faster than in the previously reported Ru^{2+}, In^{3+}, or TiO^{2+} complexes.[1] For R = Et_2N the rate of phenyl ring rotation at 323 K is about 1000 times faster for MXY = GaCl than for Ru(CO)(*t*–Bu(py)). The electronic spectra of the gallium complexes are quite similar to those previously reported for the analogous indium and titanyl complexes.[1] Since the Ga^{3+} ion is smaller than the other ions studied, it seems plausible that it would cause greater distortion of the porphyrin core when coordinated thereby facilitating ring rotation.[1] It appears that the effect of the metal ion may be largely conformational rather than electronic for these d^0 and d^{10} complexes. Crystallographic data are not available to check this hypothesis.

Effect of Axial Ligand. The rates of phenyl ring rotation in Ga(*p*-R-TPP)X with R = CH_3 and CF_3 are faster by about a factor of 2 for X = Cl than for X = OH. This observation is in marked contrast to results for In^{3+} and Ru^{2+} complexes where for a limited range of axial groups the rates of phenyl ring rotation appeared to be insensitive to changes in the axial ligand.[1] It is particularly surprising that for In(*p*-Cl-TPP)X the rates of ring rotation for X = OH and Cl are within about 10% but for Ga(*p*-R-TPP)X, rates of ring rotation for X = OH and Cl differ by about a factor of 2. Further work is necessary to assess the effect of axial ligands on rates of phenyl ring rotation.

Overall, considering the effects of metal ion and para substituents on the rate of phenyl ring rotation, the fastest rates observed to date are for Ga(*p*-Et_2N-TPP)Cl. Ring rotation in this complex at 323 K is about 10^4 times faster than for Ru(CO)(*p*-CF_3-TPP)(*t*-Bu(py))[1] which exhibits the slowest ring rotation yet observed in a metal complex of a para-substituted tetraphenylporphyrin.

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Registry No. Ga(*p*-CF_3-TPP)OH, 65930-55-4; Ga(*p*-CF_3-TPP)Cl, 65930-56-5; Ga(*p*-Cl-TPP)Cl, 65930-57-6; Ga(*p*-Me-TPP)OH, 65930-59-8; Ga(*p*-Me-TPP)Cl, 65930-60-1; Ga(*p*-*i*-Pr-TPP)Cl, 65930-61-2; Ga(*p*-OMe-TPP)Cl, 65930-62-3; Ga(*p*-Et_2N-TPP)Cl, 65930-63-4; Ga(*o*-Me-TPP)Cl, 65930-64-5.

References and Notes

(1) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **99**, 6594 (1977), and references therein.
(2) Abbreviations used throughout: *p*-R-TPP, tetrakis(*p*-R-phenyl)porphyrin dianion; *p*-CF_3-TPP, tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin dianion; p-Cl-TPP, tetrakis(*p*-chlorophenyl)porphyrin dianion; *p*-Me-TPP, tetrakis(*p*-methylphenyl)porphyrin dianion; *p*-*i*-Pr-TPP, tetrakis(*p*-isopropylphenyl)porphyrin dianion; *p*-OMe-TPP, tetrakis(*p*-methoxyphenyl)porphyrin dianion; *p*-Et_2N-TPP, tetrakis(*p*-(diethylamino)phenyl)porphyrin dianion; *o*-Me-TPP, tetra-*o*-tolylporphyrin dianion.
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Coordination Sphere Flexibility at Copper: Chemistry of a Unipositive Copper(II) Macrocycle, [Cu(cyclops)]$^+$

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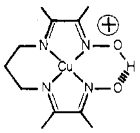
The complex of Cu^{2+} with cyclops, an N_4 macrocycle of −1 charge, has been investigated and square-pyramidal adducts of formula [Cu(cyclops)X] and [Cu(cyclops)L]ClO_4 have been isolated, where X represents a series of anionic Lewis bases and L represents a series of neutral Lewis bases. These adducts are notable for their strong axial interaction. The redox behavior of Cu(cyclops)$^+$ and its adducts was studied by cyclic voltammetry, and equilibrium constants have been determined for the 1:1 interactions of both oxidized and reduced Cu(cyclops)$^+$ with pyridine, γ-picoline, methyl phenyl sulfide, and benzyl isocyanide. The relationship of the chemistry of Cu(cyclops)$^{+/0}$ to copper biochemistry is discussed.

Introduction

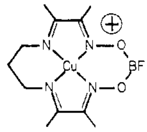
Accelerated progress[2] in the field of inorganic biochemistry has stimulated the study of model systems for protein copper. Recent work has increased our appreciation of the roles of phenoxide[3] and sulfur[4-7] coordination, of tetrahedral coordination geometry,[4,7-9] and of binucleation[10] in the optical absorption[3-6] and electron spin resonance[6-8] spectroscopic and redox[5,8-10] properties of copper proteins. Galactose oxidase[11] and superoxide dismutase[12] are examples of copper enzymes with "type 2" copper sites. In the latter, the copper(II) is bound to four nitrogen donors in a nearly square-planar array[13] and is capable of binding an exogenous Lewis base in both the cuprous and cupric states.[12,15]

We wished to synthesize a model system which might increase our understanding of type 2 copper chemistry by (a) having a nearly square-planar $(Cu^{II}N_4)^+$ chromophore as is observed in the crystal structure of the bovine dismutase,[13] (b) having a high affinity for one exogenous ligand in the cupric and cuprous state, and (c) exhibiting at least quasi-reversible redox behavior.

In this paper we shall discuss the chemistry of copper(II) chelates **1** and **2** and shall show that the latter system in particular exhibits the three properties which are required of our model system.



1 Cu(Pre H)$^+$



2 Cu(cyclops)$^+$

The neutral dioxime ligand $PreH_2$ was first prepared by Uhlig and Friedrich[16] who briefly reported on its complexes with Ni(II). Subsequently Gagnê[17] has reported the prep-

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aration of both $Cu(PreH)^+$ and $Cu(cyclops)^+$ along with adducts of $Cu(cyclops)^0$.

Experimental Section[18]

Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer. Samples were either mulled in Nujol between KBr plates or pelleted in KBr.

Electronic spectra were recorded on a Cary 14 spectrophotometer. ESR spectra were obtained on a Varian E-3 X-band spectrometer, calibrated with DPPH and an NMR probe. Cyclic voltammetry and polarography at a hanging mercury drop (0.020 cm^2), platinum disk (0.300 cm^2), or mercury-coated gold disk (0.289 cm^2) electrode were performed (at 25 ± 0.2 °C in solutions deoxygenated by bubbling nitrogen or argon) using a PAR-173 potentiostat and PAR-176 i/E converter. Voltammetric data were recorded on a storage oscilloscope or X–Y recorder. Current (i) vs. charge (q) plots were obtained by electronic integration (McKee-Pedersen MP-1012A integrator) of the current and by using the capacitively damped current and its time integral as inputs for the X–Y recorder. The three-electrode cell included as the reference an $Ag(s)|AgClO_4$ (0.01 M), TEAP (0.1 M), CH_3CN electrode. We have measured this to be 0.30 V positive of the SCE in acetonitrile at 25 °C, and all potentials are thus referred to the SCE.

