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Magnetic Interactions in Chloro-Bridged Copper(II) Dimers. Structural and Magnetic Characterization of Bis(μ-chloro)bis[chloro(*N*,*N*,*N'*-triethylethylenediamine)copper(II)], $[Cu(Et_3en)Cl_2]_2$

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The crystal and molecular structure of the compound bis(μ-chloro)bis[chloro(*N*,*N*,*N'*-triethylethylenediamine)copper(II)] has been determined from single-crystal, three-dimensional X-ray diffraction counter data. The compound crystallizes as blue-green tablets in space group $P\bar{1}$ of the triclinic system with $Z = 1$ and unit cell dimensions $a = 8.536$ (2) Å, $b = 9.194$ (5) Å, $c = 7.766$ (2) Å, $\alpha = 93.78$ (3)°, $\beta = 101.43$ (2)°, and $\gamma = 94.50$ (3)°. The observed and calculated densities are 1.53 (3) and 1.559 g cm^{-3}, respectively. The structure was refined by full-matrix least-squares techniques with final agreement factors $R = 0.0406$ and $R_w = 0.0450$. The structure consists of dimeric molecules, $[Cu(Et_3en)Cl_2]_2$, in which copper ions are bridged by chloride ligands. The geometry at copper is distorted trigonal bipyramidal with the bridging ligands occupying apical and equatorial sites of each copper ion. The apical Cu–Cl bridging distance is 2.284 (1) Å while the equatorial Cu–Cl bridging separation is 2.728 (1) Å; the terminal equatorial Cu–Cl bond length is 2.307 (1) Å, while the Cu–N(apical) and Cu–N(equatorial) separations are 2.015 (3) and 2.121 (3) Å, respectively. Magnetic susceptibility and EPR data give evidence for exchange coupling with the best fit to the data of the magnetization expression for a pair of exchange-coupled $S = {}^1/_2$ ions yielding $g = 2.092$ and $2J = +0.06$ cm^{-1}. It is concluded that $|J|$ is <0.2 cm^{-1}, but the sign of the exchange coupling constant remains uncertain. The singlet–triplet splitting of <0.2 cm^{-1} adheres to the correlation of $2J$ with ϕ/R (ϕ is the Cu–Cl–Cu′ angle and R is the longer bond in the Cu_2Cl_2 bridged unit) that has been observed to hold for bis(μ-chloro)-bridged copper(II) dimers.

The development of empirical relationships that relate the structural characteristics of binuclear and polynuclear transition-metal complexes to their magnetic properties has been vigorously pursued in many laboratories for several years. Studies of this kind have provided significant results in a variety of complexes, including bis(μ-hydroxo) copper(II)[2,3] and chromium(III)[4-9] dimers, square-planar bis(μ-chloro) copper(II)[10] dimers, and polymeric bis(μ-chloro) copper(II)[11-13] complexes. Work performed by several research groups has sought to relate the isotropic exchange coupling constant, J, to specific structural quantities, which can then be related to the metal–ligand bonding and antibonding orbitals involved in the exchange pathway between the metal centers.[2,7-9,14-22] To determine the extent to which empirical relationships can, in a general manner, be developed for exchange-coupled transition-metal complexes and for which a semiquantitative molecular orbital treatment may be useful, we and others have attempted to prepare and investigate a series of parallel-planar copper(II) halide complexes. The study of complexes of the types CuA_2X_2 and $CuLX_2$ (where A is a unidentate ligand, L is a bidentate ligand, and X is a halide) is more complicated than those discussed above, partly because of the presence of low-lying d orbitals on the bridging X atom and also because of the large number of structural types that are observed for complexes of this formulation. For example, complexes where L (or A) is a pyridine derivative have been shown to exist in monomeric,[23-25] dimeric,[25-28] and at least four distinctly different polymeric forms.[29-33] We have recently been focusing our attention on five-coordinated dimeric species, and here, also, there is a range of structures from tetragonal-pyramidal to trigonal-bipyramidal geometry at copper. Most of the

