</sub> ]		1.73 (CH <sub>2</sub> Cl <sub>2</sub> )	1.85
[Cu(MePhTIM)(NCS) <sub>2</sub> ]			1.83
[Cu(MePhTIM)]ZnCl <sub>4</sub>			1.80

<sup>a</sup> Units: cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup>. Solutions were 1 × 10<sup>-3</sup> M in CH<sub>3</sub>NO<sub>2</sub>. <sup>b</sup> Units: μ<sub>B</sub>. <sup>c</sup> 4-Mepy (18 equiv) added to sample and reference solutions. <sup>d</sup> Axial ligand (33 equiv) added to sample and reference solutions.

curved plots of the equivalent conductance vs. the square root of equivalent concentration. These are consistent<sup>18</sup> with further dissociation according to eq 1. Comparison of the visible



spectra with those of solutions containing excess axial ligand showed that at 10<sup>-3</sup> M the dissociation is negligible.

The complexes having a single neutral axial ligand are all 1:2 electrolytes in CH<sub>3</sub>NO<sub>2</sub> as expected. The visible spectral studies in CH<sub>3</sub>NO<sub>2</sub> indicated that, in contrast to the compounds with a single anionic axial ligand, the pyridine and 4-Mepy derivatives are significantly dissociated at 10<sup>-3</sup> M according to eq 2. Large excesses of axial ligand, up to 33



equiv for py, were required to convert the complex quantitatively to the five-coordinate adduct in CH<sub>3</sub>NO<sub>2</sub>. Spectrophotometric titrations were consistent with 1:1 stoichiometry and in the case of NMI showed that the binding constant is high, similar to the anionic ligands. However, for py and 4-Mepy the binding constants are much smaller and could be evaluated from spectrophotometric titration data. The titration of [Cu(MePhTIM)]<sup>2+</sup> with 4-Mepy in CH<sub>3</sub>NO<sub>2</sub> is shown in Figure 1. The method recently described by Brown<sup>19</sup> was used to calculate the binding constants from linear plots of ΔA vs. ΔA/L<sub>eq</sub>. Least-squares analysis of the plots for py and 4-Mepy resulted in binding constants of 390 ± 10 and 1050 ± 20

Table III. Visible Spectra

compd	$\lambda_{\text{max}}^a$		
	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	solid
[Cu(MePhTIM)](PF <sub>6</sub> ) <sub>2</sub>	510 (136)	<i>b</i>	487
[Cu(MePhTIM)py](PF <sub>6</sub> ) <sub>2</sub>	582 (206) <sup>d</sup>	592 (199) <sup>d</sup>	596
[Cu(MePhTIM)(4-Mepy)](PF <sub>6</sub> ) <sub>2</sub>	591 (202) <sup>d</sup>	602 (217) <sup>d</sup>	600
[Cu(MePhTIM)NMI](PF <sub>6</sub> ) <sub>2</sub>	610 (218) <sup>d</sup>	626 (220) <sup>d</sup>	634
[Cu(MePhTIM)NCS]PF <sub>6</sub>	589 (185)	610 (180)	675
[Cu(MePhTIM)I]PF <sub>6</sub>	602 (215)	630 (206)	635
[Cu(MePhTIM)Br]PF <sub>6</sub> ·H <sub>2</sub> O	628 (215)	640 (217)	615
[Cu(MePhTIM)Cl]PF <sub>6</sub> <sup>c</sup>	639 (212)	652 (217)	
[Cu(MePhTIM)I <sub>2</sub> ]	<i>b</i>	<i>e</i>	<i>e</i> , 775
[Cu(MePhTIM)Br <sub>2</sub> ]	<i>b</i>	626 (172) <sup>d</sup>	550, 750
[Cu(MePhTIM)Cl <sub>2</sub> ]·2H <sub>2</sub> O	<i>b</i>	634 (179) <sup>d</sup>	542, 700
[Cu(MePhTIM)(NCS) <sub>2</sub> ]	<i>b</i>	<i>b</i>	525, 740

<sup>a</sup> Units: nm. Values in parentheses are  $\epsilon$  values in L mol<sup>-1</sup> cm<sup>-1</sup>. <sup>b</sup> Insoluble. <sup>c</sup> Prepared in situ by adding 2 equiv of Bu<sub>4</sub>NCl to [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub>. <sup>d</sup> 0.1 M excess axial ligand added. <sup>e</sup> Masked by charge-transfer band.

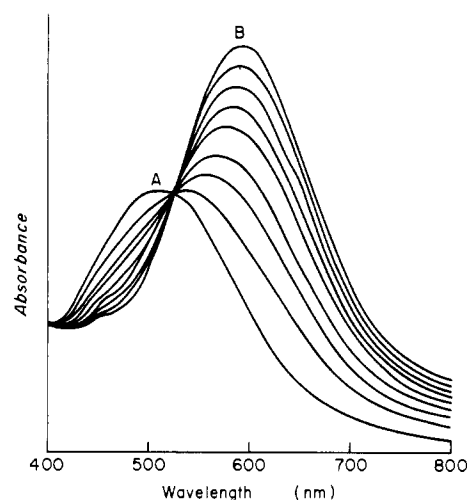
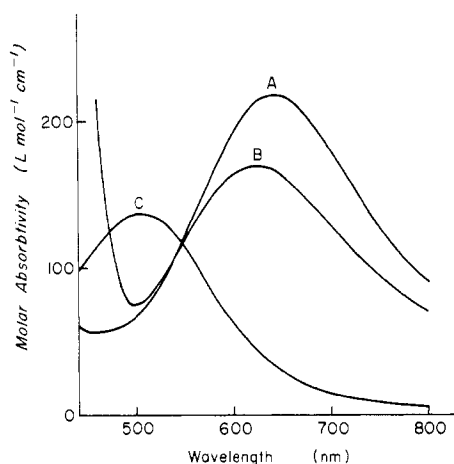


