Complexes of Binucleating Ligands. VI.
Some Copper(II) Complexes of a Tetraamine Ligand

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The new binucleating ligand with flexible, fully saturated side arms 2,6-bis(N-2'-aminoethylaminomethyl)-p-cresol, represented LH, was isolated as the unusual benzene-soluble binuclear sodium derivative, Na_2L_2. A series of binuclear cupric derivatives of L^- was isolated in which either anionic or neutral species occupy an exchangeable bridging site between the two metal ions. The structures of these complexes have been studied by conductance, spectroscopic, and magnetic measurements, and it appears that a range of stereochemical types is allowed by the marked flexibility of the ligand. In one case, Cu-LClO$_4$, the ligand was found, unexpectedly, to be able to wrap itself around a single cupric ion providing a distorted N_4O ligand field.

Introduction

Earlier reports in this series[1,2] have described complexes derived from binucleating ligands with comparatively rigid Schiff base side arms flanking a phenoxide ion, which serves to bridge two metal ions. These ligands were designed to provide, in their metal complexes, an accessible bridging site for the incorporation and possible activation of a range of species. Okawa and Kida[3] have reported a number of variants on the basic binucleating system first introduced by us,[4] using different amino groups to generate the Schiff base.

One of our ultimate goals in the application of binucleating ligands is to study the reactivity of complexes providing an accessible bridging site between two powerfully reducing cations.[1] A possible drawback of the Schiff base binucleating ligands, in this regard, is that the ligand itself may become involved in some redox process with the reducing ions. For this reason binucleating ligands with fully saturated, nonreducible side arms were of interest to us. The present report describes some complexes of a new tetraamine binucleating ligand with fully saturated side arms, 2,6-bis(N-2'-aminoethylaminomethyl)-p-cresol, I (hereafter LH), which appears,


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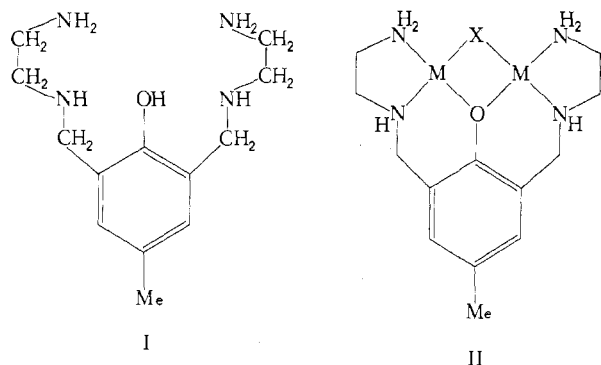
from an examination of framework molecular models, to be very much more flexible than the Schiff base binucleating ligands and to provide a wider range of stereochemical possibilities. In this case, as with other binucleating ligands, we have found it essential as a preliminary step to determine by model studies whether the ligand is able to impose the desired basic binuclear arrangement, II, and, if so, to study the gross stereochemical features of the complexes, *e.g.*, the metal co-

ordination number, whether counteranions are coordinated or not, the range of species X which can be incorporated, etc. The present report describes some model cupric complexes of L.

Results and Discussion

The Ligand. The ligand was prepared by reaction of 2-hydroxy-5-methylisophthalaldehyde with an excess of ethylenediamine in boiling methanol, followed by reduction of the condensation product (which was not isolated) with sodium borohydride. The ligand was conveniently isolated, stored, and used for complex preparations as its sodium derivative which was soluble in water, alcohols, and many organic solvents, including boiling benzene, from which it was readily recrystallized.

The molecular weight of the sodium derivative, determined by ebulliometry in benzene, was 560 ± 45 suggesting the presence in solution of electrically neutral Na_2L_2 (calcd mol wt 548). Examination of framework molecular models indicates that the ligand readily adopts a number of conformations allowing formation of 2:2 metal–ligand complexes with both metals in a roughly octahedral ligand environment, one example of which is III. Nickel(II) appears to have a strong preference for the formation of 2:2 complexes with L^- and in these cases physical properties clearly point to structures of the type III.[5] A number of examples of sodi-
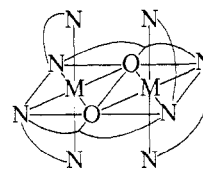
III

um ion in an approximately octahedral environment have been established recently by X-ray crystallography[6] and a structure of type III would appear reasonable for Na_2L_2.

The mass spectrum of the sodium derivative showed a peak at m/e 548, the relative heights of immediately adjacent peaks being consistent (assuming % C^{13} = 1.1) with $Na_2L_2^+$ (calcd m/e 548). Peaks corresponding to fragments of higher mass than Na_2L_2 with m/e up to *ca.* 860 were also observed which may indicate either a polymeric arrangement on the direct insertion probe or, more likely, polymerization of Na_2L_2 under the insertion conditions used. A very strong

(1) R. Robson, *Aust. J. Chem.*, **23**, 2217 (1970).
(2) W. D. McFadyen, R. Robson, and H. Schaap, *Inorg. Chem.*, **11**, 1777 (1972).
(3) H. Okawa, T. Tokh, Y. Nonaka, Y. Muto, and S. Kida, *Bull. Chem. Soc. Jap.*, **46**, 1462 (1973), and references therein.
(4) R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970).

(5) I. E. Dickson and R. Robson, unpublished results.
(6) M. R. Truter, *Chem. Brit.*, **7**, 203 (1971); C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

peak at m/e 297 is assigned to Na_2L^+ and this is supported by the relative heights of adjacent peaks (% C^{13} taken as 1.1). Na_2L^+ probably arises from $Na_2L_2^+$ by loss of the resonance-stabilized neutral ligand radical fragment, L.

The ir spectrum (Nujol) of the sodium derivative was complex and showed N-H stretching frequencies at 3360, 3290, and 3260 cm^{-1}.