Solvents for electrochemistry were distilled off P_4O_{10} (acetonitrile) or KOH (2-methoxyethanol) under nitrogen. Pyridine was distilled off phthalic anhydride. The salt $KC(CN)_3$ was prepared by the method of Trofimenko, Little, and Mower.[19] All other chemicals were obtained from commercial sources. Oxygenation at −45 °C was performed in a Dewar cell thermostated with a chlorobenzene slurry.

C, H, and N analyses were performed at the University of British Columbia by Mr. P. Borda.

2-Oximino-10-oximinato-3,9-dimethyl-4,8-diazaundeca-3,8-dienecopper(II) Perchlorate Dihydrate $[Cu(PreH)]ClO_4{\cdot}2H_2O$ (1). Copper(II) acetate hydrate (10 g, 50 mmol), sodium acetate (15 g, 175 mmol), 1,3-propanediamine (55 mmol), and diacetyl monoxime (11 g, 110 mmol) were refluxed together in methanol (50 mL) for 12 h. The crude product was precipitated by addition of sodium perchlorate (15 g), filtered off, recrystallized from water, and air-dried to yield brick red prisms (14.6 g, 72%). The salt releases water reversibly when desiccated over P_4O_{10}. If desiccated over $CaSO_4$, it forms a stable monohydrate.

1,1-Difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,12-tetraenatocopper(II) Perchlorate Monohydrate, $[Cu(cyclops)]ClO_4{\cdot}H_2O$ (2). A total of 8.8 g (20 mmol) of the precursor compound **1** was slurried in redistilled boron fluoride ethyl etherate (60 mL) and allowed to stand on the steam bath for 10 min, with occasional stirring. The deep red solution was cooled and poured [*caution*] onto a mixture of crushed ice (800 g) and sodium acetate (200 g). The ether was removed on the rotary evaporator and the product, precipitated by addition of sodium perchlorate (20 g), was recrystallized from 10% acetic acid as purple platelets (6.1 g, 65%). Desiccation in vacuo over P_4O_{10} causes the purple crystals to become red; this dehydration is reversed immediately by exposure to the atmosphere.

The adducts $[Cu(cyclops)L]ClO_4$, L = pyridine, γ-picoline, imidazole, and pyrazole, were prepared by adding the ligand (0.4 mmol) to a hot solution of $Cu(cyclops)ClO_4{\cdot}H_2O$ (100 mg, 0.21 mmol) in methanol (10 mL) and allowing the product to crystallize by remaining at 0 °C for 24 h. The resulting crystals were washed with cold methanol and dried.

The adducts $[Cu(cyclops)X]$, where X is a uninegative anion, were prepared by mixing appropriate ratios of $[Cu(cyclops)]ClO_4{\cdot}H_2O$ and the sodium, potassium, or tetrabutylammonium salt of the anion in methanol.

$X^- = Cl^-, Br^-, I^-$. These adducts were prepared by adding the salt Bu_4NX (0.4 mmol) to a hot solution of $Cu(cyclops)ClO_4{\cdot}H_2O$ (100 mg, 0.21 mmol) in 10 mL of methanol and isolating the product as above.

$X^- = NCO^-, CN^-, N(CN)_2^-$. These adducts were prepared by adding the salt NaX (0.4 mmol) to a hot solution of $Cu(cyclops)ClO_4{\cdot}H_2O$ (100 mg, 0.21 mmol) in 20 mL of methanol[20] and isolating the product as above.

$X^- = NCS^-, C(CN)_3^-$. These adducts were prepared by adding a solution of the salt KX (0.4 mmol) in 10 mL of water to a hot solution of $Cu(cyclops)ClO_4{\cdot}H_2O$ (100 mg, 0.21 mmol) in 10 mL of methanol. The product was isolated as above but was washed first with H_2O to dissolve the coprecipitated $KClO_4$.

Table I. Analytical Results for the Compounds

Formula	Calcd %C	Calcd %H	Calcd %N	Found %C	Found %H	Found %N
$[Cu(PreH)]ClO_4{\cdot}2H_2O$	30.1	5.25	12.8	30.2	5.27	13.0
$[Cu(PreH)]ClO_4{\cdot}H_2O$	31.4	5.04	13.3	31.7	4.91	13.6
$[Cu(cyclops)]ClO_4{\cdot}H_2O$	28.2	4.28	12.0	28.3	4.37	12.0
$[Cu(cyclops)Cl]{\cdot}CH_3OH$	34.5	5.27	13.4	34.6	5.36	13.7
$[Cu(cyclops)Br]{\cdot}CH_3OH$	31.2	4.76	12.1	31.1	4.60	12.4
$[Cu(cyclops)I]$	27.7	3.80	11.7	27.7	3.91	11.7
$[Cu(cyclops)CN]H_2O$	36.5	5.11	17.7	36.3	4.93	17.6
$[Cu(cyclops)NCO]{\cdot}{}^1/_2CH_3OH$	36.7	4.90	17.1	36.7	4.88	17.0
$[Cu(cyclops)NCS]{\cdot}CH_3OH$	35.4	5.00	15.9	35.3	5.13	16.0
$[Cu(cyclops)NCSe]{\cdot}CH_3OH$	32.2	4.58	14.5	32.1	4.50	14.6
$[Cu(cyclops)N(CN)_2]$	37.5	4.32	23.5	37.3	4.50	23.3
$[Cu(cyclops)C(CN)_3]$	40.9	4.12	22.2	40.6	4.20	22.5
$[Cu(cyclops)(pyridine)]ClO_4$	36.3	4.38	13.2	36.4	4.18	13.2
$[Cu(cyclops)(\gamma\text{-picoline})]ClO_4$	37.6	4.64	12.9	37.8	4.53	12.8
$[Cu(cyclops)(imidazole)]ClO_4$	32.5	4.28	16.2	32.5	4.40	15.9
$[Cu(cyclops)(pyrazole)]ClO_4$	32.5	4.28	16.2	32.8	4.40	16.4

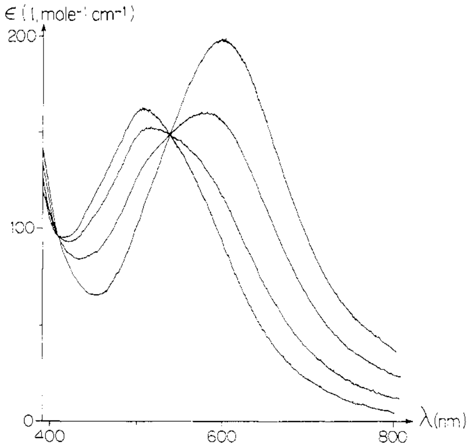

Figure 1. Pyridine adduct formation from 7.42 mM $[Cu(cyclops)]^+$ in CH_3NO_2 at ambient temperature. Curves of increasing absorbance at 600 nm correspond to [total added pyridine] = 0, 2.1, 5.7, and 57 mM, respectively.

$X^- = NCSe^-$. This adduct was prepared by mixing methanol solutions (10 mL) of $Cu(cyclops)ClO_4{\cdot}H_2O$ (0.5 mmol) and KNCSe (3 mmol), immediately filtering off the $KClO_4$ precipitate, and allowing the product to crystallize.

All adducts were desiccated over P_4O_{10} or BaO and characterized without further purification. Analytical results are given in Table I.

