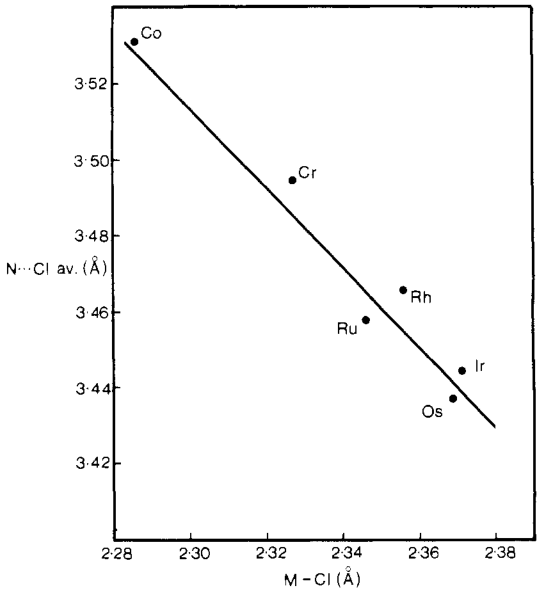

Figure 5. M-Cl bond lengths plotted against the average N···Cl contacts for the intercomplex hydrogen bonds.

in bond lengths of the order of 5-6%. The importance of this contraction, due to hydrogen bonding, is seen in the cell parameters of Ru and Os (Table I), where the *a* parameter for Os is significantly shorter than that for Ru, despite the longer Os-ligand bonds.

The increase along the *b* axis in going from Co to Os is larger (~1.7%), but still much smaller than the increase in average M-L bond lengths. From these results, it would be predicted that the exchange coupling between $[Os(NH_3)_5Cl]^{2+}$ centers should be larger than that observed between the $[Ru(NH_3)_5Cl]^{2+}$ centers,[1] if indeed the coupling occurs via intercomplex hydrogen bonding. This prediction awaits experimental verification at present. However, the postulate that this intercomplex hydrogen bonding provides a pathway for weak exchange coupling of paramagnetic ions and hence unusual magnetic and spectroscopic behavior would appear to be reasonable, since all of the $[M(NH_3)_5Cl]Cl_2$ structures have the same intercomplex hydrogen bonding.

Conclusions

The expected increase in π bonding in M-Cl bonds in going from a d^6 to d^5 or d^3 electronic configuration was observed experimentally. Changes in hydrogen bonding between the complex ions and the counterions are small, but are dominated by polarization of the N-H bonds due to the changes in M-N bond lengths. The intercomplex hydrogen bonds show a much larger variation with the nature of M and their strengths decrease with decreasing M-Cl bond length. Again, this is attributed to an increased polarization of the ligand electron density toward the metal ion as its charge:radius ratio decreases.

Acknowledgment. P.A.L. is grateful for support from the Australian Research Grants Scheme.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated atomic positions of hydrogen atoms for $[M(NH_3)_5Cl]Cl_2$ (M = Cr, Ru, Os, Ir) (8 pages); tables of observed and calculated structure factors for $[M(NH_3)_5Cl]Cl_2$ (M = Cr, Ru, Os, Ir) (19 pages). Ordering information is given on any current masthead page.

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Crystal Structure of $[(C_2H_5)_4N]_4Cu_4Cl_{12}$, a New Structural Type for a Tetranuclear Copper(II) Halide Complex