Table I. Crystal Data for $[Cu(Et_3en)Cl_2]_2$

a, Å	8.536 (2)	*V*, Å^3	593.5 (6)
b, Å	9.194 (5)	space group	$P\bar{1}$
c, Å	7.766 (2)	*Z*	1
α, deg	93.78 (3)	D_{calcd}, g cm^{-3}	1.559
β, deg	101.43 (2)	D_{obsd}, g cm^{-3}	1.53 (3)
γ, deg	94.50 (3)	μ(Mo Kα), cm^{-1}	23.14

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Table II. Positional Parameters in $[Cu(Et_3en)Cl_2]_2$

atom	x	y	z	atom	x	y	z
Cu	0.04197 (7)	0.19580 (6)	−0.03277 (7)	H3	−0.284 (6)	0.282 (6)	−0.225 (7)
Cl1	0.1433 (1)	0.0526 (1)	0.1844 (1)	H3′	−0.252 (5)	0.190 (4)	−0.345 (5)
Cl2	−0.0915 (2)	0.3325 (1)	0.1416 (1)	H4	−0.397 (6)	0.360 (6)	−0.460 (7)
N1	−0.0467 (4)	0.3071 (4)	−0.2399 (5)	H4′	−0.254 (6)	0.491 (6)	−0.401 (6)
N2	0.2463 (4)	0.1908 (4)	−0.1495 (5)	H4″	−0.259 (6)	0.344 (6)	−0.554 (7)
C1	0.0435 (6)	0.2771 (6)	−0.3786 (6)	HN1	−0.016 (5)	0.398 (4)	−0.194 (5)
C2	0.2176 (6)	0.2882 (6)	−0.2940 (6)	H5	0.251 (5)	−0.027 (5)	−0.130 (6)
C3	−0.2234 (6)	0.2870 (6)	−0.3039 (6)	H5′	0.154 (5)	0.013 (5)	−0.298 (6)
C4	−0.2853 (6)	0.3858 (6)	−0.4437 (7)	H6	0.390 (6)	−0.096 (5)	−0.341 (6)
C5	0.2567 (6)	0.0369 (6)	−0.2208 (6)	H6′	0.389 (6)	0.056 (6)	−0.418 (7)
C6	0.3918 (7)	0.0135 (6)	−0.3164 (7)	H6″	0.482 (5)	0.044 (5)	−0.247 (6)
C7	0.3973 (6)	0.2442 (6)	−0.0208 (6)	H7	0.420 (5)	0.168 (5)	0.037 (5)
C8	0.3793 (7)	0.3713 (7)	0.1014 (7)	H7′	0.477 (5)	0.278 (5)	−0.095 (6)
H1	0.028 (5)	0.358 (5)	−0.458 (5)	H8	0.483 (6)	0.403 (6)	0.178 (7)
H1′	0.006 (5)	0.188 (5)	−0.422 (5)	H8′	0.352 (6)	0.435 (6)	0.046 (7)
H2	0.242 (5)	0.376 (5)	−0.251 (5)	H8″	0.319 (6)	0.346 (6)	0.175 (7)
H2′	0.283 (5)	0.269 (5)	−0.383 (5)				

compounds to date are distorted from these ideal geometries, thus further complicating the classification of their properties and the analysis of the superexchange interactions in terms of orbital pathways. An empirical relationship between the exchange coupling constant and structural features has been detected in this series of bis(μ-chloro) copper(II) complexes, and studies of additional complexes are necessary to determine the extent of the correlation. We here report the synthesis and structural and magnetic characterization of such a compound, namely, bis(μ-chloro)bis[chloro(*N*,*N*,*N*′-triethylethylenediamine)copper(II)], $[Cu(Et_3en)Cl_2]_2$.