Results and Discussion

Adduct Formation. The 1:1 adducts isolated fall into two groups, viz., $[Cu(cyclops)L]^+$ and $[Cu(cyclops)X]$ where L and X are neutral molecules and monoanions, respectively. Binuclear species of the type $[Cu_2(cyclops)_2L]^{2+}$ and $[Cu_2(cyclops)_2X]^+$ have also been prepared, and these will be discussed elsewhere.

For donors such as pyridine, which are incapable of binding to two copper(II) ions simultaneously, adduct formation in solution is exemplified by Figure 1 which shows the spectral changes occurring upon addition of pyridine to a solution of $[Cu(cyclops)]ClO_4{\cdot}H_2O$ in nitromethane. These are interpretable only in terms of 1:1 adduct formation, with the limiting spectrum being indistinguishable from that observed for $[Cu(cyclops)py]ClO_4$ in the solid state. Attempts to form the 2:1 (L:Cu) adduct, using very high concentrations of pyridine, have resulted in an irreversible reaction yielding a brown product. Similar irreversible reactions have been observed with lower concentrations of strong organic bases, such as piperidine and phenoxide.

For potentially bridging donors, rather different behavior may be observed in solution. When a spectrophotometric

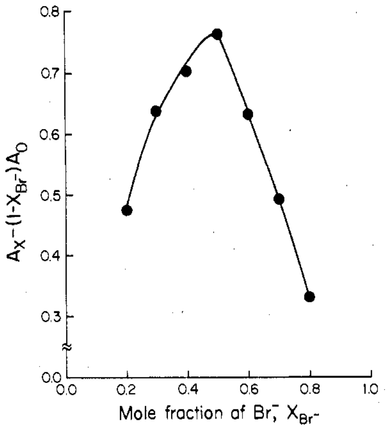

Figure 2. Job plot for titration of 9.4 mM [Cu(cyclops)]$ClO_4 \cdot H_2O$ in nitromethane with tetraethylammonium bromide at 640 nm. A_x is the absorbance of the solution with bromide mole fraction x_{Br}; A_0 is the absorbance of Cu(cyclops)$^+$.

Table II. Vibrational Frequencies for the Polyatomic Anions in Cu(cyclops)X

Anion, X^-	ν, cm^{-1}
CN^-	2134 w
NCO^-	2196 s, 1316 m, 625 m
NCS^-	2082 s, 795 sh, 455 w
$NCSe^-$	2090 s
$C(CN)_3^-$	2255 m, 2180 s, 1239 m, 566 m
$N(CN)_2^-$	2266 s, 2219 s, 2157 s, 1342 m, 663 w, 517 m

titration of Cu(cyclops)$^+$ with tetrabutylammonium bromide in CH_3NO_2 was performed, the absorption spectrum was transformed to that observed for [Cu(cyclops)Br]$\cdot CH_3OH$ in the solid state; however, the isosbestic point in this case was not well developed. a Job plot for the bromide titration (Figure 2) shows curvature on the side corresponding to less than one bromide per Cu^{2+}, which is consistent with a minor contribution to the equilibrium from 1:2 adduct formation in solution, as is expected for a ligand capable of bridging.

The solution chemistry of adduct formation by Cu(cyclops)$^+$ could involve at least four distinct species:

$$2Cu(cyclops)^+ + X^- \rightarrow Cu_2(cyclops)_2X^+ \tag{1}$$

$$Cu_2(cyclops)_2X^+ + X^- \rightarrow 2Cu(cyclops)X \tag{2}$$

$$Cu(cyclops)X + X^- \rightarrow Cu(cyclops)X_2^- \tag{3}$$

Dimer or possibly oligomer formation (eq 1) can occur with ligands capable of bridging, and we have detected spectrophotometrically such behavior in the CN^-, I^-, and Br^- systems, for example.[21] In no case, however, do we have any evidence for *significant* 2:1 adduct formation in solution.

Whereas adducts of the type [Cu(cyclops)X] can readily be isolated, we have not been able to isolate compounds of the type [Cu(PreH)X] from methanol solution. We attribute this to the enhanced Lewis acidity of Cu^{2+} in Cu(cyclops)$^+$, undoubtedly due to the strong electron-withdrawing ability of its BF_2 group.[22] Thus cyclops$^-$ should be a much weaker σ-donor macrocycle than PreH$^-$ and consequently Cu(cyclops)$^+$ will more readily form 1:1 adducts with Lewis bases.[23]

Infrared Spectra. For the 1:1 copper(II) axial adducts, infrared spectroscopy was used to ascertain the bonding mode of the potentially ambidentate donors NCO^-, NCS^-, $NCSe^-$, $C(CN)_3^-$, $N(CN)_2^-$, and CN^- in the complexes Cu(cyclops)X, and the bonding mode of ClO_4^- in the series [Cu(cyclops)L]ClO_4. Infrared bands attributable to these anions are listed in Table II. Two representative spectra are shown in Figure 3.

The cyanide adduct shows a sharp, weak CN^- stretching vibration at 2134 cm^{-1}. This is in the range expected for terminal cyanide binding to copper(II).[24] The pseudohalides NCX^- have three infrared-active modes labeled ν_{NC}, ν_{CX}, and δ_d, in the order of decreasing frequency.[25] For the NCO^- and NCS^- adducts the vibrational frequencies (particularly ν_{CX}) are consistent with N bonding. For the $NCSe^-$ adduct, bands attributable to ν_{CSe} and δ_d were masked by strong macrocycle vibrations; however, we have no evidence to counter the deduction that it should be N bonded.

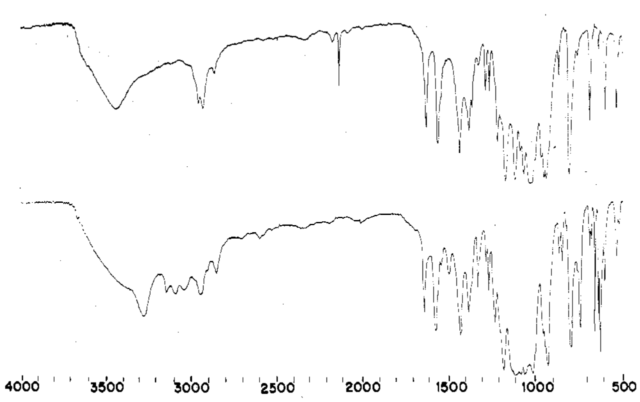

Figure 3. Infrared spectra of Cu(cyclops)$CN \cdot H_2O$ (upper) and [Cu(cyclops)(imidazole)]ClO_4 (lower).

The free dicyanamide anion is angular and of C_{2v} symmetry[26] while the free tricyanomethanide anion is planar and of approximately D_{3h} symmetry.[27] In both cases coordination to a metal ion should occur through a cyano nitrogen;[28,29] the infrared spectra of both adducts are consistent with such bonding. For Cu(cyclops)$C(CN)_3$, two infrared-active CN vibrations are found at 2255 and 2180 cm^{-1}. The former is due to the totally symmetric CN stretching vibration of the coordinated CN, while the latter is due to the unsplit infrared-active $a_1 + b_2$ CN stretching vibration. The two remaining bands at 1239 and 566 cm^{-1} are the C$=$C stretching mode and the C—CN out-of-plane bending mode.[30]

For $N(CN)_2^-$, three bands are found in the "cyanide" region. The highest energy band at 2266 cm^{-1} is a C–N combination band, $\nu_s + \nu_a$, of the C$=$N stretching modes,[26] where C$=$N refers to the central nitrogen atom. The two remaining bands at 2219 and 2157 cm^{-1} are the stretching vibrations for the coordinated and free C$\equiv$N groups. The asymmetric C$=$N stretch is found at 1342 cm^{-1}, but the symmetric stretch is masked by a very strong macrocycle absorption centered at 940 cm^{-1}. The remaining bands at 663 and 517 cm^{-1} are bending modes.