Copper(II) Complexes. The complexes isolated, which included examples with Cu(II):ligand ratios of both 2:1 and 1:1, are listed with some properties in Table I.

Cu_2L Complexes. All the 2:1 complexes were isolated in crystalline form from methanolic solution except for $Cu_2L(OH)(ClO_4)_2$ and $Cu_2L(C_3H_3N_2)(ClO_4)_2$ which were obtained from aqueous solution. The series Cu_2LX_3, $Cu_2LX_2(ClO_4)$, and $Cu_2LX(ClO_4)_2$ (where X = Cl, Br) were prepared in the hope that comparison of physical properties would reveal whether one or more X groups were bridging in Cu_2LX_3 and $Cu_2LX_2(ClO_4)$: this question was initially of some concern to us because L^-, unlike the Schiff base binucleating ligands,[1,2] seemed on the basis of molecular models to present a distinct possibility in its metal complexes of incorporating two bridging species. The series could not be completed when X = CNS because all attempts to isolate $Cu_2L(CNS)(ClO_4)_2$ yielded $Cu_2L(CNS)_2(ClO_4)$. The ready isolation of the thiocyanato derivatives of Cu_2L is in contrast to the behavior of the Cu(II) and Ni(II) complexes of the Schiff base binucleating ligands with which repeated efforts to incorporate thiocyanate ion failed.[2] A further point of contrast between the two types of ligand system is provided by our failure, despite repeated efforts, to isolate alkoxo- and amido-bridged complexes of Cu_2L while these derivatives were exceptionally stable and easy to isolate with the Schiff base binucleating ligands.

Ir Spectra. The ir spectra of the complexes are complex and somewhat variable; however the detailed patterns are effectively identical within certain pairs of complexes ($Cu_2LCl_2(ClO_4)MeOH$ and $Cu_2LBr_2(ClO_4)MeOH$, $Cu_2L\cdot Br_3(H_2O)$ and Cu_2LCl_3, and $Cu_2L(CNS)_3$ and $Cu_2L(CNS)_2(ClO_4)$), suggesting that the ligand conformation is the same for the two members of a particular pair. Some bands arising from species other than L^-, which could be assigned with some confidence, are listed in Table I and discussed below.

While no conclusions concerning the coordination of the perchlorate ion in the perchlorate salts could be drawn from the ν_3 perchlorate band near 1100 cm^{-1} because of the presence in this region of strong ligand bands, the single sharp band at 625 cm^{-1} (Nujol) in all cases indicates uncoordinated perchlorate.[7]

The O-H stretching band of $Cu_2L(OH)(ClO_4)_2$ at 3420 cm^{-1} is broadened, presumably by H bonding, compared with the OH bands of some related hydroxo-bridged cupric complexes of Schiff base binucleating ligands.[1,2] Broadening by H bonding appears to be responsible for the lack of observable O-H stretching bands in $Cu_2LX_2(ClO_4)MeOH$ (X = Cl, Br) and in $Cu_2LBr_3(H_2O)$ for there is good analytical evidence for the presence of the solvent molecules and unambiguous X-ray evidence in the case X = Br.

The pyrazole ring vibration of $Cu_2L(C_3H_3N_2)(ClO_4)_2$ at 1635 cm^{-1} is consistent with bridging in which one nitrogen is attached to one copper atom and the other nitrogen to the second copper atom.[2]

A band at 1205 cm^{-1} assignable to the N-O stretching

frequency of the pyridine N-oxide fragment in $Cu_2L(C_5H_5-NO)(ClO_4)_3H_2O$ appears to be characteristic of bridging through the oxygen atom.[8]

Although useful generalizations, based on the examination of large numbers of thiocyanato complexes, can be made regarding the ir spectra of terminal N-bonded, terminal S-bonded, and M-SCN-M bridging thiocyanate groups[9-11] unfortunately little information is available on $(M)_2SCN$ and $(M)_2NCS$ bridging modes which, for geometrical reasons, are the more likely in the thiocyanato derivatives of Cu_2L^{3+}. On the basis of simple arguments concerning the relative contributions of $^-S-C\equiv N$ and $S=C=N^-$, which seem to be valid in this case,[9] the uncommon bridging mode $(M)_2SCN$ would be expected to lead to exceptionally high ν_{CN} and exceptionally low ν_{CS} frequencies which were not observed (Table I). Bridging of the type Cu_2NCS (probably but not necessarily within Cu_2L units) would appear most likely in both cases. In addition, a second type of thiocyanate is probably present in $Cu_2L(CNS)_3$ (two distinct ν_{CN} peaks) which is either terminally N bonded or ionic. The striking similarity of the detailed ir pattern for the two thiocyanates suggests closely similar ligand conformations and the presence in both cases of much the same cation, $Cu_2L(NCS)_2^+$, is supported by the almost identical magnetic behavior, although the electronic spectra are not identical (see below).

Electronic Spectra. The 2:1 complexes appear to fall into three groups, indicated in Table I, on the basis of their diffuse reflectance electronic spectra. Despite a report questioning the value of spectra in assigning structures to Cu(II) complexes[12] we believe that, in the present related series, the division of the spectra into three groups in turn implies a division into three structural types.

Complexes in group 1, having d $\longleftrightarrow$ d bands of the highest energy, are all of the composition $[Cu_2L(X)](ClO_4)_y$ (where X is neutral or monoanionic and y = 2 or 3) in which the perchlorate ions are uncoordinated (ir). These complexes are assigned basically square-planar ligand environments in essentially discrete $[Cu_2L(X)]^{2+ \text{ or } 3+}$ cations of the type shown in structure II, although the observed energies are somewhat lower than those generally quoted for square-planar Cu(II) complexes.[13] We ascribe this discrepancy either to some degree of tetrahedral distortion, which is not unlikely with the ligand L^-, or to relatively weak axial interactions within the lattice or to both of these effects. For comparison, we have measured the diffuse reflectance spectrum of *cis*-bis(α-alaninato)copper(II) which has been shown to possess a cis N_2O_2 square-planar donor set with a single long Cu-O axial interaction;[14] the observed band at 578 mμ compares very well with the spectrum of the presumably most closely analogous member of group 1, $Cu_2L(OH)(ClO_4)_2$.