Experimental Section

Synthesis. The complex, $[Cu(Et_3en)Cl_2]_2$, was prepared by the method of Hein and Rittersdorf.[34] Suitable crystals for X-ray analysis were obtained by recrystallization of the complex from hot ethanol. Some of these crystals were ground into a powder for chemical analysis and subsequent magnetic measurements. Anal. Calcd for $Cu(C_8H_{20}N_2)Cl_2$: C, 34.48; H, 7.23; N, 10.05. Found: C, 34.26; H, 7.12; N, 9.97.

X-ray Data Collection and Reduction. A blue-green crystal of $[Cu(Et_3en)Cl_2]_2$ was placed on an Enraf-Nonius CAD-4 automated diffractometer; preliminary analysis indicated that the crystals belong to the triclinic system, the space group being either $P\bar{1}(C_i^1)$ or $P1(C_1^1)$. The former (centrosymmetric) was chosen and was confirmed by the successful refinement of the structure. Cell constants and other parameters are listed in Table I. With one dimeric formula unit in the cell, in space group $P\bar{1}$ the dimers are constrained to lie on a crystallographic inversion center.

The diffracted intensities and their estimated standard deviations were corrected for Lorentz and polarization effects and for absorption. A total of 2710 independent intensities was processed, of which 1823 had $I \geq 3\sigma(I)$; only these latter data were considered observed and used in subsequent calculations.

Solution and Refinement of the Structure. The solution of the structure was effected by the use of a three-dimensional Patterson function to locate the position of the copper atom. After the initial least-squares refinement of the copper position, the locations of all non-hydrogen atoms were obtained from a difference Fourier map. All least-squares calculations were carried out on F with the function minimized being $\sum w(|F_o| - F_c|)^2$, where w is assigned to be $4F_o^2/\sigma^2(I)$. After anisotropic refinement of the non-hydrogen atoms, the positions of the 20 independent hydrogen atoms were discovered in the difference Fourier map. The final cycles of least squares involved anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms. Upon convergence, the final values of the usual agreement factors, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|]^{1/2}$, were 0.041 and 0.045, respectively. No parameter experienced a shift of more than 0.20σ, which was taken as evidence of covergence. A final difference Fourier map was featureless with no peak higher than 0.4 e Å^{-3}. The atomic positions derived from the final cycle, along with their estimated standard deviations, are presented in Table II. Compilations of atomic thermal librations and observed and calculated structure factors are available as supplementary material.

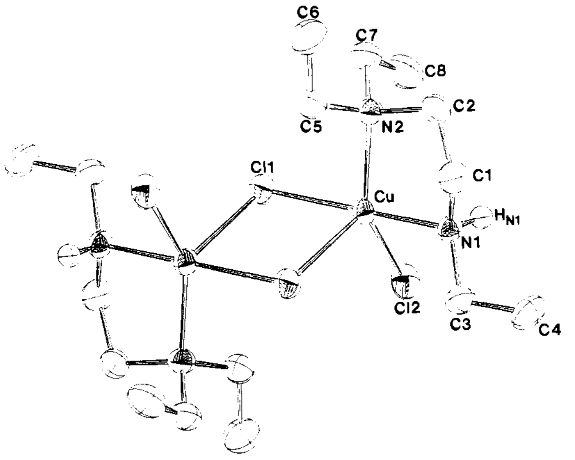

Figure 1. View of the dimeric unit in $[Cu(Et_3en)Cl_2]_2$. Thermal ellipsoids are drawn at the 50% probability level, but the amine hydrogen atom is shown as a sphere of arbitrary site and other hydrogen atoms are omitted for clarity.