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The crystal structure of the compound with the empirical formula $(C_2H_5)_4NCuCl_3$ has been determined. The crystals are monoclinic, space group $P2_1/c$, with $a = 13.799$ (3) Å, $b = 11.316$ (2) Å, $c = 17.883$ (3) Å, and $\beta = 106.04$ (2)°, with $Z = 2$. The compound is shown to have the chemical formula $[(C_2H_5)_4N]_4Cu_4Cl_{12}$ and to consist of discrete $(C_2H_5)_4N^+$ cations and $Cu_4Cl_{12}^{4-}$ anions. The centrosymmetric anions contain copper atoms in two distinct coordination geometries: the central pair of copper(II) ions have 4 + 1 coordination while the outer pair have a distorted-tetrahedral geometry. The central pair are joined by two symmetrical Cu-Cl-Cu bridges with bridging bond angles of 96.35° each. One symmetrical Cu-Cl-Cu bridge and one asymmetrical Cu-Cl···Cl bridge link each outer copper ion to a central ion. The bridging angles are 95.51 and 88.3°, respectively. The magnetic properties are indicative of a weak ferromagnetic interaction for both bridges, but the data did not allow specific values for the exchange coupling to be determined.

Introduction

The structural chemistry of copper(II) chlorides and bromides is extremely diverse as a result of that metal's flexible coordination geometry coupled with the bridging capability of the halide ions. The former characteristic leads to situations where two or more coordination geometries coexist within a structure, e.g., square pyramidal and distorted tetrahedral in $[C_6H_{18}N_3]_4Cu_5Cl_{22}$,[2] tetrahedrally distorted 4 + 1 and 4 + 2 geometries in $[(CH_3)_2CHNH_3]_2CuCl_4$,[3] and distorted tetrahedral and 4 + 2 geometry in $[(C_2H_5)_2NH_2]_2Cu_4Br_{10}\cdot EtOH$.[4] The relative flatness of the potential surface defining the coordination geometry is further seen by the ability of the square-pyramidal $CuCl_5^{3-}$ ion in $M(NH_3)_6CuCl_5$ salts[5] to undergo dynamic reorientation of its C_4 axis. The ability to transform between coordination geometries is demonstrated by the phenomenon of thermochromism,[6] in which the stereochemistry changes as materials pass through structural phase transitions.

The capability of the halides to act as bridging ligands between copper ions leads to a variety of oligomeric and polymeric species. In a recent review,[7] we summarized the findings on $ACuCl_3$ salts. These included structures containing isolated $Cu_2Cl_6^{2-}$ ions, stacks of $Cu_2Cl_6^{2-}$ ions linked by semicoordinate linkages, bibridged chains with square-pyramidal coordination geometry, and tribridged chains with 4 + 2 coordination geometry. In particular, we argued that the presence of bulky, non-hydrogen-bonding

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Table I. Diffraction Data for $(Et_4N)CuCl_3$

compd name	tetraethylammonium trichlorocuprate(II)
empirical formula	$C_8H_{20}NCuCl_3$
diffractometer system	Nicolet R3m/E
cryst class	monoclinic
space group	$P2_1/c$
systematic absences	$h0l$, l odd; $0k0$, k odd
lattice constants	$a = 13.799$ (3) Å $b = 11.316$ (2) Å $c = 17.883$ (3) Å $\beta = 106.04$ (2)° $V = 2684.7$ Å^3 based on 25 reflcns in the range $30 < 2\theta < 40°$
$F(000)$	1159.8
radiation	Mo Kα with Zr filter
abs coeff	21.89 cm^{-1}
calcd density	1.48 g cm^{-3} ($Z = 8$, based on $C_8H_{20}NCuCl_3$)
type of abs cor	empirical ψ scan
max transmission	0.437
min transmission	0.576
data collection technique	θ–2θ scan
scan range	1.8°
scan speed	3.9°/min (min), 29.3°/min (max)
check reflecns	2,0,4; 5,2,–4; 2,3,0 (monitored every 50 reflecns)
total reflecns	2839 out to $2\theta = 40°$
unique reflecns	2531, 1999 with $F > 3\sigma$
R for equiv reflecns	0.0234
structure soln package	Nicolet SHELXTL
structure soln technique	direct methods
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.036
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.039
total parameters refined	236
thermal parameters	anisotropic on all non-H atoms
H atoms	constrained to C–H and N–H = 0.96 Å, thermal parameters fixed at 1.2 times heavy-atom parameters
largest peak on final diff map	0.5 e/Å^3 near N(11)
extinction cor	none

cations would lead to the formation of isolated $Cu_2Cl_6^{2-}$ ions with a distorted-tetrahedral coordination around the copper(II) ion, as had been observed in the Ph_4P^+,[8] Ph_4As^+,[9] and Ph_4Sb^+ [10] salts. With these ideas in mind, an investigation of the properties of $(Et_4N)CuCl_3$ was begun.[11]