For the class of complexes [Cu(cyclops)L]ClO_4, where L is a neutral nitrogen donor base, the infrared spectra show absorptions characteristic of the neutral ligands L and also perchlorate. In no case is there any evidence for ClO_4^- coordination. The ν_3 band at $\sim$1100 cm^{-1} and the ν_4 band at $\sim$620 cm^{-1} are unsplit, while the totally symmetric ν_1 band at $\sim$920 cm^{-1} is not evident.

Electronic Spectra. The optical absorption spectrum of Cu(cyclops)$^+$ is quite solvent sensitive, as is expected for a system which is susceptible to axial ligation. In an acidic solvent system (CH_3NO_2/TFAA) the d–d band envelope peaks at 502 nm and shifts systematically to longer wavelength as solvent systems of increasing donor power are used (Table III). Much larger shifts are observed for the 1:1 adducts [Cu(cyclops)L]ClO_4 and [Cu(cyclops)X], with Cu(cyclops)NCO having the lowest energy band envelope maximum at 735 nm.

If one devises a spectrochemical series for the axial ligands from the data in Table III, the following order results: $H_2O \ll C(CN)_3^- <$ pyridine $<$ imidazole $< I^- \sim Br^- < N(CN)_2^- < Cl^- < NCS^- \ll CN^- \sim NCO^-$.

This is not, however, the "normal" order which is observed in inorganic spectroscopy.[31] Most unusual is the position of

Table III. Optical Absorption Spectra

Compound	Medium	λ, nm	ϵ, M^{-1} cm^{-1}
$[Cu(PreH)]ClO_4 \cdot H_2O$	H_2O	490	150
	Nujol mull	472	
$[Cu(cyclops)]ClO_4 \cdot H_2O$	Nujol mull	520	
	$CH_3NO_2/TFAA^a$	500	162
	H_2O	516	149
	Cyclopentanone^b	520	175
	$CH_3OCH_2CH_2OH^b$	520	170
	CH_3CN^b	545	183
	DMA[18,b]	560	166
$[Cu(cyclops)(pyridine)]ClO_4$	$CH_3NO_2{}^c$	600	198
	Nujol mull	593	
$[Cu(cyclops)(\gamma\text{-picoline})]ClO_4$	$CH_3NO_2{}^c$	605	199
	Nujol mull	608	
$[Cu(cyclops)(pyrazole)]ClO_4$	$CH_3NO_2{}^c$	603	193
	Nujol mull	578	
$[Cu(cyclops)(imidazole)]ClO_4$	$CH_3NO_2{}^c$	620	198
	Nujol mull	617	
$[Cu(cyclops)CN]$	Nujol mull	730	
$[Cu(cyclops)Cl]$	$CH_3CN^{c,d}$	660	210
	Nujol mull	665	
$[Cu(cyclops)Br]$	CH_3CN^c	638	184
	Nujol mull	638	
$[Cu(cyclops)I]$	CH_3CN^c	642	187
	Nujol mull	635	
$[Cu(cyclops)C(CN)_3]$	CH_3CN^c	566	173
	Nujol mull	588	
$[Cu(cyclops)N(CN)_2]$	Nujol mull	659	
$[Cu(cyclops)NCO] \cdot {}^1/_2CH_3OH$	Nujol mull	735	
$[Cu(cyclops)NCS] \cdot CH_3OH$	Nujol mull	675	
$[Cu(cyclops)NCSe] \cdot CH_3OH$	Nujol mull	630	

[a] 10% TFAA. [b] 10% CH_3NO_2. [c] Containing 0.1 M X^- or L. [d] Shoulder at 585 nm.

the neutral ligands H_2O, pyridine, imidazole, etc., relative to the anions in the above series. Normally one expects the progression ... $Cl^- < H_2O <$ pyridine ....[31] The same reversal of Cl^- and H_2O, albeit unexplained, was encountered by Musker and Hussain[32] in their study of the 1:1 adducts of square-planar $Cu(homopiperazine)_2{}^{2+}$. Also, in our observed spectrochemical series, the anions CN^- and NCO^- are juxtaposed from their normal order. All the other anions seem to be reasonably placed in the above series, including the infrequently encountered $N(CN)_2{}^-$ and $C(CN)_3{}^-$.[33]

With simple crystal field arguments, the above observations can be explained readily. In the process of adduct formation the Cu^{2+} d-orbital energies are perturbed by two factors: (a) approach of the donor L or X^- along the axis orthogonal to the N_4 plane and (b) movement of the Cu^{2+} ion out the N_4 plane toward this approaching axial ligand. This is schematically illustrated in Figure 4. Assuming Cu^{2+} is displaced by the same distance ρ in all adducts $Cu(cyclops)L^+$ and Cu(cyclops)X, a "normal" spectrochemical series should be observed. This is clearly not the case here and implies that ρ must vary substantially in these complexes. In this series the displacement ρ must be related to the "strength" of the axial ligand. Neutral donors such as pyridine, H_2O, etc., cannot have as strong a charge density on their donor atoms as do anionic donors such as Cl^-, NCO^-, etc. Thus the anionic donors, assuming the charge is not too diffusely distributed as possibly in $C(CN)_3{}^-$, will induce larger Cu^{2+} out-of-plane displacements and stronger axial binding. According to Figure 4, an increase in ρ causes compression of the d-orbital energy levels and a concomitant shift of the d–d band envelope to longer wavelength;[34] hence neutral axial donors appear at the low end of the observed spectrochemical series.

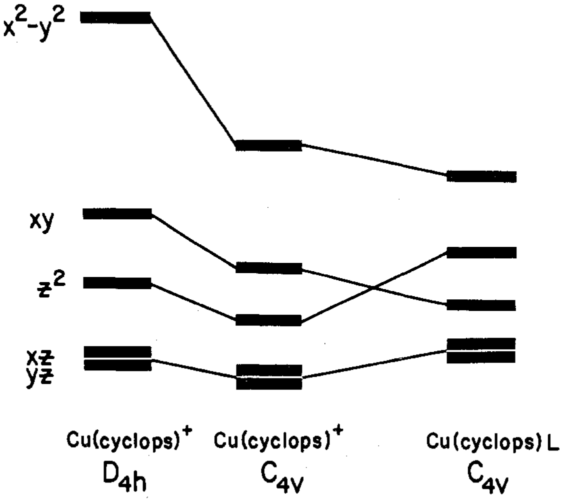

Figure 4. Orbital energy diagram for $Cu(cyclops)^+$ + L.