The d $\longleftrightarrow$ d bands for the complexes of group 1 were all comparatively sharp which is consistent with both Cu(II) centers of each binuclear unit having the same or not very different environments. By comparison, the d $\longleftrightarrow$ d bands of the complexes of group 2, which were at lower energies,

(7) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(8) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschel, *Inorg. Chem.*, **4**, 97 (1965); Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Jap.*, **39**, 58 (1966).

(9) R. A. Bailey, S. L. Kozak, T. W. Michelson, and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).

(10) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(11) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(12) E. D. McKenzie, *J. Chem. Soc. A*, 3095 (1970).

(13) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

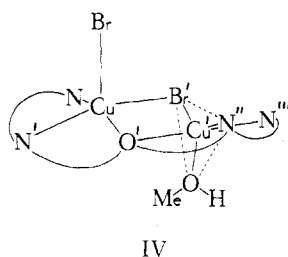(14) R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 155 (1966).

Table I. Physical Properties of Copper(II) Complexes

		Electronic spectra,[b] mμ	Ir bands,[c] cm^{-1}	Molar conductance,[d] ohm^{-1} cm^2 mol^{-1}	Magnetic properties			
					μ_{eff}[e]	$-2J$,[f] cm^{-1}	g[f]	$N\alpha$,[f] cgsu
Group 1	Cu$_2$L(OH)(ClO$_4$)$_2$	570	3420 (O-H str)	179 (1.00)	0.66 (290)			
	Cu$_2$L(C$_3$H$_3$N$_2$)(ClO$_4$)$_2$,[a]	585	1635 (C$_3$H$_3$N$_2$ ring vibration)	198 (1.00)	0.81 (292)			
	Cu$_2$L(C$_5$H$_5$NO)(ClO$_4$)$_3$(H$_2$O)	590	1205 m (NO str), 844 (NO bend)	288 (4.33)	0.58 (292)			
	Cu$_2$LCl(ClO$_4$)$_2$	607		347 (0.86)	1.61 (280)			
	Cu$_2$LBr(ClO$_4$)$_2$	592		318 (1.58)	1.69 (290)			
Group 2	Cu$_2$LCl$_2$(ClO$_4$)·MeOH	650	No OH str obsd	318 (1.04)	1.55 (292)	195	2.05	60
	Cu$_2$LBr$_2$(ClO$_4$)·MeOH	650	No OH str obsd	316 (1.48)	1.73 (296)	139	2.11	80
	Cu$_2$L(CNS)$_2$(ClO$_4$)	670	2094 vs, 2110 sh (ν_{CN}); 800 sh (ν_{CS}); 473 (δ_{NCS})	304 (1.04)	1.47 (299)	250	2.06	57
	Cu$_2$L(CNS)$_3$	685	2080 vs, 2102 vs (ν_{CN}); 800 sh (ν_{CS}); 475 w, 469 sh (δ_{NCS})		1.43 (295)	250	2.02	45
Group 3	Cu$_2$LCl$_3$	725		366 (0.50)	1.46 (291)	250	2.05	65
	Cu$_2$LBr$_3$(H$_2$O)	765	No OH str obsd	342 (1.00)	1.54 (297)	236	2.11	60
	CuL(ClO$_4$)	615		81 (0.99)	1.83 (294)			

[a] C$_3$H$_3$N$_2$ = conjugate base of pyrazole. [b] Diffuse reflectance. An additional band at 425–450 mμ was observed in all cases. [c] Arising from species other than L; KBr disk. [d] Aqueous solution; molarities × 10^3 in parentheses; temperature 20°. [e] Temperatures (°K) in parentheses. [f] Values taken to yield the agreement indicated in Figure 1 between experimental data and data calculated on the basis of the Bleaney–Bowers equation.[17] 2J taken as the singlet–triplet separation.

showed distinct broadening on the lower energy side of the maxima, which, in the case of Cu$_2$LCl$_2$(ClO$_4$)MeOH appeared as a well-defined shoulder at *ca.* 760 mμ. One member of group 2, Cu$_2$LBr$_2$(ClO$_4$)MeOH, has been examined independently by X-ray crystallography[15] and has been shown to contain discrete [Cu$_2$LBr$_2$MeOH]$^+$ cations and ClO$_4$$^-$ anions. One bromide in the cation, represented schematically as IV, is

IV

bridging, the other is terminal, and the two Cu(II) environments, while both five-coordinate, are significantly different. The cupric ion with the N$_2$OBr$_2$ donor set has an environment close to square pyramidal with a bromide ion at the apex, while the other cupric ion, Cu$'$, has an N$_2$O$_2$Br donor set which is intermediate between trigonal bipyramidal (represented in IV) and square pyramidal (MeOH at apex) but approximating more closely to the former. Some important dimensions are as follows (see structure IV): Cu-O$'$-Cu$'$, 111.2°; Cu-Br$'$-Cu$'$, 78.6°; Br$'$-Cu-O$'$, 84.7°; Br$'$-Cu$'$-O$'$, 83.7°; Cu-Cu$'$, 3.19 Å; Cu-Br, 2.73 Å; Cu-N, 1.98 Å; Cu-N$'$, 2.01 Å; Cu-O$'$, 1.94 Å; Cu-Br$'$, 2.50 Å; Cu$'$-O$'$, 1.93 Å; Cu$'$-O, 2.21 Å; Cu$'$-N$''$, 1.99 Å; Cu$'$-N$'''$, 1.98 Å; Cu$'$-Br$'$, 2.54 Å. For the two complexes Cu$_2$LX$_2$(ClO$_4$)MeOH (X = Cl, Br) the similar ligand conformations suggested by the ir spectra and the very similar electronic spectra indicate essentially identical structures.
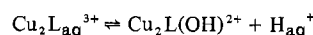
On the basis of the electronic spectra the two remaining members of group 2, Cu$_2$L(CNS)$_3$ and Cu$_2$L(CNS)$_2$(ClO$_4$), are also assigned five-coordinate Cu(II) environments, the two donor sets within each binuclear unit quite possibly having significantly different geometries. Combined ir and electronic spectral evidence and also the almost identical magnetic behavior (see below) tend to indicate essentially