Experimental Section

An 8.5-g sample of tetraethylammonium chloride was dissolved in 70 mL of 1-propanol and mixed with a solution of 8.5 g of anhydrous copper chloride in 120 mL of a 1:1 (volume) mixture of 1-propanol and 12 M hydrochloric acid at 40 °C. This solution was boiled down to one-sixth of its original volume and then cooled with ice overnight. A brown precipitate formed initially, which tarnished green. The green compound could be dissolved by addition of extra propanol and hydrochloric acid, and after heating and cooling, a reddish brown precipitate remained. This was filtered and washed with cold propanol (batch 1). Upon addition of propanol to the filtrate, an orange precipitate formed. This was also filtered and washed with ethanol (batch 2). Both products were dried in a vacuum desiccator. Crystals were grown by a temperature gradient technique with ethyl acetate or an ethyl acetate/acetone mixture as the solvent. Anal. Found (batch 1, 2) (calcd) for $[(C_2H_5)_4N]CuCl_3$: C, 29.75, 32.31 (32.01); H, 6.09, 6.72 (6.72); N, 4.29, 4.72 (4.67); Cl, 35.21, 33.66 (40.72); Cu, 24.93, NA (21.17).

It is quite likely that the tetraethylammonium salt is identical with the compound prepared by Piovesana and Selbin[11] from the reaction of copper chloride with $[(C_2H_5)_4N]_3VOCl_3(OSO_3)(H_2O)$ in hot ethanol. Those authors claim that the trichloride, as well as a salt of stoichiometry $[(C_2H_5)_4N]_5Cu_3Cl_{11}$, do not form in the absence of vanadyl ion.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (10^3 Å^2)

	x	y	z	U^a
Cu(1)	1192 (1)	4645 (1)	5566 (1)	41 (1)
Cu(2)	2501 (1)	2027 (1)	5808 (1)	39 (1)
Cl(1)	922 (1)	2385 (1)	5872 (1)	46 (1)
Cl(2)	347 (1)	4820 (2)	4255 (1)	48 (1)
Cl(3)	2083 (1)	5495 (2)	6667 (1)	62 (1)
Cl(4)	2601 (1)	3880 (2)	5274 (1)	56 (1)
Cl(5)	3328 (1)	1056 (2)	5104 (1)	67 (1)
Cl(6)	3042 (1)	1015 (2)	6904 (1)	49 (1)
N(1)	4697 (3)	7378 (4)	1262 (3)	42 (2)
C(1)	4283 (5)	7079 (6)	410 (4)	70 (3)
C (2)	3382 (5)	7776 (7)	–29 (5)	92 (4)
C(3)	5679 (4)	6724 (6)	1563 (4)	57 (3)
C(4)	5598 (5)	5398 (6)	1573 (4)	73 (4)
C(5)	4886 (5)	8698 (6)	1375 (4)	58 (3)
C(6)	5610 (5)	9213 (6)	976 (4)	71 (3)
C(7)	3923 (5)	7011 (7)	1680 (5)	75 (4)
C(8)	4280 (6)	7090 (7)	2545 (5)	92 (4)
N(11)	62 (3)	4040 (4)	8230 (3)	32 (2)
C(11)	723 (5)	4842 (6)	8834 (4)	59 (3)
C(12)	1308 (5)	5760 (6)	8528 (4)	67 (3)
C(13)	659 (5)	3455 (6)	7740 (4)	59 (3)
C(14)	1570 (4)	2751 (6)	8183 (4)	57 (3)
C(15)	–762 (5)	4772 (6)	7699 (4)	58 (3)
C(16)	–1578 (5)	4064 (6)	7129 (4)	59 (3)
C(17)	–361 (5)	3113 (6)	8655 (4)	63 (3)
C(18)	–1070 (5)	3562 (6)	9108 (4)	60 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III