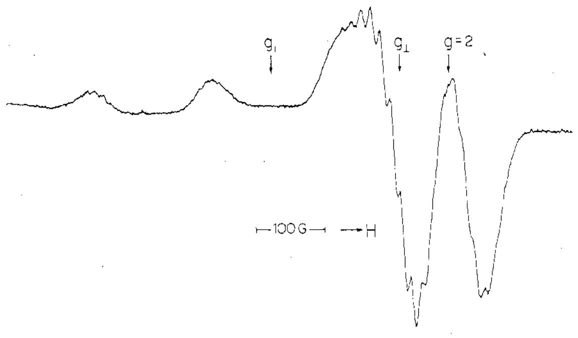

Figure 5. First derivative X-band ESR spectrum of 0.46 mM $Cu(cyclops)ClO_4 \cdot H_2O$ in 5% v/v TFAA/nitromethane at 77 K.

One other spectrochemical series reversal bears comment. The fact that NCO^- from our series has an *apparent* ligand field strength at least equal to that of CN^- must imply that $\rho(NCO)$ is large and surely greater than $\rho(CN)$. The structure of Cu(cyclops)NCO has recently been determined by single-crystal x-ray diffraction[35] and confirms our suspicion of a truly large out-of-plane Cu^{2+} displacement. It was found that $\rho = 0.58$ Å, which is the largest value we have encountered for square-pyramidal copper(II).[36]

The ESR spectra of $[Cu(PreH)]ClO_4 \cdot H_2O$ and of the $[Cu(cyclops)]^+$ derivatives obtained at 77 K in nitromethane solution are essentially axial (Figure 5) and are all quite similar in appearance. There is considerable overlap between the $g_\parallel$ and $g_\perp$ regions, which renders accurate analysis nontrivial; we have not attempted any spectral simulation here. Values for $g_\perp$ and $A_\perp$ were estimated by application of the simple first-order relationships $g_\perp = {}^1/_2(3g_0 - g_\parallel)$ and $A_\perp = {}^1/_2(3A_0 - A_\parallel)$. It was evident from the fluid solutions' spectra (Table IV) that A_0 decreases as more strongly interacting axial donors are encountered, and for the case of $[Cu(cyclops)(CN)]H_2O$, the isotropic nuclear hyperfine structure is not completely resolved at ambient temperature. Decrease in A_0 has been observed previously to parallel the donor strength of the axial addend and is a consequence of axial ligand coordination causing $A_\perp$ to decrease.[37] This decrease in $A_\perp$ is clearly evident in Table IV. There is also a (less systematic) tendency for $g_\perp$ to increase as stronger donors are used, the value of $(g_\perp - 2)$ increasing by ca. 50% when a pyridine addend binds to the $[Cu(cyclops)]^+$ moiety. This is consistent with the expression for $g_\perp$ in C_{4v} symmetry:[38]

$$g_\perp - 2 = -2k_\perp{}^2\lambda/E({}^2E - {}^2B_1)$$

where λ is the spin–orbit coupling constant (-829 cm^{-1} for Cu^{2+}) and $k_\perp$ is an orbital reduction factor. Axial adduct formation decreases the energy of the optical transition, and $g_\perp$ increases consequently. In contrast, there are no systematic

Table IV. ESR Spectra of Copper Complexes[a]

Species	$10^4\lvert A_0\rvert$, cm^{-1}	g_0	$10^4\lvert A_\parallel\rvert$, cm^{-1}	$g_\parallel$	$10^4\lvert A_\perp\rvert$,[b] cm^{-1}	$g_\perp$
$[Cu(PreH)]ClO_4 \cdot H_2O$ in CH_3NO_2	88	2.081	191	2.158	37	2.043
$[Cu(cyclops)]ClO_4 \cdot H_2O$ in CH_3NO_2	88	2.090	186	2.181	39	2.045
$[Cu(cyclops)]ClO_4 \cdot H_2O$ in CH_3NO_2/TFAA[c]	86	2.090	193	2.181	32	2.045
$[Cu(cyclops)]ClO_4 \cdot H_2O$ in CH_3NO_2/DMA[c]	79	2.095	197	2.107	20	2.089
$[Cu(cyclops)]ClO_4 \cdot H_2O$ in CH_3NO_2/pyridine[d]	72	2.105	195	2.183	11	2.066
$[Cu(cyclops)]ClO_4 \cdot H_2O$ in CH_3NO_2/Bu_4NCl[d]	69	2.108	184	2.189	12	2.100
$[Cu(cyclops)(CN)]H_2O$ in CH_3NO_2	61[e,f]	*f*	172	2.187	6	*f*

[a] Via first-order spectral analysis. $g_\parallel$, $A_\parallel$ determined at 77 K; A_0, g_0 at ambient temperature for 10^{-3} M solutions. No allowance was made for dependence of coordination mode on temperature. g_0 assumed temperature independent: F. G. Herring and R. L. Tapping, *Can. J. Chem.*, **52,** 4016 (1974). [b] $\pm 0.005\ cm^{-1}$. A_0, $A_\parallel$, and $A_\perp$ have the same sign. [c] 10%. [d] 0.25 M. [e] Estimated from highest and lowest field features of spectrum. [f] Poorly resolved at 300 K.

changes in $A_\parallel$ or $g_\parallel$, apart from replacement of the macrocycle oxime proton by the more electron-withdrawing BF_2 unit causing $g_\perp$ to increase and $\lvert A_\parallel\rvert$ to decrease, in agreement with previously observed trends.[39]

Redox Chemistry. Cyclic voltammetry of $Cu(cyclops)^+$ in acetonitrile/TEAP reveals two reduction processes. The first of these at $E_{1/2} = -0.40$ V is chemically reversible and, while non-Nernstian at a platinum electrode ($E_{p,a} - E_{p,c} = 80$ mV), approaches Nerstian behavior at a mercury electrode, where the peak potential separation (65 mV) is consistent with a one-electron process. Assuming $n = 1$, a reasonable value can be calculated for the diffusion coefficient, D, in acetonitrile and in other solvents (Table V).[40] The assumption of reversibility yields a value near unity for $n^{1/2}$ from combined voltammetry and chronoamperometry at mercury,[41] while voltammetry and RDE polarography at mercury both yield $D = 1.02 \times 10^{-5}\ cm^2\ s^{-1}$, $n = 1$, in acetonitile/TEAP. Finally, controlled potential reduction at a platinum mesh cathode in TEAP/acetonitrile at -0.58 V vs. SCE caused a pink solution of the complex to become deep greenish blue. The current–charge plot[42] after a few half-lives extrapolated linearly to zero current at $n = 0.97 \pm 0.06$ F mol^{-1}. The ESR signal associated with the Cu(II) center disappeared, and the solution evidenced a strong absorption band at 673 nm, with $\epsilon \simeq 6000$. The intensity is somewhat greater ($\epsilon \simeq 8000$) in 2-methoxyethanol solution (Figure 6).[43] In acetonitrile, the reduced species reacts with O_2, the 673-nm absorption band being destroyed. The reaction is, however, rapid and irreversible, both at 25 and -45 °C. The second reduction process at $E_{1/2} = -1.75$ V is irreversible and was not investigated further.

A one-electron oxidation was also observed in acetonitrile/TFAA/TEAP, which at the RPE exhibited an $E_{1/2}$ of $+1.05$ V vs. SCE. Its chemical reversibility was poorly reproducible, and this process may well be associated with oxidation of an imine group.