the same cation, CuL(NCS)$_2$$^+$, in both cases. This may be a discrete binuclear species with two N-bridging thiocyanate groups or may be polymeric with one intermolecular and one intramolecular N-bridging thiocyanato group, both Cu(II) centers being five-coordinate in either case.

For the two members of group 3 the low energies of the d ↔ d bands and also the very pronounced tailing into the infrared region suggest distorted octahedral ligand sets.[16] Intermolecular halogen bridges would be an essential feature of any structure of this type.

Solution Behavior. Some aqueous conductance data are presented in Table I. Cu$_2$L(OH)(ClO$_4$)$_2$ behaved as a 2:1 electrolyte in aqueous solution at 20°; the plot of molar conductance *vs.* the square root of concentration was linear in the observed concentration range, molar conductances increasing from 169 ohm^{-1} cm^2 mol^{-1} at 2.00 × 10^{-3} *M* to 197 ohm^{-1} cm^2 mol^{-1} at 2.03 × 10^{-5} *M*, consistent with the presence of Cu$_2$L(OH)$^{2+}$ as the only significant Cu(II) species at all concentrations studied. The behavior of Cu$_2$L(C$_3$H$_3$N$_2$)(ClO$_4$)$_2$ was very similar, giving a linear molar conductance *vs.* square root of concentration plot in the concentration range 1.00 × 10^{-3} *M* (198 ohm^{-1} cm^2 mol^{-1}) to 5.04 × 10^{-5} *M* (218 ohm^{-1} cm^2 mol^{-1}), but in more dilute solution there was some evidence of a significant increase in molar conductance although, under these conditions, relative uncertainties in the measurements were large.

The remaining Cu$_2$L complexes showed molar conductances at *ca.* 10^{-3} *M* typical of 3:1 electrolytes (Table I). Plots of molar conductance *vs.* the square root of concentration were similar in all these cases, showing a marked increase in conductance at lower concentrations; molar conductances rose sharply to 500–600 ohm^{-1} cm^2 mol^{-1} at concentrations of *ca.* 10^{-5} *M*. The behavior at *ca.* 10^{-3} *M* suggests the presence of Cu$_2$L$_{aq}$$^{3+}$ cations plus three compensating anions. The large increase in conductance at higher dilution can be explained in terms of the following hydrolytic process in which the apparently stable [Cu$_2$L(OH)]$^{2+}$ cation is formed with liberation of highly conducting protons

Cu$_2$L$_{aq}$$^{3+}$ ⇌ Cu$_2$L(OH)$^{2+}$ + H$_{aq}$$^+$

In agreement with this proposal dissolution of Cu$_2$LCl$_3$ in water was accompanied by a marked decrease in pH and also

(15) D. G. Vince, Ph.D. Thesis, University of Melbourne, 1973. The structure was determined from 3088 independent reflections using a Seimens automatic diffractometer and refined to an *R* value of 0.043 using a least-squares method.

(16) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968, p 355.

conductometric titration of Cu_2LCl_3 with NaOH in aqueous solution gave a very sharp end point at 1 mol of OH^- per Cu_2LCl_3. No indication of the uptake of a second hydroxyl was obtained.

Apparent molecular weights of Cu_2LCl_3 in water by vapor pressure osmometry were measured as a function of concentration. Extrapolation to infinite dilution by a least-squares method gave an apparent molecular weight at infinite dilution of 99. If, as proposed above, each mole of Cu_2LCl_3 is liberating five entities, namely, $Cu_2L(OH)^{2+}$, H^+, and 3 Cl^-, at infinite dilution, the theoretically expected apparent molecular weight would be one-fifth of the molecular weight of Cu_2LCl_3, i.e., 97, in excellent agreement with the observed figure.

As would be expected from the above solution behavior $Cu_2L(OH)(ClO_4)_2$ showed a concentration-independent electronic spectrum in aqueous solution (λ_{max} 602 mμ, ϵ_{max} 125) whereas the remaining complexes, except Cu_2L-$(C_3H_3N_2)(ClO_4)_2$, showed concentration-dependent spectra approaching that of $Cu_2L(OH)(ClO_4)_2$ with increasing dilution (λ_{max} 620-605 mμ, apparent ϵ_{max} 110-140). The 2:1 electrolyte behavior of $Cu_2L(C_3H_3N_2)(ClO_4)_2$ in aqueous solution suggested the liberation of $Cu_2L(C_3H_3N_2)_{aq}^{2+}$ cations and while the aqueous solution spectrum (2.9 $\times$ 10^{-3} M) in this case showed a single maximum (600 mμ) in much the same position as for $Cu_2L(OH)(ClO_4)_2$, the much higher extinction coefficient (185) supported the presence of a cation other than $Cu_2L(OH)_{aq}^{2+}$.