(a) Bond Lengths (Å)

Cu(1)–Cl(1)	2.662 (2)	Cu(1)–Cl(2)	2.320 (2)
Cu(1)–Cl(3)	2.230 (2)	Cu(1)–Cl(4)	2.316 (2)
Cu(1)–Cl(2a)	2.313 (2)	Cu(2)–Cl(1)	2.250 (2)
Cu(2)–Cl(4)	2.324 (2)	Cu(2)–Cl(5)	2.212 (2)
Cu(2)–Cl(6)	2.215 (2)	Cl(2)–Cu(1a)	2.313 (2)
N(1)–C(1)	1.511 (8)	N(1)–C(3)	1.507 (7)
N(1)–C(5)	1.520 (8)	N(1)–C(7)	1.521 (10)
C(1)–C(2)	1.498 (10)	C(3)–C(4)	1.505 (10)
C(5)–C(6)	1.497 (11)	C(7)–C(8)	1.491 (12)
N(11)–C(11)	1.509 (7)	N(11)–C(13)	1.512 (9)
N(11)–C(15)	1.512 (7)	N(11)–C(17)	1.504 (9)
C(11)–C(12)	1.509 (10)	C(13)–C(14)	1.514 (9)
C(15)–C(16)	1.522 (9)	C(17)–C(18)	1.520 (11)

(b) Bond Angles (deg)

Cl(1)–Cu(1)–Cl(2)	103.3 (1)	Cl(1)–Cu(1)–Cl(3)	107.9 (1)
Cl(2)–Cu(1)–Cl(3)	148.8 (1)	Cl(1)–Cu(1)–Cl(4)	82.0 (1)
Cl(2)–Cu(1)–Cl(4)	91.3 (1)	Cl(3)–Cu(1)–Cl(4)	93.8 (1)
Cl(1)–Cu(1)–Cl(2a)	92.1 (1)	Cl(2)–Cu(1)–Cl(2a)	83.8 (1)
Cl(3)–Cu(2)–Cl(2a)	94.0 (1)	Cl(4)–Cu(1)–Cl(2a)	171.4 (1)
Cl(1)–Cu(2)–Cl(4)	91.5 (1)	Cl(1)–Cu(2)–Cl(5)	141.0 (1)
Cl(4)–Cu(2)–Cl(5)	96.6 (1)	Cl(1)–Cu(2)–Cl(6)	98.2 (1)
Cl(4)–Cu(2)–Cl(6)	141.9 (1)	Cl(5)–Cu(2)–Cl(6)	98.4 (1)
Cu(1)–Cl(1)–Cu(2)	88.3 (1)	Cu(1)–Cl(2)–Cu(1a)	96.2 (1)
Cu(1)–Cl(4)–Cu(2)	95.5 (1)	C(1)–N(1)–C(3)	107.6 (5)
C(1)–N(1)–C(5)	110.9 (5)	C(3)–N(1)–C(5)	109.3 (4)
C(1)–N(1)–C(7)	108.3 (5)	C(3)–N(1)–C(2)	112.0 (5)
C(5)–N(1)–C(7)	108.8 (5)	N(1)–C(1)–C(2)	116.0 (6)
N(1)–C(3)–C(4)	115.6 (5)	N(1)–C(5)–C(6)	115.6 (6)
N(1)–C(7)–C(8)	114.8 (6)	C(11)–N(11)–C(13)	111.1 (5)
C(11)–N(11)–C(15)	108.7 (4)	C(13)–N(11)–C(15)	108.2 (5)
C(11)–N(11)–C(17)	107.4 (5)	C(13)–N(11)–C(17)	109.7 (5)
C(15)–N(11)–C(17)	111.7 (5)	N(11)–C(11)–C(12)	115.6 (5)
N(11)–C(13)–C(14)	115.6 (5)	N(11)–C(15)–C(16)	114.9 (5)
N(11)–C(17)–C(18)	115.7 (5)		