$[Cu(PreH)]^+$ has similar cathodic properties. The quasi-reversible first reduction process appears at a slightly more negative potential, and the voltammetric peak current is consistent with a slightly greater diffusion coefficient. As with $Cu(cyclops)^+$, the second reduction wave is irreversible.

That $Cu(cyclops)^+$ is reduced more readily than $Cu(PreH)^+$ can be directly attributed to the electron-withdrawing ability of BF_2^+ relative to H^+. As the in-plane σ-donor power of the macrocyclic ligand is decreased, the affinity of the Cu(II) ion in $Cu(cyclops)^+$ for electronic charge is simultaneously increased. Thus the reduction potential becomes more positive by 230 mV.

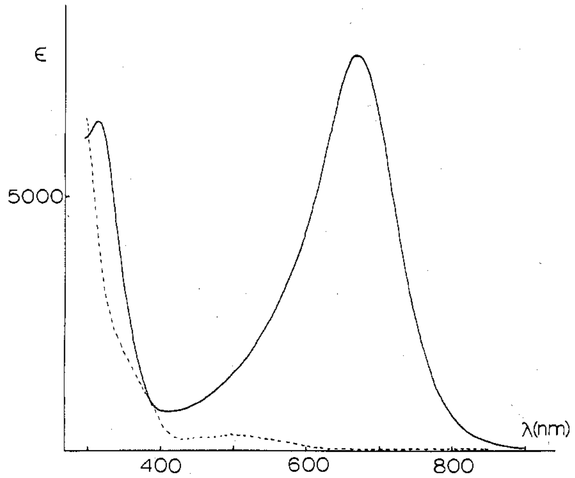

Figure 6. Optical absorption spectra of 1.0 mM $[Cu(cyclops)]^+$ (dotted line) in 2-methoxyethanol/0.2 M $NaClO_4$ and its one-electron reduction product (solid line).

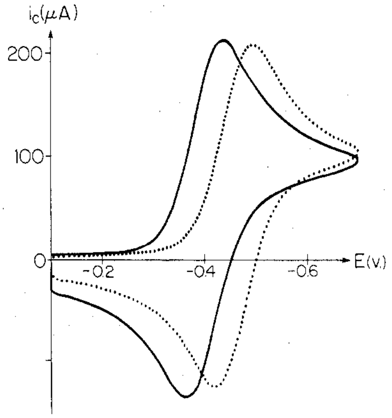

Figure 7. Cyclic voltammogram of 2.6 mM $[Cu(cyclops)]^+$ in acetonitrile/0.2 M TEAP, before (solid line) and after (dotted line) addition of pyridine (0.2 M). Scan rate 0.10 V s^{-1} at Pt disk electrode. Potential referred to SCE.

All of the above electrochemical data are consistent with the recent brief report on $Cu(PreH)^+$ and $Cu(cyclops)^+$ by Gagné[17] and show unequivocally that the first reduction is a chemically reversible one-electron reduction.

The presence of a Lewis base X^- or L in solution with $Cu(cyclops)^+$ has a definite effect on the value of the reversible reduction potential. For example, when an acetonitrile solution which is 0.97 mM in $Cu(cyclops)^+$ is made 0.144 M in pyridine, $E_{1/2}$ is shifted by -50 mV (Figure (7). Assuming the presence in solution of the species $[Cu(cyclops)(py)]^+$ as

Table V. Redox Properties of the Compounds[a]

Species[b]	Solvent	Supporting electrolyte	$E_{1/2}$,[c] V vs. SCE	D,[d] $cm^2\ s^{-1}$
$[Cu(PreH)]^+$	CH_3CN	0.2 M TEAP	−0.63	1.37×10^{-5}
			−1.82[e]	
$[Cu(cyclops)]^+$	CH_3CN	0.2 M TEAP	−0.40	1.08×10^{-5}
	CH_3OH	0.4 M $NaClO_4$	−0.40	6.00×10^{-6}
	CH_3NO_2	0.1 M TEAP	−0.33	6.66×10^{-6}
	$CH_3OCH_2CH_2OH$	0.2 M TEAP	−0.41	2.52×10^{-6}
$[Cu(cyclops)Br]$	CH_3CN	0.1 M Bu_4NBr	−0.55	
			−1.73[e,f]	
$[Cu(cyclops)CN]$	CH_3CN	0.1 M TEAP	−0.39	
$[Cu(cyclops)Cl]$	CH_3CN	0.1 M Et_4NCl	−0.60	
$[Cu(cyclops)I]$	CH_3CN	0.1 M Bu_4NI	−0.55	
$[Cu(cyclops)C(CN)_3]$	CH_3CN	0.1 M $KC(CN)_3$	−0.40	

[a] At Pt-disk electrode. [b] Perchlorate salt, unless denoted otherwise, at 0.1–3 mM. [c] $\frac{1}{2}(E_{p,c} + E_{p,a})$. Unless otherwise noted, $i_{p,a}/i_{p,c} = 0.95 \pm 0.05$ at $\nu = 0.0167\ V\ s^{-1}$. [d] ±10%. [e] $E_{p,c}$ for irreversible process. [f] This second reduction process occurs near here for other $Cu(cyclops)^+$ adducts also.

the only copper(II) chromophore—note the agreement between λ_{max} for solution and mull electronic spectrum (Table III)—it is evident that axial ligation by pyridine makes the copper(II) less susceptible to reduction. In general, addition of σ-donor Lewis bases, whether anionic or neutral, stabilizes copper(II) relative to copper(I), thus shifting $E_{1/2}$ to more negative potential. Half-wave potentials for some selected adducts are listed in Table V.

Binding Constants for Axial Adduct Formation. The affinity of $Cu(cyclops)^+$ for axial adduct formation with Lewis bases in solution can be ascertained quantitatively by electrochemical determination of the binding constants. For a Cu(II)/Cu(I) redox couple with half-wave potential E_0, addition of a donor L which can bind to Cu(II) and/or Cu(I) will shift the observed potential $E_{1/2}$ as follows:[44]

$$E_{1/2} = E_0 - \frac{RT}{nF} \ln\left(\frac{1 + \sum_i \beta_i^{II}[L]^i}{1 + \sum_j \beta_j^{I}[L]^j}\right) \tag{4}$$

Here β_i^{II} and β_j^{I} are the cumulative stability constants of the $Cu^{II}L_i$ and $Cu^{I}L_j$ species, respectively, and E_0 refers to the $Cu(cyclops)^+/Cu(cyclops)^0$ couple.[45] Determination of $E_{1/2}$ as a function of [L] and use of eq 4 enables the composition and formation constants of adducts in solution to be deduced.