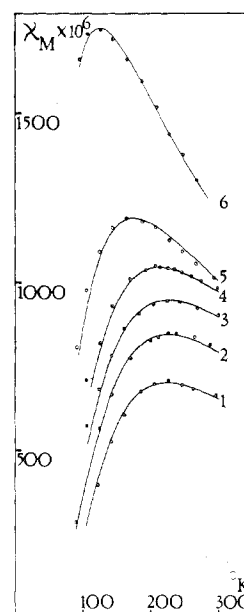$Cu_2L(OH)(ClO_4)_2$ and $Cu_2L(C_3H_3N_2)(ClO_4)_2$ were the only solid complexes we were able to isolate from aqueous solution and all attempts to prepare from aqueous solution complexes with species other than OH^- and $C_3H_3N_2^-$ at the bridging site yielded the former solid.

Magnetic Properties. The magnetic behavior of the Cu_2L series varies from very weak paramagnetism to only slightly depressed paramagnetism (Table I). All magnetic susceptibility data were corrected for the diamagnetism of anions, exchangeable bridging species, and solvent molecules using Pascal's constants and for the diamagnetism of L$^-$ (169 $\times$ 10^{-6} cgsu) derived from measurements on Zn_2LBr_3[5] but not for any temperature-independent paramagnetism.

The paramagnetic susceptibility per Cu(II) ion for Cu_2L-$(OH)(ClO_4)_2$ over the temperature range 300-90°K was invariant at 185 $\times$ 10^{-6} cgsu, a high value compared with the temperature-independent paramagnetism of *ca.* 60 $\times$ 10^{-6} cgsu normally associated with Cu(II). The susceptibility per Cu(II) for $Cu_2L(C_3H_3N_2)(ClO_4)_2$ fell from 278 $\times$ 10^{-6} cgsu at 292°K to 73 $\times$ 10^{-6} cgsu at 103°K and for $Cu_2L(C_5H_5NO)$-$(ClO_4)_3(H_2O)$ from 141 $\times$ 10^{-6} cgsu at 292°K to 44 $\times$ 10^{-6} cgsu at 226°K. Very strong antiferromagnetic coupling within binuclear units would appear to operate in these three cases.

The smallest degree of coupling was exhibited by Cu_2LCl-$(ClO_4)_2$ which obeyed the Curie-Weiss law over the temperature range 300-90°K with a Weiss constant of 76°K in the antiferromagnetic sense.

The remaining Cu_2L complexes all showed susceptibility *vs.* temperature curves with a maximum below room temperature (Figure 1). In all these cases, except Cu_2LBr-$(ClO_4)_2$, the experimental data could be satisfactorily fitted (Figure 1) to curves calculated from the Bleaney-Bowers equation[17] for antiferromagnetically coupled cupric dimers taking the $2J$, g, and $N\alpha$ values indicated in Table I. How-

(17) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

Figure 1. Plots of molar susceptibility per cupric ion, χ_M, *vs.* temperature for (1) $Cu_2L(CNS)_3$, (2) Cu_2LCl_3, (3) $Cu_2L(CNS)_2(ClO_4)$, (4) $Cu_2LBr_3(H_2O)$, (5) $Cu_2LCl_2(ClO_4)MeOH$, and (6) $Cu_2LBr_2(ClO_4)MeOH$. Full lines represent theoretical curves taking the values for $2J$, g, and $N\alpha$[17] indicated in Table I. Theoretical curves and experimental points are lowered 100 $\times$ 10^6 cgsu for 2 and 200 $\times$ 10^6 cgsu for 1 to avoid confusion in the figure.

ever, the Bleaney-Bowers equation is based on a model in which the two cupric ions are equivalent, whereas X-ray crystallography[15] shows that the two cupric ions of Cu_2LBr_2-$(ClO_4)MeOH$ are in different environments. It is possible that, in the Cu_2L series, the two Cu(II) ions may generally have different g values. Griffith has recently treated the general case of coupling between two nonequivalent spin centers[18] and when his results are applied to the case of two nonequivalent cupric ions[19] the molar susceptibility per cupric ion, χ_{Cu}, is given by

$$\chi_{Cu} = \frac{N\beta^2 g^2}{3kT}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} + N\alpha + \delta\chi \qquad (1)$$

In this expression $\delta\chi$ is temperature dependent but small and g is an "average" related to the individual g tensors by the following expression derived by Griffith[18]

$$g^2 = {}^1/_3 \sum_{jk} g_{jk}{}^2 = {}^1/_3[{}^1/_4\sum_j (g_j^{(1)})^2 + {}^1/_4\sum_j (g_j^{(2)})^2 + {}^1/_2\sum_{jk} g_j^{(1)} g_k^{(2)} l_{jk}{}^2]$$

where superscripts (1) and (2) refer to the individual copper centers and j, $k = x$, y, z and l_{jk} are the direction cosines of the axes at one copper center relative to those at the other. When the two centers are equivalent, $\delta\chi$ reduces to zero and the g values for the two centers are equal in which case the expression for χ_{Cu} adopts the Bleaney-Bowers form. In those cases where χ_{Cu} changes by hundreds $\times$ 10^{-6} cgsu between 300 and 100°K the corresponding change in $\delta\chi$ is negligibly small.[19] In this way the "successful" application of the Bleaney-Bowers equation to many binuclear cupric systems, including members of the present Cu_2L series, in which the two paramagnetic centers are known to be or may be nonequivalent, can be understood.

(18) J. S. Griffith, *Struct. Bonding (Berlin)*, **10**, 87 (1972).
(19) W. D. McFadyen, Ph.D. Thesis, University of Melbourne, 1973.

No attempt was made to evaluate J and g parameters for the three very strongly coupled examples $Cu_2L(OH)(ClO_4)_2$, $Cu_2L(C_3H_3N_2)(ClO_4)_2$, and $Cu_2L(C_5H_5NO)(ClO_4)_3(H_2O)$ nor for the apparently weakly coupled system $Cu_2LCl(ClO_4)_2$.