Table III. Selected Internuclear Separations (Å) in $[Cu(Et_3en)Cl_2]_2$

Cu-Cl(1)	2.284 (1)	Cu-Cl(1)′	2.728 (1)
Cu-Cl(2)	2.307 (1)	Cu-N(1)	2.015 (3)
Cu-N(2)	2.121 (3)	Cu-Cu′	3.703 (1)

Magnetic Measurements. Magnetic susceptibility data were collected with the use of a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) operating at an applied field strength of 10 kOe. Temperatures at the sample were measured with a calibrated GaAs diode by observing the voltage on a Fluke 8502A 6.5-place digital multimeter; further details of the apparatus and temperature measurement have been given elsewhere.[6,12] A finely ground polycrystalline sample was packed in a Lucite sample holder. The sample weighed approximately 136 mg. The data were corrected for the diamagnetism of the Lucite holder and for the underlying diamagnetism of the constituent atoms with use of Pascal's constants. A value of 60×10^{-6} cgsu was assumed for the temperature-independent paramagnetism (TIP) of copper.

EPR spectra of a polycrystalline sample and of a dichloromethane solution of the complex, $[Cu(Et_3en)Cl_2]_2$, were recorded at room temperature and 77 K on a Varian E-3 X-band spectrometer.

Description of the Structure

The complex consists of dimeric $[Cu(Et_3en)Cl_2]_2$ units that are essentially isolated from each other. A view of a single dimer is shown in Figure 1, and bond distances and angles for the complex are given in Tables III and IV. The bridging

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Table IV. Selected Internuclear Angles (deg) in $[Cu(Et_3en)Cl_2]_2$

Cl(1)-Cu-Cl(1)′	85.16 (4)	Cl(1)-Cu-Cl(2)	94.72 (4)
Cl(1)-Cu-N(1)	174.91 (10)	Cl(1)-Cu-N(2)	93.28 (8)
Cl(1)′-Cu-Cl(2)	110.96 (4)	Cl(1)′-Cu-N(1)	91.02 (10)
Cl(1)′-Cu-N(2)	102.93 (8)	Cl(2)-Cu-N(1)	89.78 (9)
Cl(2)-Cu-N(2)	145.69 (9)	N(1)-Cu-N(2)	84.29 (11)
Cu-Cl(1)-Cu′	94.84 (4)		

Cu_2Cl_2 unit is constrained to be planar by the presence of the crystallographic inversion center in the middle of the dimer. The geometry at each copper can be described as either a distorted tetragonal-pyramidal or a distorted trigonal-bipyramidal arrangement. As will be noted later, from a magnetic viewpoint, this distinction appears to lose meaning.

With use of the trigonal-bipyramidal description, the apical sites are occupied by Cl(1) and N(1) with atoms Cl(2), N(2), Cl(1)′, and Cu making up the equatorial plane (see Figure 1) with deviations from the best least-squares plane being 0.02, 0.03, 0.01, and −0.06 Å, respectively. The apical atoms, Cl(1) and N(1), are located −2.330 and 1.951 Å, respectively, on either side of this plane. The dihedral angles between the three trigonal planes defined by atoms Cu, Cl(1), N(1), and N(2), by Cu, Cl(1), N(1), and Cl(2), and by Cu, Cl(1), N(1), and Cl(1)′ are 35.8, 74.9, and 69.2°, while the idealized value is 60°.

For the tetragonal-pyramidal description, the base plane would consist of the atoms Cl(1), Cl(2), N(1), and N(2) with the bridging chloride, Cl(1)′, occupying the apical site. The best least-squares plane through the basal atoms shows deviations from the plane of 0.30, −0.32, 0.39, and −0.38 Å, respectively, with the copper atom sitting 0.29 Å from this the plane on the side of the apical atom Cl(1)′. These distortions from the ideal tetragonal-pyramidal geometry appear greater than in the trigonal-bipyramidal model; however, this classification will be discussed further in the Discussion in conjunction with the structures of several other complexes.

The Cu-N distances are observed to be considerably different from one another with the Cu-N(2) distance being 2.121 (3) Å and the Cu-N(1) distance being 2.015 (3) Å. This behavior is inconsistent with the electron-donating capability of the ethyl groups on N(2), which would lead to an enhancement of electron density at N(2) over that at N(1). However, this enhancement is presumably offset by the greater steric crowding at N(2), thereby accounting for the observed difference in bond lengths. This trend is analogous to that which was observed in the *N*,*N*-dimethylethylenediamine complexes[35] $Cu(dmen)Cl_2$ and $Cu(dmen)Br_2$, where the presence of the two methyl groups at one nitrogen atom produced a lengthening of this Cu-N bond over the other by about 0.08 Å.