Figure 1. Spectrophotometric titration of [Cu(MePhTIM)]PF<sub>6</sub><sub>2</sub> with 4-methylpyridine in CH<sub>3</sub>NO<sub>2</sub> at ambient temperature. Spectrum A is of [Cu(MePhTIM)]<sup>2+</sup> and spectrum B is after complete conversion to [Cu(MePhTIM)(4-Mepy)]<sup>2+</sup> (18 equiv of 4-Mepy per [Cu(MePhTIM)]<sup>2+</sup>). Intermediate spectra resulted from the following equivalents of 4-Mepy per [Cu(MePhTIM)]<sup>2+</sup>: 0.3, 0.6, 0.9, 1.5, 2.0, 3.0, 5.0.

mol/L, respectively. These values are quite comparable to the binding constant of 250 mol/L reported<sup>5</sup> for [Cu(cyclops)]<sup>+</sup> and pyridine in CH<sub>3</sub>NO<sub>2</sub> and indicate the great similarity of MePhTIM complexes and those of cyclops in spite of the

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**Figure 2.** Visible spectra of four-, five-, and six-coordinate Cu(MePhTIM) derivatives: spectrum A,  $[\text{Cu}(\text{MePhTIM})\text{Br}]\text{PF}_6 \cdot \text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$ ; spectrum B, after 1 equiv of  $\text{Bu}_4\text{NBr}$  added to A and the same as  $[\text{Cu}(\text{MePhTIM})\text{Br}_2]$  in  $\text{CH}_2\text{Cl}_2$ ; spectrum C,  $[\text{Cu}(\text{MePhTIM})](\text{PF}_6)_2$  in  $\text{CH}_3\text{NO}_2$ .

differences in ligand charge and structure. As expected the MePhTIM complex binds axial ligands slightly more strongly. No spectral evidence was found for 2:1 adducts of neutral ligands with  $[\text{Cu}(\text{MePhTIM})]^{2+}$  in  $\text{CH}_3\text{NO}_2$ . The aniline derivative is formulated as six-coordinate in solid state on the basis of the similarity of its solid-state visible spectrum with those of the bis halide derivatives. However, in solution it dissociates to give  $[\text{Cu}(\text{MePhTIM})]^{2+}$  and free aniline. Its isolation is most likely a consequence of insolubility in methanol/water rather than an indication of the major ligating properties of aniline.

The bis bromide, iodide, and thiocyanate derivatives are insoluble in most polar organic solvents and in water. They are quite soluble in  $\text{CH}_2\text{Cl}_2$ , giving very low molar conductivities, less than  $10 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  for  $10^{-3} \text{ M}$  solutions. However, the  $[\text{Cu}(\text{MePhTIM})\text{X}]\text{PF}_6$  derivatives also give similar low conductivities in  $\text{CH}_2\text{Cl}_2$ . Drago and Rosenthal<sup>20</sup> have criticized the use of  $\text{CH}_2\text{Cl}_2$  for conductivity studies due to extensive ion pairing and poor solvating properties, but  $\text{CH}_2\text{Cl}_2$  has been used successfully in other cases.<sup>21</sup> More convincing evidence of the nature of the bis halide derivatives in  $\text{CH}_2\text{Cl}_2$  comes from visible spectra such as those shown in Figure 2. Spectrum A is of  $[\text{Cu}(\text{MePhTIM})\text{Br}]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$ . Spectrum B is produced when 1 equiv of  $\text{Bu}_4\text{NBr}$  is added and is identical with the spectrum of  $[\text{Cu}(\text{MePhTIM})\text{Br}_2]$  in  $\text{CH}_2\text{Cl}_2$ . Spectrum C, for comparison, is  $[\text{Cu}(\text{MePhTIM})](\text{PF}_6)_2$  in  $\text{CH}_3\text{NO}_2$ . The shift in the spectral maximum to higher energy and the decrease in molar absorptivity are to be expected when a five-coordinate square-pyramidal complex is converted to a six-coordinate tetragonal complex.<sup>22,23</sup> On the basis of these results, the bis halide and thiocyanate derivatives are all formulated as six-coordinate both in the solid state and in  $\text{CH}_2\text{Cl}_2$  solutions. It is notable that for the bis adducts the solid-state spectra differ significantly from the solution spectra. This may be indicative of weaker axial ligation in solution due to solvation (see below). In more polar solvents such as alcohols or DMF these complexes dissociate to form the five-coordinate adducts.

Magnetic moments were measured in the solid state and solution at room temperature (Table II). In all cases the solid-state moments are in the range of  $1.8\text{--}2.0 \mu_B$  expected

for monomeric, noninteracting copper ions.<sup>23</sup> The solution moments are consistently lower than those in solid state but also have more uncertainty associated with them (estimated at  $\pm 0.1 \mu_B$ , whereas the solid measurements are  $\pm 0.02 \mu_B$ ). The solution magnetic moment of  $[\text{Cu}(\text{MePhTIM})\text{NCS}]\text{PF}_6$  could not be measured accurately due to low solubility.