Crystals of the salt grow as red needles. A small crystal, approximately 0.1 × 0.2 × 0.3 mm^3, was selected for data collection on a Nicolet R3m/E diffractometer system.[12] The system is monoclinic, $P2_1/c$, with $a = 13.799$ (3) Å, $b = 11.316$ (2) Å, $c = 17.883$ (3) Å, and $\beta = 106.04$

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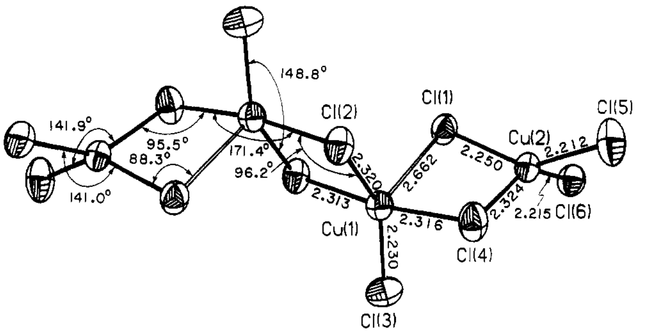

Figure 1. Illustration of the $Cu_4Cl_{12}^{4-}$ ion in $(Et_4N)CuCl_3$.

(2)° (λ = 0.71069 Å) with $Z = 2$ for $\rho_{calcd} = 1.48$. Structure solution and refinement proceeded in a straightforward fashion with use of the version 4.1 SHELX programs.[13] A final value of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.036$ and $R_w = (\sum w(F_o - F_c)^2/\sum w|F_o|^2)^{1/2} = 0.035$ was obtained. Data collection parameters are given in Table I and final positional and isotropic thermal parameters in Table II. Bond distances and angles are given in Table III. Anisotropic thermal parameters and $|F_o|$ and $|F_c|$ values as well as a stereographic packing diagram are available as supplementary material. Scattering factors are taken from ref 14.

Crystal Structure Description

The structure consists of discrete Et_4N^+ cations and tetrameric $Cu_4Cl_{12}^{4-}$ anions. The latter are illustrated in Figure 1, along with pertinent bond distances and angles. The centrosymmetric tetrameric unit contains two distinctly different coordination environments for the copper(II) ions. The central pair, Cu(1), have a 4 + 1 coordination geometry with four short Cu–Cl bonds (2.295 Å, average) and one longer, semicoordinate Cu–Cl bond at 2.662 Å. The distances and angles indicate a geometry that, arguably, shows a substantial distortion toward trigonal bipyramidal with one of the "trans" Cl–Cu–Cl bonds, Cl(2)–Cu(1)–Cl(3), bent away from the semicoordinate chloride to 148.8°, while the other, Cl(2′)–Cu(1)–Cl(4), is nearly linear at 171.4°. The distance to the semicoordinate chloride, Cl(1), is similar to those in other compounds with similar coordination geometry. In contrast to the case for Cu(1), the terminal copper(II) ions, Cu(2), have a distorted-tetrahedral geometry. The typical D_{2d} distortion is quite pronounced, with Cl(1)–Cu(1)–Cl(5) = 141.0° and Cl(4)–Cu(1)–Cl(6) = 141.9°. Contacts between tetramers are all greater than van der Waals distances (3.6 Å). For the tetraethylammonium cation, the N–C bond lengths and angles are in the usual range. Most of the hydrogen atoms were located on different maps with no evidence of disorder and then were refined as rigid CH_2 and CH_3 groups.