The Cu-Cl(1) and Cu-Cl(2) distances are 2.284 (1) and 2.307 (1) Å, respectively, with the bond to the nonbridging atom, Cl(2), having the slightly longer length. These bond lengths are normal for bis(μ-chloro) copper(II) complexes. The Cu-Cl(1)′ distance of 2.728 (1) Å is also within the previously observed range for these complexes, which exhibit values from 2.447 Å in the guaninium complex[43] $[Cu(GuaH)Cl_3]_2 \cdot 2H_2O$ to 3.364 Å in the 2-methylpyridine complex[25] $[Cu(2\text{-pic})_2Cl_2]_2$. Furthermore, the bridging angle (ϕ) Cu-Cl(1)-Cu′ of 94.84 (4)° and the Cu-Cu′ distance of 3.703 (1) Å are in the middle of their respective ranges. The structure of the dimer is compared to those of related dimers in Table V.

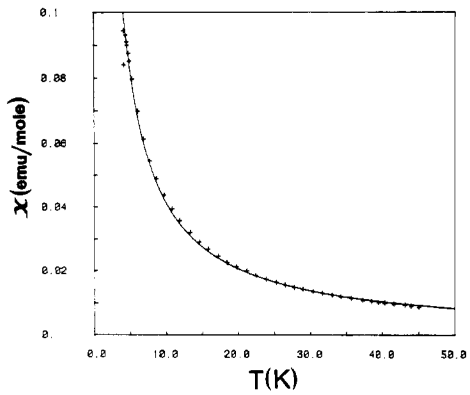

Figure 2. Temperature dependence of the magnetic susceptibility of $[Cu(Et_3en)Cl_2]_2$. The solid line represents the fit to the magnetization expression (eq 1) with the parameters $g = 2.092$ and $J = 0.032$ cm^{-1}.

The geometry and structural parameters within the triethylethylenediamine ligand are normal as can be seen in Tables VI and VII (supplementary material). The only significant feature of the ethylenediamine geometry is that the hydrogen atom attached to N(1) forms a hydrogen bond to a terminal chloride on a dimer situated one cell length away along the *b* axis. The $N(1)\cdots Cl(2)^y$ and $HN1\cdots Cl(2)^y$ distances and the $N1\text{-}HN1\cdots Cl(2)^y$ angle are 3.413 (4) Å, 2.55 (4) Å, and 165°, respectively. These values are within the ranges observed for other N-H···Cl hydrogen bonds.[48]

Magnetic Properties

The magnetic susceptibility of a powdered sample of the complex is plotted as a function of temperature in Figure 2. Analysis of the temperature variation of the inverse susceptibility with use of the Curie-Weiss law yields a *g* value of 2.09 and a Θ value of −0.02 K, suggestion a very small exchange coupling constant. Since the exchange coupling constant is expected to be small, the application of the Bleaney-Bowers susceptibility expression[55] is inappropriate since here $|J|$ cannot be greater than $g\mu_B H$. Consequently, the data were

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Table V. Structural and Magnetic Properties of Bis(μ-chloro) Copper(II) Dimers[a]