For a 1:1 adduct, say $[Cu(cyclops)py]^+$, the relationship

$$\Delta E = E_{1/2} - E_0 = -(RT/nF) \ln (1 + K_1^{II}) \tag{5}$$

which can be written

$$e^{-nF\Delta E/RT} = K_1^{II}[L] + 1 \tag{6}$$

might at first seem appropriate, the assumption being that $[Cu(cyclops)]^0$ has no affinity for pyridine. However, a plot of $(e^{-nF\Delta E/RT} - 1)$ vs. $[py]$[46] for data from acetonitrile solutions was clearly nonlinear, demonstrating the nonvalidity of the assumption above. If formation of $[Cu(cyclops)py]^0$ is considered of possible significance, eq 7 must be used.

$$\frac{1}{e^{-nF\Delta E/RT} - 1} = \frac{1}{K_1^{II} - K_1^{I}}\,\frac{1}{[L]} + \frac{K_1^{I}}{K_1^{II} - K_1^{I}} \tag{7}$$

ΔE data from cyclic voltammetry experiments gave a linear plot (Figure 8) of $(e^{-nF\Delta E/RT} - 1)$ vs. $[py]^{-1}$, yielding $K_1^{II} = 61.6 \pm 1.8$ and $K_1^{I} = 2.7 \pm 0.4$ at 25 °C (Table VI). At pyridine concentrations above ca. 0.3 M ($py:Cu^{2+} \geq 10^2$), a slight curvature signals onset of the influence of $Cu(cyclops)(py)_2^+$ formation, but the system is not amenable to experiments at the high base concentration required for evaluation of K_2^{II} (vide supra).

Formation constants for adducts with γ-picoline and the soft Lewis bases methyl phenyl sulfide (thiaanisole), bis(p-tolyl) disulfide, and benzyl isocyanide were also estimated from their cyclic voltammograms (Table VI). The very weak interaction revealed with the copper(II) state prevented isolation of any 1:1 adducts of the S or C donors with $Cu(cyclops)^+$. Binding constants were not determined for the anion adducts $[Cu(cyclops)X]^0$. We considered analysis of the redox data obtained from these systems to be outside the scope of this work, as it involves taking into account the formation of other than mononuclear species of Cu(II).[21]

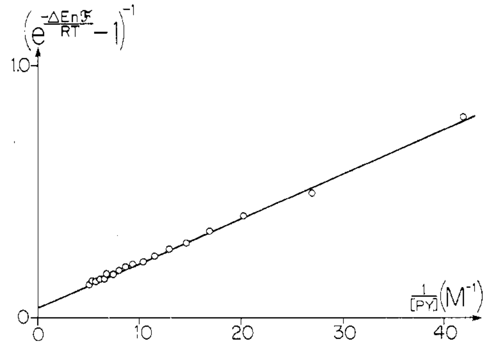

Figure 8. Plot for determination of binding constants for pyridine with $[Cu(cyclops)]^{+/0}$ in acetonitrile/0.1 M TEAP at 25 °C. [Cu] = 0.97 mM.

Table VI. Ligand Binding Constants[a] for $[Cu(cyclops)]^{+/0}$

Solvent	Ligand	K_1^{I}	K_1^{II}
Acetonitrile	Pyridine	2.7 (0.4)	61.6 (1.8)
Acetonitrile	γ-Picoline	2.7 (1.0)	129 (6.0)
Acetonitrile	Methyl phenyl sulfide	0.90 (0.10)	0[b]
2-Methoxyethanol	Methyl phenyl sulfide	1.90 (0.20)	0.01 (0.02)
2-Methoxyethanol	Bis(p-tolyl) disulfide	<1	0[b]
2-Methoxyethanol	Benzyl isocyanide[c]	3×10^6	0[b]

[a] Determined electrochemically at 25 °C. Units are M^{-1}. Errors (2σ) in parentheses estimated from least-squares analyses. [b] Relative to K_1^{I}, i.e., $100K_1^{II} < K_1^{I}$. [c] Estimated at $[L] >> [Cu]$.

The thermodynamic stability of the copper(II) adducts parallels the σ-donor ability of the ligand, as K_1^{II} for pyridine is lower than K_1^{II} for the more basic γ-picoline, while K_1^{II} is very much lower for the poor σ-donor sulfur species.[47] In addition, the ability of the solvent to compete with an added base (e.g., pyridine) is greatest in the case of CH_3CN, less so for $CH_3OCH_2CH_2OH$, and least for nitromethane, in which solvent the results from Figure 1 enable one to estimate log $K_1^{II} = 2.4 \pm 0.4$ for pyridine binding.

The nature of the equilibria, to which the calculated K_1^{I} values relate, is not revealed by the voltammetry experiments alone. Of the two processes,

$$[\mathrm{Cu(cyclops)}]^0 + \mathrm{L} \rightleftarrows [\mathrm{Cu(cyclops)L}]^0 \qquad (8)$$

and

$$[\mathrm{Cu(cyclops)}]^0 + \mathrm{L} + n\mathrm{S} \rightleftarrows [\mathrm{CuS}_n\mathrm{L}]^+ + \mathrm{cyclops}^- \qquad (9)$$

where S represents a solvent molecule, Gagnê's isolation[48] of stable crystalline five-coordinate species, $[\mathrm{Cu(cyclops)L}]^0$, strongly supports eq 8 as the applicable equilibrium in solution. In no case was any evidence found at all for K_2^1 becoming significant.

Relative to the stabilities of their copper(II) analogues, the thermodynamic stabilites (K_1^{I}) of the copper(I) adducts appear to follow the increasing π-acceptor and decreasing σ-donor abilities of the axial ligand, as suggested previously.[49] That is, good π acceptors complex Cu(I) preferentially and shift $E_{1/2}$ anodically, while good σ-donors complex Cu(II) preferentially and $E_{1/2}$ is cathodically shifted. The results in Table VI also indicate that forced coordination of an axial donor to a square $\mathrm{CuN_4}$ system, as may be achieved by the tertiary structure of a copper-containing protein, will significantly affect the E^0 of the copper center in a fashion strongly dependent on the nature of the axial ligand.

The optical spectroscopic properties of the axial adducts are also worthy of comment in this regard. Out-of-plane displacement of the metal ion as the explanation for the anomalous spectrochemical series associated with the five-coordinate adducts of $\mathrm{Cu(cyclops)}^+$ is in itself quite normal. Indeed, displacement of the metal out of the basal plane toward the axial ligand in otherwise square-pyramidal geometry appears to be the rule, rather than the exception.[50] The range of displacements, ρ, suggested by the absorption spectra of the various ligands, implies that the copper(II) ion has considerable geometric flexibility with respect to its static position in the macrocyclic ligand plane. This in turn implies that in a given, essentially planar $\mathrm{N_4}$ donor atom environment with suitable properties the copper(II) ion may have *dynamic* flexibility. Such dynamic flexibility will endow the metal center with a means of adjusting readily to the dissimilar geometric requirements normally associated with the copper(I) and copper(II) oxidation states, which must be alternated rapidly on the time scale of enzyme redox chemistry. Moreover, the existence of five-coordinate copper(I) species in such a system also provides a means whereby the Franck–Condon barrier to geometric reorganization is minimized during the redox step. Thus, in a five-coordinate model[51] for protein-bound copper(II), there is no need to require that the coordination number decrease in the copper(I) state, although this appears to be a possibility for the copper–zinc dismutases.[52]

Similarly, the likelihood of isocyanides acting as a fifth ligand to copper(I) in the system we report here means that binding of ethyl isocyanide by reduced hemocyanin[53] may be associated with an otherwise preserved coordination sphere about copper(I) and not necessarily with displacement of a native ligand.