The two distinct coordination geometries force two different bridging arrangements within the dimer. The central bridging between equivalent Cu(1) ion is of the symmetric bibridged type found in $Cu_2Cl_6^{2-}$ dimers in the bibridged chains in $ACuCl_3$ salts. The bridging angle, 96.2°, is about 0.5–0.7° larger than typically found in these systems.[15,16] The central Cu_2Cl_6 moiety exhibits what we have labeled as a bifold or sedia geometry with a bifold angle, σ, of 31.6° between the plane of the bridging Cu_2Cl_2 unit and the folded $CuCl_3$ unit (Cu(1), Cl(2), Cl(3), and Cl(4)). However, the bibridge between the two crystallographically different copper(II) ions is unique in copper halide crystal chemistry in that one symmetric bridge, Cu(1)–Cl(4)–Cu(2), and one asymmetric bridge, Cu(1)–Cl(1)–Cu(2), exist. The bridging angles are 95.5 and 88.3°, respectively. The effect of bridging upon the Cu–Cl distances is clearly seen. Those involved in symmetric bridges are in the range 2.313–2.324 Å, terminal bonds are 2.212–2.215 Å (tetrahedral) and 2.230 Å (4 + 1 coordination), and the Cu–Cl distance in the asymmetric bridge is intermediate (2.250 Å). The dihedral angle between the Cu(2), Cl(1), Cl(4) plane and the Cu(2), Cl(5), Cl(6) plane is 53°.

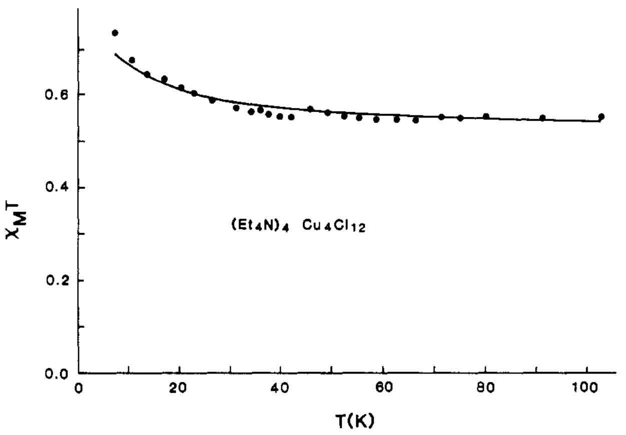

Figure 2. Plot of χT vs. T for $(Et_4N)CuCl_3$. The solid curve is calculated for J_{12}/k = 10 K and J_{23}/k = 10 K.

Magnetic Properties

Magnetic susceptibility measurements[17] were made in the temperature range 4.2–100 K with a PAR vibrating-sample magnetometer. Figure 2 shows the product of molar susceptibility and temperature vs. temperature for tetraethylammonium trichlorocuprate(II). The compound shows an enhanced moment, even at the high end of the temperature scale.

For the observed tetrameric species, the appropriate Hamiltonian is

$$\mathcal{H} = -2J_{12}\vec{S}_1\cdot\vec{S}_2 - 2J_{23}\vec{S}_2\cdot\vec{S}_3 - 2J_{34}\vec{S}_3\cdot\vec{S}_4$$

with, in this case, $J_{12} = J_{34}$. Solutions for the susceptibility of copper(II) tetramers have been obtained for several Hamiltonians,[18] as well as for our specific case.[19] The results from a mean field corrected dimer model indicated that both interactions, J_{12} and J_{23}, are ferromagnetic. Unfortunately, attempts to fit the data to the model did not allow a unique determination of these two exchange constants because of the strong correlation of J_{12} with J_{23}. It did demonstrate that both interactions had to be positive. The solid curve in Figure 2 is calculated for J_{12}/k = 10 K and J_{23}/k = 10 K. Similar curves were obtained for a range of positive J_{12} and J_{23} values.