**Infrared Spectra.** The infrared spectra of Cu(MePhTIM) derivatives are all very similar to the spectra for other MePhTIM complexes.<sup>12</sup> Bands attributed to functional groups in the macrocycle are observed in the following regions (in  $\text{cm}^{-1}$ ): 3000–3100, aromatic  $\nu_{\text{C-H}}$ ; 2900–3000, aliphatic  $\nu_{\text{C-H}}$ ; 1602–1612,  $\nu_{\text{C-N}}(\text{asym})$  (w); 1585–1595,  $\nu_{\text{C-N}}(\text{sym})$ ; 1569–1590,  $\nu_{\text{C=C}}$  (sh);  $\sim 710$  and  $745$ , C–H out of plane bending of phenyl. Weaker bands in the 900–1400  $\text{cm}^{-1}$  region are associated with the ligand framework. A sharp band seen for most TIM complexes<sup>15,16</sup> at about  $1200 \text{ cm}^{-1}$  is observed for these complexes in the 1226–1238- $\text{cm}^{-1}$  region.  $[\text{Co}(\text{MePhTIM})\text{Cl}_2]\text{PF}_6$ , for which an X-ray structural analysis has shown the ligand to be approximately planar,<sup>24</sup> has an infrared spectrum highly similar to those of the copper complexes. Therefore, no gross differences in ligand conformation between the four-, five-, and six-coordinate copper complexes and the cobalt complex are to be expected.

The infrared and visible spectra of the two derivatives containing water provide some indication of whether the water is coordinated or present in the lattice.  $[\text{Cu}(\text{MePhTIM})\text{Br}]\text{PF}_6 \cdot \text{H}_2\text{O}$  has two relatively sharp bands at 3650 and 3490  $\text{cm}^{-1}$ . The bis chloride derivative has an additional broad band between 450 and 600  $\text{cm}^{-1}$  which is not observed for any other derivatives. In general, lattice water often gives rise to bands near 3500, 1650, and 300–600  $\text{cm}^{-1}$ . For coordinated water a band is seen in the 650–880- $\text{cm}^{-1}$  region.<sup>25</sup> For the bromide derivative the bands near 3000  $\text{cm}^{-1}$  indicate hydrogen-bonded water, but the 800- $\text{cm}^{-1}$  region is obscured by a  $\text{PF}_6^-$  band, and no additional band is observed in the 300–600- $\text{cm}^{-1}$  region. From a comparison of the solid-state and solution visible spectra (Table III) it is seen that  $\lambda_{\text{max}}$  in the solid state is at shorter wavelength than the maximum in either of the solution spectra. This behavior is opposite that observed in the other five-coordinate derivatives and is suggestive of the spectral differences previously noted between five- and six-coordination. Thus, it is probable that a water molecule is interacting with the metal center in  $[\text{Cu}(\text{MePhTIM})\text{Br}]\text{PF}_6 \cdot \text{H}_2\text{O}$ . It is well established that even a weakly interacting sixth ligand can have an appreciable effect on the electronic properties of otherwise square pyramidal copper(II) complexes.<sup>26</sup> Alternatively, the effect could be due to hydrogen bonding between coordinated bromide and water in the lattice. For  $[\text{Cu}(\text{MePhTIM})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  both the infrared and visible spectra are consistent with lattice water and two chloride ions coordinated.

The thiocyanate derivatives are of interest because copper(II) is known to form both N- and S-bonded complexes.<sup>27</sup> While many efforts have been made to identify the type of linkage from infrared band frequencies, there are many exceptions which make such arguments very tentative. However, electronic spectra can aid in making assignments since NCS is considerably higher in the spectrochemical series than is  $\text{SCN}^-$ .<sup>28</sup>  $[\text{Cu}(\text{MePhTIM})\text{NCS}]\text{PF}_6$  has a very strong band at 2075  $\text{cm}^{-1}$  which is in the region associated with N-bonded thiocyanate.<sup>25</sup> The CS stretching and NCS bending regions are masked by macrocyclic ligand vibrations. In  $\text{CH}_2\text{Cl}_2$  solution  $\nu_{\text{CN}}$  shifts to 2095  $\text{cm}^{-1}$ , and a 65-nm shift to higher energy is also observed for the d–d band maximum of the

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Table IV. UV Spectra in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

compd	$\lambda_{\max}$ ( $\epsilon$ )
[Cu(MePhTIM)py](PF <sub>6</sub> ) <sub>2</sub>	270 sh (7600)
[Cu(MePhTIM)(4-Mepy)](PF <sub>6</sub> ) <sub>2</sub>	252 (9600), 280 (5760)
[Cu(MePhTIM)NMI](PF <sub>6</sub> ) <sub>2</sub>	277 (16 200) <sup>b</sup>
[Cu(MePhTIM)NCS]PF <sub>6</sub>	280 sh (7800), 340 sh (3000)
[Cu(MePhTIM)I]PF <sub>6</sub>	286 (9240), 360 (4040), 400 sh (3300)
[Cu(MePhTIM)Br]PF <sub>6</sub> ·H <sub>2</sub> O	280 sh (8400), 340 sh (3400)
[Cu(MePhTIM)I <sub>2</sub> ]	292 (14 500), 364 (7380)
[Cu(MePhTIM)Br <sub>2</sub> ]	270 (15 640), 350 (3640)
[Cu(MePhTIM)Cl <sub>2</sub> ]·2H <sub>2</sub> O	280 sh (7500), 340 sh (2800)

<sup>a</sup> Units:  $\lambda_{\max}$ , nm;  $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>. Key: sh, shoulder. <sup>b</sup> 0.1 M NMI added.