complex	Cu-Cu', Å	Cu-Cl' (R), Å	Cu-Cl-Cu' (ϕ), deg	ϕ/R, deg/Å	$2J$, cm^{-1}	geom	ref
1. $[Cu(PAN)Cl_2]_2$	3.416	2.647 (1)	87.79 (3)	33.17		TP	36
2. $[Cu(dmgH)Cl_2]_2$	3.445	2.698	88.0	32.62	+6.3	TP	37-39
3. $[Cu(dmen)Cl_2]_2$	3.458 (3)	2.734 (3)	86.13 (8)	31.50	−2.1	TP	35, 40
4. $[Cu(9M6MP)Cl_2]_2$	3.519 (1)	2.737 (1)	88.17	32.21		TP	41
5. $[Cu(Me_3en)Cl_2]_2$	3.558 (1)	2.937 (2)	84.84 (4)	28.89		TP	42
6. $[Cu(GuaH)Cl_3]_2$	3.575	2.447 (1)	97.9	40.01	−82.6	TBP	43, 44
7. $[Cu(AETA)Cl_2]_2$	3.592	2.767 (5)	90.1 (2)	32.56		TP	45
8. $[Cu(BTMH)Cl_2]_2$	3.631 (3)	2.735 (2)	92.83 (5)	33.94		TP	46
9. $[Cu(Et_3en)Cl_2]_2$	3.703 (1)	2.728 (1)	94.84 (4)	34.75	+0.1	TBP	this work
10. $[Cu(4\text{-}Metz)(DMF)Cl_2]_2$	3.721	2.724	95.3	34.99	−3.6	TBP	47
11. $[Co(en)_3]_2[Cu_2Cl_8]Cl_2$	3.722 (5)	2.703 (5)	95.2 (1)	35.22	−14.6	TBP	48, 49
12. $[Cu(TMSO)Cl_2]_2$	3.737 (2)	3.020 (2)	88.5 (1)	29.30	−17.0	TP	50
13. $[Cu(BBTE)Cl_2]_2$	3.749 (2)	2.825 (2)	94.22 (5)	33.35		TP	51
14. $[Cu(TMPD)Cl_2]_2$	3.958 (1)	2.980 (1)	96.5 (1)	32.35		TP	52
15. $[Cu(tmen)Cl_2]_2$	4.089 (4)	3.147 (4)	96.8 (1)	30.76	−5.6	TP	40, 53
16. $[Cu(2\text{-}pic)_2Cl_2]_2$	4.404 (1)	3.364 (1)	100.63 (3)	29.91	−7.4	TP	25, 26, 54

[a] Abbreviations: PAN = 1-(2-pyridylazo)-2-naphtholate; dmgH = dimethylglyoxime; dmen = *N,N*-dimethylethylenediamine; 9M6MP = 9-methyl-6-mercaptopurine; Me_3en = *N,N,N'*-trimethylethylenediamine; GuaH = guaninium; AETA = *N*-(2-aminoethyl)thiophene-2-carbaldimine; BTMH = benzoyltrimethylhydrazine; Et_3en = *N,N,N'*-triethylethylenediamine; 4-Metz = 4-methylthiazole; DMF = *N,N*-dimethylformamide; TMSO = tetramethylene sulfoxide; BBTE = $BuSCH_2CH_2SBu$; TMPD = *N,N,N',N'*-tetramethyl-*o*-phenylenediamine; tmen = *N,N,N',N'*-tetramethylethylenediamine; 2-pic = 2-methylpyridine; TP = tetragonal pyramidal; TBP = trigonal bipyramidal.

fitted to the magnetization expression[56] for a pair of exchange-coupled $S = {}^1/_2$ ions (eq 1), where the exchange Hamiltonian is given by eq 2 and $\hat{S}$ is the total spin (i.e., $\hat{S} = \hat{S}_1 + \hat{S}_2$).

$$M = \frac{Ng\mu_B \sinh (g\mu_B H/kT)}{\exp(-2J/kT) + 2 \cosh (g\mu_B H/kT) + 1} \quad (1)$$

$$H_{ex} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (2)$$

The experimental susceptibility data were fitted to eq 1 with use of the relationship

$$\chi = M/H \quad (3)$$

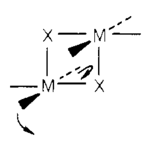
where χ is the magnetic susceptibility. The parameters g and J were treated as variables in a SIMPLEX fitting routine.[12] The results of the fit, shown as the solid line in Figure 2, lead to values of $g = 2.092$ and $2J = +0.06$ cm^{-1}. The average g value obtained from the magnetic susceptibility data agrees reasonably well with the average g value of 2.12 determined from EPR spectra.