These magnetic results are consistent with the structural characteristics within the tetramer. We have examined the magnetic behavior of a series of salts containing chains of $Cu_2Cl_6^{2-}$ dimers.[15,16] These dimers exhibit the sedia distortion, with the bifold angle ranging from nearly zero up to σ = 31.7°. With a bridging angle of 95.5–96°, the dimers exhibit antiferromatic coupling for $\sigma < 20°$ and are ferromagnetically coupled when $\sigma \geq 25°$. With a bifold angle near 32° and a bridging angle of 96.2°, the central Cu_2Cl_6 unit is expected to have a ferromagnetic interaction ($J/k \approx 30 \pm 15$ K). The magnetic behavior associated with the terminal bridges is harder to interpret because of their unique nature. The distorted D_{2d} tetrahedral coordination geometry at Cu(2) would normally be expected to yield a ferromagnetic coupling of $J/k \approx 30$ K for the symmetric bridge.[8-10] However, the bridging angle here is ~2° larger than in the tetrahedrally distorted bibridged dimers; thus, the magnitude of the exchange constant is expected to be smaller. For the asymmetric bridge, a ϕ/R value of 34.46 has been correlated with an

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exchange coupling of near zero.[20] Thus, a ferromagnetic interaction is anticipated for this pathway, but the maximum value is indeterminant.

The correlation between structural characteristics and magnetic coupling can be placed on a firmer basis through the application of extended Hückel calculations in the Hay, Thibeault, and Hoffmann formalism.[21] In their approximation, the exchange coupling is given as the sum of two forms, one ferromagnetic in nature, the other antiferromagnetic, viz.

$$J = K_{ab} - (\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab})$$

where the exchange and Coulomb integrals, $K_{ab} > 0$ and $J_{aa} > J_{ab}$, are slowly varying functions of molecular geometry and ϵ_1 and ϵ_2 are the one-electron energies of the symmetric and antisymmetric combinations of magnetic orbitals. We have found an excellent correlation of observed magnetic coupling parameters and the magnitude of $(\epsilon_1 - \epsilon_2)^2$ within a series of copper(II) chloride compounds when closely related structures are compared.[15-17] In particular, for the sedia dimers, $|\epsilon_1 - \epsilon_2|$ values greater than 0.11 eV correspond to systems with antiferromagnetic coupling.[14,15] The calculation for the central pair of copper ions (including both the coordinated and semicoordinated chloride ions) yields $|\epsilon_1 - \epsilon_2| = 0.0921$ eV. This clearly places this interaction in the ferromagnetic regime. For the outer pair of copper(II) ions, a value of $|\epsilon_1 - \epsilon_2| = 0.050\,19$ eV is obtained. There is no exact structural analogue for comparison purposes. However, our calculations for the isolated, twisted dimers in $Ph_4AsCuCl_3$ and related compounds[8-10] give $|\epsilon_1 - \epsilon_2| \approx 0.03$ eV. Since these contain ferromagnetically coupled dimers, the theoretical calculations support the proposed ferromagnetic nature of the coupling between the terminal pairs of copper(II) ions.