visible spectrum (see Table III). Evaporation of the CH<sub>2</sub>Cl<sub>2</sub> regenerates a solid with the original characteristics. The shift in visible spectral maximum could be due to solvent interaction with the vacant coordination site, to linkage isomerism of thiocyanate, or to formation of thiocyanate-bridged dimers. Of those possibilities, the first is not considered to be important. This is primarily because of the large magnitude of the visible spectral shift and the fact that no such shifts are observed for any other five-coordinate derivatives in CH<sub>2</sub>Cl<sub>2</sub>. The formation of thiocyanate-bridged dimers must be considered since low dielectric solvents such as CH<sub>2</sub>Cl<sub>2</sub> are known to promote their formation.<sup>29</sup> Anion-bridged dimers have been reported for Cu(cyclops),<sup>11</sup> though not with SCN<sup>-</sup>. The visible spectral maxima for these dimers are at shorter wavelength than the five-coordinate derivatives, e.g., 539 nm for [Cu<sub>2</sub>(cyclops)<sub>2</sub>N<sub>3</sub>]ClO<sub>4</sub> vs. 617 nm for [Cu(cyclops)N<sub>3</sub>] in CH<sub>3</sub>NO<sub>2</sub>. Also by way of comparison, a cyanide-bridged complex, [Cu<sub>2</sub>([14]-4,11-dieneN<sub>4</sub>)<sub>2</sub>CN](ClO<sub>4</sub>)<sub>3</sub>, has a magnetic moment of 1.95  $\mu_B$  at room temperature and a visible spectrum with three bands at 614, 736, and 950 nm.<sup>30</sup> In contrast, only one visible band is observed at 610 nm for [Cu(MePhTIM)NCS]PF<sub>6</sub> in solution and one at 675 nm in the solid state.

The third possibility, a linkage isomerism between solution and solid state, is consistent with both the visible and infrared spectral shifts. Thus interpreted, the complex would be N-bonded in the solid state and S-bonded in solution. Marzilli has observed that the S-bonded isomer of [Co(DMGH)<sub>2</sub>(*t*-Bupy)SCN] is favored over the N-bonded isomer in solvents of low dielectric constant.<sup>31</sup> A solid-solution linkage isomerism has been well documented for Mn(CO)<sub>5</sub>SCN.<sup>32</sup> The fact that the starting material [Cu(MePhTIM)NCS]PF<sub>6</sub> is regenerated upon evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution to dryness is consistent with this proposed behavior.

[Cu(MePhTIM)(NCS)<sub>2</sub>] has two strong sharp  $\nu_{\text{CN}}$  bands of approximately the same intensity and half-width at 2067 and 2040 cm<sup>-1</sup>. The solid-state visible spectrum is similar to those of the six-coordinate bis halide derivatives and is quite different from that of [Cu(MePhTIM)NCS]PF<sub>6</sub>, suggesting that the complex is six-coordinate in the solid state. The presence of two  $\nu_{\text{CN}}$  bands could be due to one N-bonded and one S-bonded thiocyanate or to both bonded the same way but interacting with copper to a different extent. The latter alternative would be favored in view of the magnitudes of the  $\nu_{\text{CN}}$ , one of which is in the N-bonded region and the other closer to ionic.

**Electronic Spectra.** The complexes were further characterized by their solution spectra (800–380 nm in CH<sub>3</sub>NO<sub>2</sub>,

800–240 nm in CH<sub>2</sub>Cl<sub>2</sub>) and spectra in the polycrystalline solid state (1500–350 nm). The results are included in Tables III and IV. Square- or rectangular-planar copper(II) tetraaza macrocycles usually exhibit a single broad d-d band near 500 nm with a molar absorptivity of about 125 M<sup>-1</sup> cm<sup>-1</sup>.<sup>33</sup> [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>NO<sub>2</sub> (Figure 2) follows this pattern with a single band at 510 nm ( $\epsilon = 136 \text{ M}^{-1} \text{ cm}^{-1}$ ). In the solid state the band is at 487 nm. In solution, as the donor ability of the solvent is increased, the maximum shifts to longer wavelength and the molar absorptivity increases. In the solvents acetone, 1:1 methanol/water, and CH<sub>3</sub>CN, the  $\lambda_{\max}$  ( $\epsilon$ ) values are 538 (148), 540 (157), and 542 nm (173), respectively. This series parallels the behavior observed for [Cu(cyclops)]<sup>+</sup> in other solvents<sup>5</sup> and for other tetraazacopper(II) complexes<sup>34,35</sup> and has been attributed to formation of five-coordinate solvent complexes. Recent proton NMR solvent line-broadening studies of two copper(II) complexes of neutral tetraaza macrocycles are consistent with five-coordination in water, methanol, and DMF at room temperature.<sup>36</sup> In contrast, complexes of  $\beta$ -diiminato macrocycles exhibit little or no solvent dependence and do not form isolable derivatives with axial ligands.<sup>37,38</sup> In general, there is lower tendency toward coordination of axial ligands in complexes of unsaturated anionic macrocycles.<sup>39</sup>

The ligand field band maxima for five-coordinate Cu(MePhTIM) derivatives in CH<sub>3</sub>NO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and the solid state are listed in Table III. Excess axial ligand was added to each of the [Cu(MePhTIM)L]<sup>2+</sup> solutions to ensure complete complex formation, but this was unnecessary for the complexes with anionic axial ligands. In comparison with the maxima in CH<sub>2</sub>Cl<sub>2</sub>, the maxima in CH<sub>3</sub>NO<sub>2</sub> are shifted by about 20 nm to shorter wavelength. This is opposite to the solvent dependence observed for [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> and is probably due to the better solvation of the fifth ligand in CH<sub>3</sub>NO<sub>2</sub> which consequently would decrease its donor ability toward the metal ion. Alternatively, solvent interaction at the sixth coordination site would produce the same result. In contrast to [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> the solid state band maxima are at longer wavelength than in any of the solution spectra, as would be expected from either of the above interpretations. When compared with data for Cu(cyclops), the band maxima and molar absorptivities are found to be quite similar with the same general trends being observed for both types of complex. This is consistent with rectangular-pyramidal geometry for the five-coordinate derivatives of Cu(MePhTIM) as has been confirmed by crystallographic studies of the Cu(cyclops) derivatives.<sup>1-4</sup>