Esr signals could not be observed for powdered samples except in the case of $Cu_2LCl_2(ClO_4)MeOH$ which showed a very broad resonance centered at $g = 2.10$ in fair agreement with the g value of 2.05 required for optimum agreement of susceptibility data with the Bleaney-Bowers equation.

The Cu-Cu distance in $Cu_2LBr_2(ClO_4)MeOH$ is 3.19 Å,[15] and this separation throughout the Cu_2L series can reasonably be expected to be generally too large for any significant direct metal-metal interaction. The observed interaction can therefore be attributed to superexchange *via* the bridging groups. No doubt the angle subtended at the phenoxy oxygen atom by the two copper atoms and also the relative orientation of the benzene ring to the Cu-O-Cu plane will change significantly when species of widely variable size are incorporated at the exchangeable bridging site; both these factors may critically affect the degree of superexchange *via* the phenoxy oxygen atom. Moreover the extent of superexchange would be expected to be dependent on the geometrical arrangement of the other (*i.e.*, nonbridging) ligand atoms around the two Cu(II) centers. It would seem unwise therefore to speculate upon the relative contributions to the total superexchange, in any particular example, of the phenoxy bridging group and the other bridging group and even less wise to attempt to compare various species occupying the exchangeable bridging site with regard to their ability to promote superexchange as Okawa, *et al.*, have attempted for related systems.[3] A striking feature of the exchange coupling constants given in Table I, no doubt related to the above considerations, is that for two pairs of halo derivatives coupling is greater for the chloro than for the related bromo derivative, the reverse of the generally observed trend.

While it is recognized that the above treatment of the magnetic data does not constitute proof of binuclear arrangements in the Cu_2L series, the general behavior does strongly support this proposal.

Magnetic data for $Cu_2LBr(ClO_4)_2$ are given in Table II. In this case the susceptibility *vs.* temperature curve could not be satisfactorily fitted to data calculated from eq 2. This possibly indicates that the binuclear units are not magnetically isolated.

The Mononuclear Species CuLClO₄. $CuLClO_4$ was obtained as a green crystalline solid by reaction of Na_2L_2 and cupric perchlorate in 1:1 proportions in methanol. The question of whether this complex should be formulated as $CuLClO_4$ or $Cu_2L_2(ClO_4)_2$ was of considerable interest to us because analogous Ni(II) complexes are binuclear.[5] However, despite the fact that molecular models indicate that the ion CuL^+ with coordination number 4 or 5 is achieved only with the introduction of strain in L, the properties of $CuLClO_4$ (Table I) clearly point to a mononuclear structure.

In aqueous solution at 19.5° the complex behaves as a strong electrolyte showing an almost linear dependence of conductance upon square root of concentration in the range 1.6×10^{-3} to 10^{-5} M, but the conductance values alone do not allow a definite choice between the two alternatives $(CuL^+)(ClO_4^-)$ and $(Cu_2L_2^{2+})(ClO_4^-)_2$. However, measurement of apparent molecular weight in aqueous solution by vapor pressure osmometry resolved this ambiguity, the observed figure of 194 being in good agreement with the theoretical figure for $(CuL^+)(ClO_4^-)$ of 205 and very different from the theoretical figure for $(Cu_2L_2^{2+})(ClO_4^-)_2$ of 273. The effective identity of the visible absorption spectrum of

Table II. Magnetic Data for $Cu_2LBr(ClO_4)_2$

Temp, °K	$10^6\chi_{Cu}$, cgsu	Temp, °K	$10^6\chi_{Cu}$, cgsu	Temp, °K	$10^6\chi_{Cu}$, cgsu
290	1215	188	1406	126	1439
260	1262	164	1451	109	1376
238	1304	141	1449	94	1308
213	1356				

the aqueous solution and the diffuse reflectance spectrum of solid $CuClO_4$ (Table I) and the fact that the perchlorate ion appears from the ir spectrum to be uncoordinated in the solid points to the presence of the same CuL^+ cation, which almost certainly cannot have coordination number greater than 5, both in the solid and in aqueous solution.

The mononuclear formulation receives further strong support from the magnetic data which obeyed the Curie-Weiss law over the temperature range 300-90°K with the low Weiss constant of 8°K in the antiferromagnetic sense.

$CuLClO_4$, in contrast to the binuclear Cu_2L derivatives, gave a well-resolved powder esr spectrum consisting of two well-defined maxima (first-derivative spectrum) above the horizontal axis and two well-defined minima below the axis. Signals due to three different principal g values at *ca.* 2.00, 2.10, and 2.22 could be distinguished.[20] Since the coordination number is almost certainly less than 6, the fact that the lowest g factor is less than 2.03 would suggest, according to Hathaway,[13] a distorted trigonal-bipyramidal ligand field. Molecular models indicate that this is the most likely way in which L^- would wrap itself around a single metal ion but that considerable strain would nevertheless be involved.

Experimental Section

Na_2L_2 **and LH.** A solution of 2-hydroxy-5-methylisophthalaldehyde[21] (1.5 g, 9.1 mmol) in methanol (50 ml) was added to a solution of ethylenediamine (50 ml) in methanol (50 ml) and the resulting solution was heated under reflux for 15 min. A solution of sodium borohydride (1.5 g, 40 mmol) in the minimum of water was added in three equal aliquots at intervals of 30 min. After a solution of sodium hydroxide (2.8 g, 70 mmol) in water (5 ml) had been added, the solution was heated under reflux for 15 min. The mixture was evaporated under vacuum to a paste and the residue extracted with boiling benzene (250 ml). The extract was allowed to cool to room temperature and the crystalline solid which separated was removed by filtration. The filtrate was evaporated at atmospheric pressure to a volume of 50 ml, was filtered while hot, and then further boiled down to a volume of 20 ml. The resultant solution was allowed to stand at 8° for 12 hr in a stoppered flask during which time colorless crystals separated, which were collected and recrystallized from benzene. The recrystallized material was dried at 78° under vacuum; yield 2.0 g; mp (uncor) 186-188°. *Anal.* Calcd for $C_{13}H_{23}N_4NaO$: C, 57.0; H, 8.4; O, 5.8; N, 20.4; Na, 8.4. Found: C, 57.3; H, 8.8; O, 5.7; N, 19.8; Na, 8.4.