The EPR spectrum of a powdered sample of $[Cu(Et_3en)Cl_2]_2$ at 77 and at 298 K showed a complete **g**-tensor anisotropy with $g_1 = 2.04$, $g_2 = 2.08$, $g_3 = 2.24$, and $g_{av} = 2.12$. Careful scans in the $\Delta M_s = \pm 2$ region (~1500 G) revealed no additional resonances.

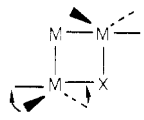
The magnetic data demonstrate that in $[Cu(Et_3en)Cl_2]_2$ the exchange coupling constant (J) is very small and that there is essentially no energy difference between the singlet and triplet states. With the present susceptibility data, little significance should be attached to the suggestion from the fit that J is positive. The proper conclusion here is that $|J|$ is very small (<0.2 cm^{-1}), and in the absence of data at extremely low temperatures the sign of J cannot be determined with certainty.

Discussion

In previous attempts[25] to analyze the relationship between the structural and magnetic properties of complexes of the types $[CuA_2X_2]_2$ and $[CuLX_2]_2$, we have considered the tetragonal-pyramidal (I) and trigonal-bipyramidal (II) complexes as being different structural types, since in the former the unpaired spin lies predominantly in the $d_{x^2-y^2}$ orbital while in the latter it is predominantly in the d_{z^2} orbital. This distinction is, however, unnecessary for the axial–equatorial dimers of the two types, since they are interconvertible by a single angular deformation, as shown:



I

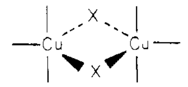


II

This deformation is, of course, well-known in inorganic chemistry and is the basis of the Berry mechanism for intramolecular rearrangement.[57]

Fundamentally, therefore, all that has occurred is a change of coordinate systems. Electronically the observed dimers of types I and II are substantially similar, and, in fact, the "trigonal-bipyramidal" (type II) complex $[Cu_2Cl_8]^{4-48}$ has been shown[58] to exhibit a predominantly $d_{x^2-y^2}$ ground state as expected for tetragonal-pyramidal geometry. Consequently, we submit that all of the complexes in Table V may be viewed as belonging to the same structural type and that their magnetic properties can be compared directly.

This statement is restricted to complexes of types I and II, since the deformation described would not transform I to the equatorial–equatorial trigonal-bipyramidal dimer (III). All



III

of the complexes in Table V are of types I and II; the only reported example of III is the benzotriazole complex $[Cu(BTAH)_2Cl_2]_2 \cdot H_2O$, whose structure is complicated by the presence of two dissimilar dimers in the cell[59] and which exhibits a weakly ferromagnetic interaction.[60]

As has been noted elsewhere for related systems,[6,8,12,19,25] the exchange coupling constants J in the present complexes might be expected to show a simple relationship with the quantity ϕ/R, where ϕ is the Cu–Cl–Cu' bridging angle and R is the (longer) Cu–Cl' separation; this latter bond distance is the axial Cu–Cl bridging distance in I and the equatorial

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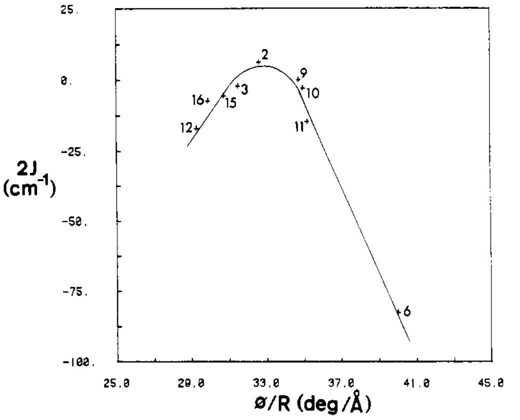