From the data in Table III the following spectrochemical series can be constructed: H<sub>2</sub>O, CH<sub>3</sub>CN < py < SCN<sup>-</sup>, 4-Mepy < I<sup>-</sup>, NMI < Br<sup>-</sup> < Cl<sup>-</sup> < NCS<sup>-</sup>. The thiocyanate derivative is assumed to be S-bonded in solution and N-bonded in the solid state (see Infrared Spectra). From the spectra of [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> in MeOH/H<sub>2</sub>O and CH<sub>3</sub>CN, it is concluded that these ligands are lower than pyridine in the series. This ordering of ligands is very similar to that found by Addison et al.<sup>5</sup> for five-coordinate derivatives of Cu(cyclops). Notably, the neutral and anionic ligands are reversed in their positions in the series compared to the order for octahedral complexes. Addison et al.<sup>5</sup> proposed a rationale for the series in terms of variability of apical displacement of the

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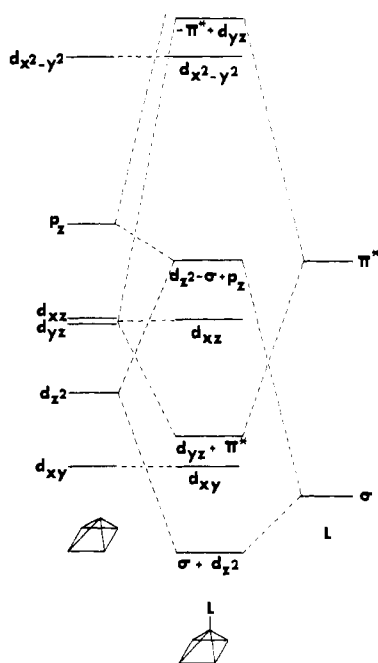
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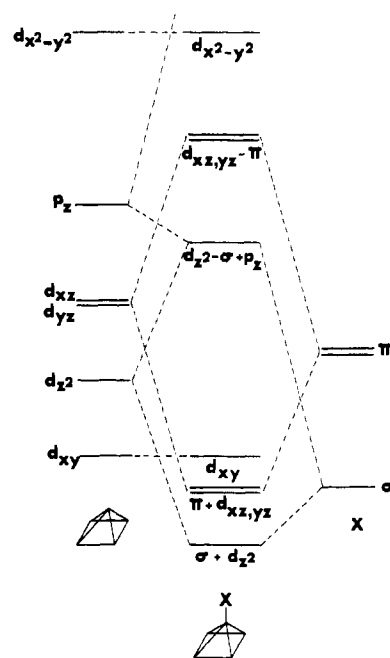
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**Figure 3.** Qualitative molecular orbital diagram for the interaction of a square-pyramidal  $C_{4v}$  metal-macrocycle fragment (on left) with a monofacial  $\sigma$ -donating,  $\pi$ -accepting apical ligand, L.

metal ion from the  $N_4$  plane and unusually strong metal-ionic ligand interaction. Both effects were verified by the structural results of Anderson and co-workers, but interestingly, [Cu(cyclops)I] with its short Cu-I bond was found to have the same apical displacement as [Cu(cyclops)py]<sup>+</sup> which has a normal Cu-py bond.<sup>3,4</sup> The iodide complex in addition has its  $\lambda_{max}$  at 40 nm longer wavelength than the pyridine complex. Thus, the strong metal-anion interactions are not accompanied by much larger apical displacements, and the spectral differences must therefore be due to the ways in which these ligands interact with the metal ion. The remarkable similarity of the spectrochemical series for cyclops and MePhTIM complexes shows that the cyclops ligand is not uniquely responsible for the series. Similar structural and electronic effects are most likely occurring in the MePhTIM series as well.

Inspired by these results, we have sought a more general explanation, at least for the two cyclops cases where the metal-ligand geometry is known to be the same. Since the two apical ligands in question, pyridine and iodide, differ not only in charge but also in bonding modes, one being  $\sigma$  donor,  $\pi$  acceptor and the other  $\sigma$  donor,  $\pi$  donor, a qualitative MO approach was explored. In order for the differences in apical ligand bonding to be emphasized, the molecule was divided into two fragments as shown at the bottom of Figures 3 and 4. One fragment includes the metal and macrocyclic ligand with the metal already displaced from the  $N_4$  plane. The other fragment is the ligand to be bound on the apical site along the  $z$  axis. To arrive at a reasonable energy level scheme for the metal-macrocycle fragment, we have used the results of Elian and Hoffmann.<sup>40</sup> In their study of square-pyramidal  $M(CO)_4$  fragments they calculated extended Hückel energy level diagrams as a function of pyramidality of the fragment. Since MePhTIM is a  $\sigma$ -donor,  $\pi$ -acceptor ligand, it should interact in roughly the same way as the carbonyls of Elian and Hoffmann but with more  $\sigma$ -donor ability relative to  $\pi$ -acceptor ability. Also, since the 3d shell of Cu(II) is almost full, the 4s and 4p orbitals are expected to be important in metal-ligand



**Figure 4.** Qualitative molecular orbital diagram for the interaction of a square-pyramidal  $C_{4v}$  metal-macrocycle fragment (on left) with a  $\sigma$ -donating,  $\pi$ -donating apical ligand, X.

bonding. Therefore, for the metal-macrocycle fragment we have used Elian and Hoffmann's energy order and descriptions of d orbital contributions for a  $C_{4v}$  fragment with approximately the same degree of apical displacement of the metal as was found for [Cu(cyclops)py]<sup>+</sup> and [Cu(cyclops)I]. Figures 3 and 4 have the same fragment energy level diagram in the left column in which the levels are labeled according to the major d orbital contribution. It should be kept in mind, however, that these levels are for the entire fragment and therefore contain ligand contributions as well.