LH could be obtained as follows. Na_2L_2 in benzene solution was acidified with the equivalent quantity of hydrochloric acid in methanol. The precipitated sodium chloride was removed by filtration and the filtrate was evaporated under vacuum to yield LH as a yellow oil. *Anal.* Calcd for $C_{13}H_{24}N_4O$: C, 61.8; H, 8.5. Found: C, 61.8; H, 8.5. All attempts at distillation of the oil produced involatile yellow glasses.

$Cu_2L(OH)(ClO_4)_2$. An aqueous solution of Na_2L_2 (0.55 g, 1 mmol) and sodium hydroxide (0.095 g, 2.4 mmol) was added slowly to a stirred aqueous solution of cupric perchlorate hexahydrate (1.48 g, 4 mmol). After removal of the initially formed red precipitate the volume of the solution was reduced under vacuum at room temperature until crystals began to appear. After standing at 0° for 12 hr the solution deposited very dark crystals which were collected, washed with water, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{13}H_{24}Cl_2Cu_2N_4O_{10}$: C, 26.3; H, 4.1; N, 9.4; Cl, 12.0; Cu, 21.3. Found: C, 26.0; H, 4.5; N, 9.3; Cl, 12.2; Cu, 21.2.

$Cu_2L(C_3H_3N_2)(ClO_4)_2$. Na_2L_2 (0.63 g, 1.15 mmol) dissolved

(20) F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).
(21) F. Ullman and K. Brittner, *Ber. Deut. Chem. Ges.*, **2539** (1909).

in water (10 ml) was added dropwise to a stirred solution of cupric perchlorate hexahydrate (1.8 g, 4.8 mmol), sodium hydroxide (0.10 g, 2.5 mmol), and pyrazole (0.17 g, 2.5 mmol) in water (30 ml). The fine green crystals which separated were collected, washed with water, and dried under vacuum at room temperature over phosphorus pentoxide; yield 0.65 g. *Anal.* Calcd $C_{16}H_{26}Cl_2Cu_2N_6O_9$: C, 29.8; H, 4.0; N, 13.0; Cl, 11.0; Cu, 19.7. Found: C, 29.9; H, 4.5; N, 12.9; Cl, 10.8; Cu, 19.6.

$Cu_2L(C_5H_5NO)(ClO_4)_3(H_2O)$. Na_2L_2 (0.22 g, 0.4 mmol) dissolved in methanol (20 ml) was added to a solution of cupric perchlorate hexahydrate (0.59 g, 1.6 mmol) and pyridine N-oxide (0.076 g, 0.8 mmol) in methanol (20 ml). The solution was evaporated at atmospheric pressure to a volume of 20 ml and was allowed to stand at room temperature for 2 days. The green crystals which separated were collected and dried under vacuum; yield 0.32 g. The solid was recrystallized from methanol and the resulting crystals were collected, washed with methanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{18}H_{30}Cl_3Cu_2N_5O_{15}$: C, 27.4; H, 3.8; N, 8.9; Cl, 13.5; Cu, 16.1. Found: C, 27.4; H, 4.0; N, 8.8; Cl, 13.4; Cu, 16.1.

$Cu_2LCl(ClO_4)_2$. Na_2L_2 (0.95 g, 1.73 mmol) in warm methanol (10 ml) was added to a warm solution of cupric perchlorate hexahydrate (2.0 g, 5.4 mmol) and cupric chloride dihydrate (0.296 g, 1.74 mmol) in methanol (30 ml). Sodium chloride precipitated and the suspension was evaporated under vacuum to *ca.* 40 ml and allowed to stand for 2 days at room temperature during which time the sodium chloride redissolved and green crystals separated. The green solid was collected, washed with methanol, and dried under vacuum at room temperature; yield 0.93 g. *Anal.* Calcd for $C_{13}H_{23}Cl_3Cu_2N_4O_9$: C, 25.5; H, 3.8; N, 9.1; Cl, 17.4. Found: C, 25.4; H, 4.2; N, 9.0; Cl, 17.1. The solid rapidly took up water from the atmosphere yielding a monohydrate which was identical in its physical properties with the anhydrous material except in its magnetic behavior; both compounds showed Curie–Weiss behavior in the range 300–90°K but the Weiss constants were significantly different, 76°K for the anhydrous solid and 110°K for the hydrate.

$Cu_2LBr(ClO_4)_2$. Na_2L_2 (0.36 g, 0.66 mmol) dissolved in methanol (20 ml) was added to a solution of cupric perchlorate hexahydrate (2.4 g, 6.5 mmol) and cupric bromide (0.146 g, 0.66 mmol) in methanol (20 ml). The solution was evaporated to 20 ml and then cooled to −5°. The very dark crystals which separated were collected, washed with methanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{13}H_{23}BrCl_2Cu_2N_4O_9$: C, 23.8; H, 3.5; N, 8.7; Br, 12.2; Cl, 10.8. Found: C, 23.9; H, 3.6; N, 8.4; Br, 12.1; Cl, 10.7.