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Registry No. $[\mathrm{Cu[PreH)]ClO_4}$, 62197-89-1; $[\mathrm{Cu(cyclops)]ClO_4}$, 64783-10-4; [Cu(cyclops)Cl], 66070-08-4; [Cu(cyclops)Br], 66070-09-5; [Cu(cyclops)I], 66070-10-8; [Cu(cyclops)CN], 66070-11-9; [Cu(cyclops)NCO], 65071-48-9; [Cu(cyclops)NCS], 66070-12-0; [Cu(cyclops)NCSe], 66070-13-1; $[\mathrm{Cu(cyclops)N(CN)_2}]$, 66197-65-7; $[\mathrm{Cu(cyclops)C(CN)_3}]$, 66197-66-8; $[\mathrm{Cu(cyclops)(pyridine)]ClO_4}$, 66070-15-3; $[\mathrm{Cu(cyclops)(\gamma\text{-}picoline)]ClO_4}$, 66070-17-5; $[\mathrm{Cu(cyclops)(imidazole)]ClO_4}$, 66070-19-7; $[\mathrm{Cu(cyclops)(pyrazole)]ClO_4}$, 66102-29-2; [Cu(PreH)], 66070-20-0; [Cu(cyclops)], 61114-07-6; $[\mathrm{Cu(cyclops)Br]^-}$, 66070-21-1; $[\mathrm{Cu(cyclops)CN]^-}$, 66069-78-1; $[\mathrm{Cu(cyclops)Cl]^-}$, 66069-79-2; $[\mathrm{Cu(cyclops)I]^-}$, 66069-80-5; $[\mathrm{Cu(cyclops)C(CN)_2]^-}$, 66197-64-6; [Cu(cyclops)(pyridine)], 66069-81-6; [Cu(cyclops)(γ-picoline)], 66069-82-7; [Cu(cyclops)(methyl phenyl sulfide)], 66069-83-8; [Cu(cyclops)(bis(*p*-tolyl) disulfide)], 66069-84-9; [Cu(cyclops)(benzyl isocyanide)], 66069-85-0; $[\mathrm{Cu(cyclops)(methyl\ phenyl\ sulfide)]^+}$, 66069-86-1; 1,3-propanediamine, 109-76-2; diacetyl monoxime, 57-71-6; boron fluoride ethyl etherate, 109-63-7.

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(18) Abbreviations: $\mathrm{Et_4N}$, tetraethylammonium; $\mathrm{Bu_4N}$, tetra-*n*-butylammonium; TEAP, tetraethylammonium perchlorate; RPE, rotating platinum electrode; TFAA, trifluoroacetic anhydride; py, pyridine; RDE, rotating disk electrode; SCE, saturated calomel electrode; DPPH, diphenylpicrylhydrazyl radical; DMA, *N,N*-dimethylacetamide.
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New Reagents for the Synthesis of Paramagnetic Organometallic, Amide, and Coordination Complexes of Trivalent Titanium, Vanadium, and Chromium

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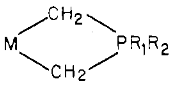
The tetrahydrofuran complexes, MCl$_3$(THF)$_3$ (M = Ti, V, Cr), react with 1 equiv of a 1,3-diketone (diket) in THF to give the air-sensitive, paramagnetic complexes M(diket)Cl$_2$(THF)$_2$. Reactions of these reagents with LiC$_6$H$_4$CH$_2$NMe$_2$, LiCH$_2$C$_6$H$_4$NMe$_2$, and LiN(SiMe$_3$)$_2$ give novel, air-sensitive organometallic and amide complexes. The coordinated THF may be readily displaced by neutral ligands such as PMe$_3$ and bipyridine to give new coordination compounds. Magnetic and spectroscopic data are presented with detailed synthetic procedures.

Introduction

We are currently investigating the coordination and organometallic chemistry of the early transition metals, with particular emphasis on paramagnetic compounds. Generally, paramagnetic organometallic complexes are less stable than their diamagnetic analogues. For example, while Cp$_2$MH$_2$ (where M = Mo and W and Cp = cyclopentadienide) are well-known, thermally stable compounds[1] Cp$_2$TaH$_2$ and Cp$_2$NbH$_2$[2] are very reactive and unstable below room temperature.



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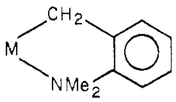

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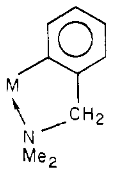

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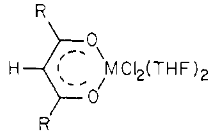
Chelated organic ligands, such as **1**–**3**, have been found[3-6] to greatly enhance the thermal stability of paramagnetic organometallic compounds, and some interesting chemistry has evolved. The reactions of organolithium reagents with CrCl$_2$ give compounds of the type [Li$_2$(sol)CrR$_2$]$_2$[7,8] (where sol = coordinating solvent such as dioxane or tetrahydrofuran), **4**. These compounds were *diamagnetic* and dimeric with quadruple metal–metal bonds postulated to account for the diamagnetism. In contrast, the lithium salts of **2** and **3** reacted with CrCl$_2$ to give *paramagnetic* organometallic compounds.[9] The interesting chemistry and unusual stability of these paramagnetic organometallic compounds prompted us to search for new systems containing chelating ligands. Our objectives were twofold: (1) to find a chelating ligand capable of stabilizing electron-rich paramagnetic organometallics by delocalization of electron density and (2) to find new reagents for the synthesis of early transition metal organometallic and coordination compounds. The diketonate ligand satisfied both requirements.[5] In this paper are described detailed preparations and some chemistry of the series of compounds **5**, where M = Ti, V, or Cr, R = Me, Ph, or *t*-Bu, and THF = tetrahydrofuran. The following abbreviations will be used for the diketonate ligands throughout the paper:



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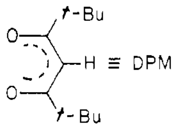

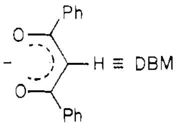

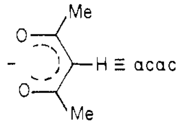

Results

A. M(diket)Cl$_2$(THF)$_2$ Complexes. The addition of a molar equivalent of a 1,3-diketone to a suspension of CrCl$_3$(THF)$_3$ or TiCl$_3$(THF)$_3$ in dry THF under an inert atmosphere gave an immediate reaction, liberating HCl. From these solutions crystalline, air-sensitive solids, whose analytical data were consistent with the formulation M(diket)Cl$_2$(THF)$_2$, were isolated nearly quantitatively. The DPM compounds are soluble in benzene, ether, THF, and toluene, whereas the acac and DBM compounds are much less soluble in these solvents. All of the compounds are quite soluble and stable in dry, oxygen-free dichloromethane, so it is an excellent solvent for recrystallizations and solution spectral and magnetic moment measurements.

The vanadium complexes **5** were isolated in only low yields from reactions of the 1,3-diketones with VCl$_3$(THF)$_3$ in THF. Improved yields were obtained by preforming the diketonate anion and reacting this salt with VCl$_3$(THF)$_3$. Thus, DBMH was dissolved in THF and solid KH was slowly added. When the formation of K$^+$DBM$^-$ was complete, as indicated by the absence of hydrogen gas evolution, the THF solution of this salt was added to a solution of VCl$_3$(THF)$_3$. KCl precipitated rapidly and VCl$_2$(THF)$_2$(DBM) was isolated in excellent yield. Large quantities of these reagents can easily be prepared directly from the appropriate anhydrous metal halide by

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