The major factors determining the character of the levels in the metal-macrocycle fragment and their order are as follows.<sup>40,41</sup> The  $d_{xy}$  orbital is nonbonding, localized between the ligands, and therefore lowest in energy. The  $d_{z^2}$  orbital is low in energy because no ligand has yet been placed on the  $z$  axis. In the lowered symmetry (compared to tetragonal or octahedral) the  $d_{z^2}$  and metal 4s and 4p<sub>z</sub> orbitals are of the same symmetry type and can mix. This effect is crucial toward understanding the bonding in the pyramidal complex.<sup>41</sup> It lowers the energy of the  $d_{z^2}$  orbital and distorts it away from the apical ligand so that its antibonding interaction with the apical ligand is diminished and at the same time its  $\pi$ -bonding interaction with the basal ligands is enhanced (due to overlap with the nitrogen p<sub>z</sub> orbitals which are situated near the  $d_{z^2}$  nodal surface). This latter important effect compensates for the loss of  $\pi$  bonding with the  $d_{xz,yz}$  orbitals and makes the metal-basal ligand  $\pi$  interaction remain relatively constant as the metal apical displacement is varied.<sup>40</sup> Several experimental facts support this notion, including the "flexing" of the macrocycle in Anderson's structures, the maintenance of relatively constant M-N and C=N distances despite wide variations in apical displacement, and the invariance of the C=N stretching frequencies in the infrared spectra of the complexes.

By the same argument as above, the  $d_{xz,yz}$  pair can mix with the metal 4p<sub>x,y</sub> pair. The consequence is that the antibonding interaction is decreased toward the basal ligands and also toward the apical ligand when it is added. However, the p<sub>x,y</sub>

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orbitals are much higher in energy than the  $p_z$  so the effects of their mixing are less than those of the  $p_z$ . The  $d_{x^2-y^2}$  level is high in energy due to  $\sigma$ -antibonding character with the basal ligands and actually should be off the scale at the top of Figures 3 and 4.

Now consider the result of adding a  $\sigma$ -donor,  $\pi$ -acceptor ligand L on the  $z$  axis as shown in Figure 3. The  $\sigma$ -donor orbital, e.g., the lone pair of a pyridine nitrogen atom, interacts with the  $d_{z^2}$  metal-macrocycle fragment orbital to make bonding and antibonding combinations. However, the effect of the contributing  $4p_z$  orbital is to decrease the antibonding character in the upper level and to lower its energy somewhat.<sup>41</sup> The plus and minus signs included in the orbital labels in the figures are not meant to imply specific phases but only to denote whether an orbital contributes in a bonding (+) or antibonding (-) way. The  $\pi^*$  (empty) orbital of a monofacial ligand interacts with one of the  $d_{xz,yz}$  pair such that the bonding combination, mainly  $d_{yz}$ , is stabilized while the antibonding combination is very high in energy and unoccupied. Filling in the electrons in the diagram indicates that the lowest energy transition predicted is from the  $d_{z^2}-\sigma + p_z$  orbital to the  $d_{x^2-y^2}$  orbital.

A slightly different situation is encountered in Figure 4 where the same metal-macrocycle fragment is now combined with a  $\sigma$ -donor,  $\pi$ -donor apical ligand, X, e.g., a halide ion. The M-X  $\sigma$  interaction is the same as in the previous case. The two  $\pi$  orbitals (occupied) interact with the  $d_{xz,yz}$  pair making a bonding, mainly ligand, and an antibonding, mainly metal, combination. Again, admixture of  $4p_{x,y}$  would tend to decrease the antibonding character in the upper orbitals but to a lesser extent than in the  $\sigma$  combination because the  $p_{x,y}$  are higher in energy and because of the counteracting effect of the basal ligands which also are combined in this orbital. In comparison with Figure 3, the important consequence is that now the lowest energy transition is from the  $d_{xz,yz}-\pi$  orbital to  $d_{x^2-y^2}$  and is much less energy than the lowest energy transition in Figure 3. It is impressive that the arguments used to predict the "reversal" of the neutral  $\pi$ -acceptor ligands and the anions in the spectrochemical series are basically the same as those used to rationalize their relative order in the octahedral series. Recent extended Hückel calculations by Burdett and Williams<sup>42</sup> on copper and nickel tetraaza macrocycles, including cyclops and TIM, quantitatively verify the bonding effects described above but have not been used to interpret the spectrochemical series.

A final point which follows from the MO diagrams is that because of the d-p mixing, which diminishes metal-ligand antibonding character in both the  $\sigma$  and  $\pi$  bonds, the anionic ligands are expected to have strong interactions with the metal. This is in agreement with the unusually short Cu-I distance in the structure of [Cu(cyclops)I]. For the  $\sigma$ -donor,  $\pi$ -acceptor case this effect applies only to the  $\sigma$  bond which thus should be much smaller. A normal Cu-N<sub>py</sub> bond distance was reported for [Cu(cyclops)py]<sup>+</sup>. It is tempting to try to rationalize the remainder of the spectrochemical series in terms of this model; however, the apical displacement is not constant and its variation may have as great or greater effect on the spectral transitions as the bonding effects considered here.

A final subject to be considered before leaving electronic spectra is that of the six-coordinate derivatives. These complexes are not as well characterized as the four- and five-coordinate derivatives because of their tendency to dissociate in polar organic solvents. Their spectra were obtained in the solid state and in CH<sub>2</sub>Cl<sub>2</sub> solution, where possible. The solid-state spectra feature two bands, one more intense near 550 nm and the other very weak at 700-775 nm. Copper(II) in an elongated tetragonal environment is known to exhibit two (or

sometimes three) bands, one in the 500-600-nm region and the other at longer wavelength.<sup>23</sup> For example, [Cu(en)<sub>2</sub>Cl<sub>2</sub>]-H<sub>2</sub>O has bands at 552 and 666 nm. On the basis of similarity of our spectra with those reported for tetragonal Cu(II) complexes, the [Cu(MePhTIM)X<sub>2</sub>] complexes are assigned as six-coordinate in the solid state. It is noteworthy that the halide-bridged dimers of Addison et al.<sup>11</sup> gave only one band in the solid state, for example, at 596 nm for [Cu<sub>2</sub>(cyclops)<sub>2</sub>Br]ClO<sub>4</sub>, whereas for [Cu(MePhTIM)Br<sub>2</sub>] we find two bands at 550 and 750 nm. Thus, it seems clear that the MePhTIM complexes are not dimers.