Figure 3. Plot of the singlet–triplet splitting $2J$ as a function of ϕ/R (see text for definitions). The solid line is a guide for the eye. The data are numbered as in Table V.

distance in II. The available $2J$ values (Table V) are plotted as a function of ϕ/R in Figure 3. It is noteworthy that the expected[6,8,12,19,25] behavior of the singlet–triplet splitting is observed in that $2J$ increases with increased ϕ/R until it reaches a maximum value, after which further increase in ϕ/R leads to a reduction in $2J$. Since there are both ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contributions to J, the existence of some values of ϕ/R where these two terms approximately cancel is predicted, and the present observation of $J \approx 0$, therefore, is an expected result. It should be emphasized that while the magnetic data in Figure 2 could be interpreted in terms of two noninteracting copper(II) centers, the correct interpretation (and the only interpretation consistent with the structure) is that of contributions to J of opposite sign that happen to cancel each other.

It is apparent from the plot in Figure 3 that all of the available structural and magnetic data for these structurally related bis(μ-chloro)-bridged dimers fit this gross trend, irrespective of their assignment as structural types I or II. It is important to note that the orbitals involved in the superexchange pathway are fundamentally the same in both cases, although the coefficients of the various orbital functions in the ground-state linear combination vary from complex to complex as a result of the chemical and structural environment of the copper ions. We expect that it will be possible to correlate exchange coupling with these coefficients. It is further expected that there will be a smooth variation of the coefficients with subtle structural changes and that this smooth variation of coefficients provides the basis for the $2J$ vs. ϕ/R correlation. As further data become available, it will be possible to replace the empirical quantity R^{-1} by a more satisfying function such as $\exp(-bR)$ as suggested by Glerup, Hodgson, and Pedersen[9] or, at least, by R^{-n}, but the present data are insufficient to justify this refinement.

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Supplementary Material Available: Tables of anisotropic thermal parameters (U_{ij}), observed and calculated structure factors (electrons × 10), and bond lengths (Table VI) and bond angles (Table VII) in the *N,N,N'*-triethylethylenediamine ligand (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Phosphite-Containing Cobalt(III) Complexes Obtained via Disproportionation Reactions of Pentacoordinate Mononitrosyl Derivatives. Crystal Structure of *trans*-Bis(isothiocyanato)tetrakis(triethyl phosphite)cobalt(III) Tetraphenylborate

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The disproportionation reactions of $Co(SCN)_2$ (in the presence of $P(OMe)_3$) and $[Co(NCS)L_3(NO)]^+$ (L = $P(OEt)_3$ or $PhP(OEt)_2$) species have been examined and have led to the synthesis of the first cobalt(III) complexes with the donor-atom set X_2L_4 (X = pseudohalogen; L = monodentate phosphite). Both the *cis*- and the *trans*-$[Co(NCS)_2L_4]BPh_4$ isomers were isolated and characterized, and the crystal structure of *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$ was determined. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of the following dimensions: $a = 19.05$ (2) Å, $b = 13.25$ (1) Å, $c = 27.46$ (3) Å, $\beta = 109.86$ (7)°. The structure was solved by the heavy-atom method from automated diffractometer data and refined to $R = 0.0935$ for 3199 reflections.

Introduction

Previous reports from our laboratories have dealt with studies of cobalt(II) halide reactions with phosphites and subsequent reactions with nitric oxide.[2] We found that CoX_2 (X = Cl, Br, I) reacts with phosphite to produce $[CoXL_4]^+$ species, which react with nitric oxide to form $[CoXL_3(NO)]^+$ cations. We have extended these studies to include the reactivity of cobalt(II) thiocyanate and found, instead of substitution products, Co(I) and Co(III) complexes. Redox reactions of this type have been only occasionally observed though the properties of cobalt(II) compounds have been extensively investigated.[3] Similar reactivity has been observed only with $Co(ClO_4)_2 \cdot 6H_2O$ in the presence of sterically con-

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