Discussion

The tetrameric unit found here is distinctly different from the previously reported copper(II) halide tetranuclear species. One common class, orginally reported by Bertrand and Kelley,[22] contains $Cu_4X_6OL_4$ clusters[23] in which the central oxygen atom is surrounded tetrahedrally by four copper ions and octahedrally by six halide ions. Each L (L = amine, phosphine oxide, halide, etc.) ligand completes the trigonal-bipyramidal coordination for the copper(II) ions by bonding to an axial site. This species is a quite common product in aqueous systems, especially when neutral solutions are subject to prolonged heating, resulting in the loss of HX. These compounds are known to be catalytically active[24] in the oxidative coupling of phenols. They present a rich transmetalation chemistry, with a $Ni(NS)_2$ species, where NS is a hydrazinecarbodithioate ligand.[25] The other class of tetranuclear species is composed of planar, bibridged $Cu_4X_{10}^{2-}$ ions, e.g. in $[(CH_3)_3NH]_2Cu_4X_{10}$ salts ($X = Cl^-, Br^-$).[26,27] These may be viewed as sections of the infinite chains present in $CuCl_2$.[28] These are one representative of a particular ubiquitous series of $A_2Cu_nX_{2n+2}$ or $Cu_nX_{2n}L_2$ compounds ($n = 2$–5), which is formed upon crystallization of solutions containing AX or L with excess copper(II) halides. Their structures were recently reviewed,[26] but many more compounds in this series have been discovered since that article appeared, including dimers,[29-31] trimers,[32] and tetramers.[33] The characteristic feature of these compounds is the stacking of the oligomers through the formation of semicoordinate Cu–X bonds between oligomers, yielding a 4 + 1 or 4 + 2 coordination geometry for the copper(II) ion.

The compound also presents a new structural type for $ACuCl_3$ salts, again demonstrating the peril of attempting to summarize the structural behavior of copper(II) halide species. Their coordination geometry is a balance of two competing processes[7]—crystal field stabilization, which favors a square-planar coordination (with possibly one or two additional semicoordinate bonds), and electrostatic repulsions between halide ions, which favor a geometry approaching tetrahedral. (The trigonal-bipyramidal geometry for copper(II) halides appears to be restricted to the $Cu_4OX_6L_4$ systems, where the geometry of the tetranuclear species forces that copper ion to assume that special geometry.) Thus, crystalline effects that are able to reduce electrostatic repulsions between the halide ions will cause the copper coordination sphere to move towards planarity. These so-called charge compensation effects include electrostatic interaction of the halides with small cations, hydrogen bonding of organic cations or other species to the halide ions, and formation of copper–halide–copper bridges. With the tetraethylammonium counterion utilized here, and other large anions, only the last mechanism can be operative. In Ph_4A^+ salts (A = P, As, Sb), isolated bibridged $Cu_2Cl_6^{2-}$ dimers are found.[8-10] Two of the chloride ions form symmetrical bridges, linking the two copper ions. No charge compensation is present for the other chloride ions, and therefore, the copper coordination sphere distorts toward a tetrahedral geometry, with a dihedral angle between the bridging Cu_2Cl_2 plane and the terminal $CuCl_2$ plane of ~48°. An even larger distortion occurs in $Cu\{(C_6H_5)_2POCH_2PO(C_6H_5)_2\}_3Cu_2Cl_6$.[31] In the Et_4N^+ salt described in this paper, three of the four chlorides bonded to Cu(1) are involved in symmetrical bridges. Thus, the distortion toward tetrahedral is smaller, allowing a fifth chloride ion to form a semicoordinate bond with Cu(1). For Cu(2), one chloride is involved in a symmetric bridge and one in an asymmetric bridge. With the electrostatic charge of the other two chloride ions uncompensated, the distortion toward tetrahedral is quite pronounced. Consequently, the formation of a larger oligomer, with more extensive bridging, is able to reduce the electrostatic repulsions at the central copper ions and lead to a more planar coordination geometry. The versatility of Cu(II) in adapting to its environment is again demonstrated by the existence of the two distinctly different coordination geometries in the same system. Finally, the mixed symmetric–asymmetric bibridging arrangement between the two types of copper ions is unique in copper halide crystal chemistry.

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Supplementary Material Available: Anisotropic non-hydrogen atom thermal parameters (Table IV) and hydrogen atom positional and thermal parameters (Table V) and a stereoview of the title compound (3 pages); observed and calculated structure factors (Table VI) (12 pages). Ordering information is given on any current masthead page.

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