In CH<sub>2</sub>Cl<sub>2</sub> solution the [Cu(MePhTIM)X<sub>2</sub>] derivatives exhibit one visible band at a wavelength intermediate between the two bands observed in the solid state. The same spectrum can be produced by adding 1 equiv of X<sup>-</sup> to [Cu(MePhTIM)X] PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The nature of the species produced in solution is not certain. Ion pairing at least is indicated since low molar conductivity values are observed. Possibilities include solvated six-coordinate complexes, dimers, or more highly associated polymers.

**Chemical Reduction of [Cu(MePhTIM)]<sup>2+</sup>.** Under anaerobic conditions and in polar organic solvents such as acetone or CH<sub>3</sub>CN, [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> reacts with Zn<sup>0</sup>, Mg<sup>0</sup>, or phenylhydrazine to give blue solutions having spectral properties ( $\lambda_{\max} = 775$  nm,  $\epsilon \approx 10^4$ ) very similar to those reported for Cu<sup>I</sup>(cyclops).<sup>8</sup> Kept anaerobic, the blue solutions are stable and disproportionate either slowly over days or not at all. In contrast, [Cu(MePhTIM)]ZnCl<sub>4</sub> in MeOH or MeOH/H<sub>2</sub>O reacts with Zn<sup>0</sup> to give Cu<sup>0</sup> and nearly colorless solutions from which [Zn(MePhTIM)Cl]PF<sub>6</sub> can be precipitated in about 40% yield. Thus, in aprotic solvents Zn<sup>0</sup> reduction gives only the blue, presumably Cu<sup>I</sup>(MePhTIM), whereas in protic solvent the disproportionation and transmetalation to Zn is facilitated. This behavior contrasts with Cu(cyclops) for which disproportionation is reported under most conditions.

Also of interest for comparison with Cu(cyclops) is the behavior toward potentially reducing ligands, iodide, cyanide, and cyanate. The mono and bis iodide derivatives of Cu<sup>II</sup>-(MePhTIM) are stable toward autoreduction in solution and in the solid state. However, stoichiometric or excess CN<sup>-</sup> or NCO<sup>-</sup> added to methanol or methanol/water solutions of [Cu(MePhTIM)]<sup>2+</sup> produced blue or green solutions which slowly turned yellow under both aerobic and anaerobic conditions. No macrocyclic complexes could be isolated from the final solutions. The blue color indicates probable reduction of copper, and yellow solutions result when the copper(I) complex reduced by other agents is exposed to air or when decomposition of the ligand is induced by base. The redox potentials of the MePhTIM complexes have not been investigated but, in view of the chemical behavior, are clearly less negative than [Cu(cyclops)]<sup>+</sup>.

**Characterization of [Zn(MePhTIM)Cl]PF<sub>6</sub>.** This compound was prepared as described above by reduction of [Cu(MePhTIM)]<sup>2+</sup> with Zn<sup>0</sup> in MeOH. Gagné and co-workers<sup>9</sup> have reported the analogous reaction utilizing [Cu(cyclops)]<sup>+</sup>. Attempts to prepare Zn(MePhTIM) by the template reaction resulted only in rapid polymerization of the diamine and diketone from which no macrocyclic product could be isolated. The fact that the template reaction proceeds to give macrocyclic products for all the other latter first-row transition metals and not for zinc is not surprising in view of results for template reactions of similar ketones, amines, and metals.<sup>43</sup> Zinc is apparently capable of catalyzing the Schiff base condensation but in most cases does not coordinate strongly enough to organize the intermediates to form the macrocyclic

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Table V. NMR Data and Assignments for [Zn(MePhTIM)Cl]PF<sub>6</sub><sup>a</sup>

type of C or H	chem shift	
	<sup>13</sup> C	<sup>1</sup> H
methyl	18.18	2.13 s
α-methylene	53.48	3.7-4.1 (m)
	54.64	
	29.43	
β-methylene	29.43	2.2-2.8 (m, br)
	128.19	
	130.71	
	131.88	
phenyl	133.38	7.4-7.8 (m)
	168.41	
	169.55	
imine		

<sup>a</sup> Solvent CD<sub>3</sub>NO<sub>2</sub>; units ppm relative to (CH<sub>3</sub>)<sub>4</sub>Si as internal standard. <sup>13</sup>C NMR data are from the proton-decoupled spectrum. Key: s, singlet; m, complex multiplet; br, broad.

product. Also, the propensity of zinc(II) to form four- or five-coordinate rather than six-coordinate complexes may be important.

The characterization of [Zn(MePhTIM)Cl]PF<sub>6</sub> is of interest for two major reasons. First, being derived from the copper complex and diamagnetic, its carbon-13 NMR spectrum is expected to reveal the arrangement of substituents on the macrocyclic ligand.<sup>12</sup> These results can be related back to the copper template reaction on the assumption of unlikelihood of isomerization during reduction transmetalation. Second, a comparison of the properties of the zinc complex with other metal-MePhTIM complexes is of interest because little π back-bonding is expected between zinc and the α-diimine ligand.