$Cu_2LCl_2(ClO_4)(CH_3OH)$. Na_2L_2 (0.225 g, 0.41 mmol) in methanol (20 ml) was added dropwise to a boiling stirred solution of cupric perchlorate hexahydrate (0.306 g, 0.83 mmol) and cupric chloride dihydrate (0.141 g, 0.83 mmol) in methanol (20 ml). The solution was evaporated to 15 ml and then maintained at −5° for 12 hr. The very dark crystals which separated were collected, washed with methanol, and dried under vacuum at room temperature; yield 0.36 g. *Anal.* Calcd for $C_{14}H_{27}Cl_3Cu_2N_4O_6$: C, 29.0; H, 4.7; N, 9.6; Cl, 18.3. Found: C, 29.1; H, 4.7; N, 9.5; Cl, 17.9.

$Cu_2LBr_2(ClO_4)(CH_3OH)$. Na_2L_2 (0.417 g, 0.76 mmol) dissolved in methanol (20 ml) was added dropwise to a solution of cupric bromide (0.34 g, 1.52 mmol) and cupric perchlorate hexahydrate (0.573 g, 1.55 mmol) in methanol (30 ml). The solution was evaporated at atmospheric pressure to 30 ml, filtered hot, and allowed to stand for 4 days at −5°. The very dark crystals which separated were collected, washed with methanol, and dried under vacuum at room temperature; yield 0.77 g. *Anal.* Calcd for $C_{14}H_{27}Br_2ClCu_2N_4O_6$: C, 25.1; H, 4.0; N, 8.4; Br, 23.9; Cl, 5.3. Found: C, 25.2; H, 4.2; N, 8.3; Br, 23.7; Cl, 5.3.

$Cu_2L(CNS)_2(ClO_4)$. Na_2L_2 (0.53 g, 0.97 mmol) dissolved in methanol (15 ml) was added to a solution of cupric perchlorate

hexahydrate (1.4 g, 3.8 mmol) in methanol (15 ml). A methanolic solution of sodium thiocyanate (0.297 g, 3.7 mmol) was added dropwise to the resulting green solution, causing the precipitation of a light green amorphous solid which was removed by filtration. The filtrate was evaporated at atmospheric pressure to a volume of 40 ml, filtered while hot, and allowed to stand at room temperature for 12 hr. The very dark crystals which separated (0.46 g) were recrystallized from methanol. The recrystallized solid was collected, washed with methanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{14}H_{23}ClCu_2N_6O_5S_2$: C, 30.3; H, 3.9; N, 14.1; S, 10.8; Cl, 6.0; Cu, 21.4. Found: C, 30.2; H, 4.2; N, 13.4; S, 10.7; Cl, 6.1; Cu, 21.6.

Cu_2LCl_3. A solution of Na_2L_2 (1.0 g, 1.8 mmol) in methanol (20 ml) was added to a stirred solution of cupric dichloride dihydrate (1.25 g, 7.35 mmol) in methanol (20 ml). After being allowed to stand for 3 days the solution had deposited very dark crystals which were collected, washed with methanol, and dried under vacuum at room temperature; yield 0.92 g. *Anal.* Calcd for $C_{13}H_{23}Cl_3Cu_2N_4O$: C, 32.2; H, 4.8; N, 11.6; Cl, 22.0. Found: C, 32.2; H, 5.0; N, 11.3; Cl, 21.8.

$Cu_2LBr_3(H_2O)$. A solution of Na_2L_2 (0.63 g, 1.15 mmol) in methanol (45 ml) was added to a stirred solution of cupric bromide (1.02 g, 4.6 mmol) in methanol (45 ml). The solution was evaporated to a volume of 45 ml, was filtered, and allowed to stand at 0°. The very dark crystals which separated were collected, washed with methanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{13}H_{25}Br_3Cu_2N_4O_2$: C, 24.5; H, 3.9; N, 8.8; Br, 37.7. Found: C, 24.6; H, 3.8; N, 8.9; Br, 37.5.

$Cu_2L(CNS)_3$. A solution of Na_2L_2 (0.65 g, 1.2 mmol) in methanol (35 ml) was added to a suspension of cupric acetate monohydrate (0.95 g, 4.8 mmol) in methanol (40 ml) and the mixture was stirred until the solid had dissolved. A methanolic solution of ammonium thiocyanate (0.54 g, 8.0 mmol) was added to the solution which was filtered and evaporated to a volume of 30 ml. The green crystals which separated after the mixture was allowed to stand at −5° for 12 hr were collected, washed with methanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{16}H_{23}Cu_2N_7OS_3$: C, 34.8; H, 4.2; N, 17.8; S, 17.4. Found: C, 34.7; H, 4.2; N, 17.6; S, 16.8.

$CuL(ClO_4)$. A solution of Na_2L_2 (0.56 g, 1.02 mmol) in methanol (40 ml) was added to a solution of cupric perchlorate hexahydrate (0.765 g, 2.07 mmol) in methanol (20 ml) and the resulting solution was evaporated to a volume of 20 ml. The green crystals, which separated after the solution had been standing at −5° for 3 days, were collected, washed with methanol, and dried under vacuum at room temperature; yield 0.69 g. *Anal.* Calcd for $C_{13}H_{23}ClCuN_4O_5$: C, 37.7; H, 5.6; N, 13.5; Cl, 8.6; Cu, 15.3. Found: C, 37.6; H, 5.9; N, 13.3; Cl, 8.8; Cu, 15.3.

Physical Measurements. Spectra were recorded using the following instruments: ir spectra, Perkin-Elmer 457 grating spectrophotometer; electronic spectra, Beckman DK-2A spectrophotometer. Magnetic moments were measured by the Gouy method using mercury cobalt(II) tetrathiocyanate as calibrant. Conductance measurements were made using a Philips PR9500 bridge. Molecular weight measurements were made with a Hitachi Perkin-Elmer Model 115 apparatus. Analyses were carried out by the Australian Microanalytical Service, Melbourne.