The molar conductivity of a 10<sup>-3</sup> M solution of [Zn(MePhTIM)Cl]PF<sub>6</sub> in CH<sub>3</sub>NO<sub>2</sub> is 81 cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup> which is indicative of a 1:1 electrolyte and a five-coordinate complex. This is not surprising in view of other known five-coordinate tetraaza zinc macrocycles with halide ligands.<sup>44,45</sup> The infrared spectrum is very similar to those of the Cu(MePhTIM)X (X = halide) complexes. It is noteworthy that in comparison with the Fe(II), Ni(II), and Co(III) complexes, both the Cu(II) and Zn(II) complexes have C=N stretching bands which are relatively more intense. This effect stems from the decreasing importance of π back-bonding in the Cu and Zn complexes due to the filling of the d<sub>x<sub>2</sub>-y<sub>2</sub></sub> orbital which interacts with the α-diimine lone pairs. The frequency of the ν<sub>C=N</sub> is also shifted slightly higher to 1615 cm<sup>-1</sup>, indicative of less antibonding electron density in the imine bonds. The only feature of the electronic spectrum of [Zn(MePhTIM)Cl]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> is a shoulder (ε ≈ 4000) at 270 nm on the low-energy side of the intense intraligand bands which start at 250 nm.

The carbon-13 and proton NMR data for [Zn(MePhTIM)Cl]PF<sub>6</sub> are listed in Table V. The proton-decoupled carbon-13 NMR spectrum has 10 resonances including only one arising from the β-methylene carbon atoms. Thus, just as in the cases previously studied,<sup>12</sup> the macrocyclic ligand has a center of symmetry indicating that the substituents are located trans to each other. Since it is unlikely that a specific ligand isomerization occurs simultaneously with the reduction of copper and transmetalation to zinc, the same constitution is indicated for the copper complexes. This product is consistent with earlier studies<sup>12</sup> of the template reaction mechanism in

which the condensation product from one molecule each of 1,3-diaminopropane and 1-phenyl-1,2-propanedione is responsible for the regiospecific ligand isomer and is formed before the metal template is added. The carbon-13 chemical shifts are comparable to those observed for the other MePhTIM complexes with the exception of the imine carbon atoms which are shifted upfield by about 12 ppm relative to the complexes with other metals.<sup>12</sup> This shift is due to decreased zinc-ligand π back-donation resulting from extensive use of metal 4s and 4p for bonding.

The proton NMR spectrum of [Zn(MePhTIM)Cl]PF<sub>6</sub> is analogous to those observed for other MePhTIM complexes. In comparison with those complexes, for which the metal is tetragonal and the ligand is approximately planar, the α-methylene pattern appears more resolved into two overlapping triplets rather than one broad triplet. Thus, in the zinc complex there is greater distinction between the two nonequivalent sets of α-methylene protons. This is most likely a result of rectangular-pyramidal coordination geometry and the flexing of the macrocycle to accommodate apical displacement of the metal ion, analogous to the Cu(cyclops) derivatives. Studies of the proton NMR spectra of other Zn(MePhTIM) derivatives are in progress to determine whether NMR is sensitive to variations in apical ligand.<sup>46</sup>

The transmetalation to [Zn(MePhTIM)Cl]<sup>+</sup> by metallic zinc reduction of [Cu(MePhTIM)]<sup>2+</sup> suggests that the metal-free macrocyclic ligand has some degree of stability in solution. The ligand coordination to zinc is not as strong as for the other metals, as evidenced by the carbon-13 NMR and infrared results. Since zinc complexes of other macrocycles have been found to undergo metal exchange reactions under acidic conditions,<sup>47</sup> we attempted some of these reactions with [Zn(MePhTIM)Cl]<sup>+</sup>. Indeed, when [Zn(MePhTIM)Cl]PF<sub>6</sub> was stirred in warm 1:1 methanol/water with CuCl<sub>2</sub> and a few drops concentrated HCl, a blue-violet solution resulted. Upon addition of KPF<sub>6</sub> in water, [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub> precipitated in about 60% yield. Similar facile reactions under appropriate conditions yielded the Co- and Ni(MePhTIM) complexes. Transmetalation to the iron complex was not attempted. The success of these transmetalation reactions to known MePhTIM complexes shows that the method is general and therefore could provide a route to new MePhTIM complexes which are probably inaccessible by the template method.

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**Registry No.** [Cu(MePhTIM)]ZnCl<sub>4</sub>, 77154-15-5; [Cu(MePhTIM)](PF<sub>6</sub>)<sub>2</sub>, 77154-14-4; [Cu(MePhTIM)NMI](PF<sub>6</sub>)<sub>2</sub>, 77154-12-2; [Cu(MePhTIM)py](PF<sub>6</sub>)<sub>2</sub>, 77154-10-0; [Cu(MePhTIM)(4-Mepy)](PF<sub>6</sub>)<sub>2</sub>, 77154-08-6; [Cu(MePhTIM)(aniline)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 77154-06-4; [Cu(MePhTIM)Br]PF<sub>6</sub>, 77154-04-2; [Cu(MePhTIM)I]PF<sub>6</sub>, 77154-02-0; [Cu(MePhTIM)NCS]PF<sub>6</sub>, 77154-00-8; Cu(MePhTIM)Br<sub>2</sub>, 77153-98-1; Cu(MePhTIM)Cl<sub>2</sub>, 77153-97-0; Cu(MePhTIM)I<sub>2</sub>, 77153-96-9; Cu(MePhTIM)(NCS)<sub>2</sub>, 77153-95-8; [Cu(MePhTIM)Cl]PF<sub>6</sub>, 77153-94-7; [Zn(MePhTIM)Cl]PF<sub>6</sub>, 77153-92-5; 1-phenyl-1,2-propanedione, 579-07-7; 1,3-diaminopropane, 109-76-2.

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