an axial methyl group would interact sterically with the pseudocoordinated solvent molecules. (ii) The second is by H bonding with the amino group H atoms. As illustrated in Figure 7, an equatorial methyl group would hinder close approach of a solvent molecule to the adjacent equatorial hydrogen on N. An axial methyl group would cause much less hindrance to such solvent approach. Thus, in a strongly H-bonding solvent, the equatorial conformer would be less favored than in a more weakly H-bonding solvent.

The solvents which would probably pseudocoordinate strongly to Pt(II) (DMSO, water, and acetonitrile) are also those which might be expected to be strongly H bonded to the diamine amino groups. The fact that the coupling is smaller (and thus the preference for the equatorial conformer) is less in these solvents suggests that (ii) is more important than (i) in influencing the conformational equilibrium (very strong pseudocoordination by the solvent could affect the coupling constant directly by altering the electron density in the Pt–N bonds, but no such effect has been observed for complexes of other diamines).

Conclusions

Results reported in this paper indicate that

$^3J_{Pt-N-C-H}$ decreases on oxidation from Pt(II) to Pt(IV) by a fairly constant factor and decreases with increasing trans influence of ligands trans to the chelate ring. When these factors are constant, a Karplus type angular dependence law is followed. Coupling constants in pmr spectra of (±)dptn complexes support assignment of chair conformation to Pt(II) complexes and skew-boat to Pt(IV) complexes.

A correlation between the conformational behavior and the four-bond platinum–methyl coupling constants in complexes containing the grouping Pt–NH₂–CH–CH₃ supports the hypothesis that, after allowing for effects of oxidation state and trans influence, the coupling constant increases with increasing preference for the conformation with the methyl group equatorial. Variation of $^4J_{Pt-N-C-CH_3}$ for [Pt(bdn)(NH₃)₂](ClO₄)₂ with different solvents reflects a solvent effect on the conformational equilibrium of the chelate ring.

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Spin–Spin Coupling in the Tetramethylammonium Salt of μ₄-Oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)), [(CH₃)₄N]₄[Cu₄OCl₁₀]

By JAMES A. BARNES, GUY W. INMAN, JR., AND WILLIAM E. HATFIELD*

The magnetic susceptibility of a powdered sample of the tetramethylammonium salt of μ₄-oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)) was measured in the temperature range 4.2–295°K. The cryomagnetic data exhibit a maximum in the magnetic susceptibility near 29°K and may be described by the Van Vleck equation for a tetrahedral arrangement of copper(II) ions with $J = -16$ cm⁻¹. A comparison of the magnetic properties of [(CH₃)₄N]₄[Cu₄OCl₁₀] and the reported data for the structurally similar Cu₄OCl₆(TPPO)₄ (TPPO = triphenylphosphine oxide) is given.

Introduction

X-Ray crystal structure studies have shown μ₄-oxo-hexa-μ-chloro-tetrakis[(triphenylphosphine oxide)copper(II)],[1] Cu₄OCl₆(TPPO)₄, and the tetramethylammonium salt of μ₄-oxo-hexa-μ-chloro-tetrakis(chlorocuprate(II)),[2] [(CH₃)₄N]₄[Cu₄OCl₁₀], to have very similar structures. In both complexes, there is a tetrahedral arrangement of copper ions bonded to the single central oxygen atom. Each of the six edges of the Cu₄ tetrahedron is occupied by a bridging chloride ion so that each copper ion is linked to each of the other three metal ions through the central oxygen and through three separate chloride bridges. The fifth coordination position of each copper ion, located on the central oxygen–copper axis on the outside of the cluster, is occupied by the oxygen of a TPPO group in the first complex and by a chloride ligand in the second, as is shown in Figure 1. Though there are minor dif-

ferences in the two structures, both Cu₄O units have nearly T_d symmetry and the octahedra of six bridging chlorides have exact or almost exact O_h symmetry. Bond distances and angles are very similar; Cu–Cu distances are 3.11 and 3.18 Å, respectively; Cu–central oxygen distances range from 1.91 to 1.95 Å; Cu–bridging chloride distances are 2.38–2.45 Å; typical bond angles are Cu–O–Cu = 109°, O–Cu–Cl = 85°, and Cu–Cl–Cu = 81°.

Although it had been suggested[1,2] on the basis of room-temperature magnetic susceptibility measurements that no spin interaction existed between the copper ions in either system, more recent studies reported by Martin[3] have demonstrated the presence of very complex interactions in Cu₄OCl₆(TPPO)₄. The effective magnetic moment of the compound rises from 1.87 BM at 295°K to 2.12 BM at 54°K and then drops

(1) J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).
(2) J. A. Bertrand and J. A. Kelley, *ibid.*, **8**, 1982 (1969).
(3) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, unpublished results, reported by R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968, p 228.

sharply to 0.76 BM at 1.5°K. "Independent ferromagnetic and antiferromagnetic couplings appear to be competing in this molecule with. . . the antiferromagnetic coupling at lower temperatures dominating the ferromagnetic interaction, which appears to be larger at higher temperatures."[3]

In an attempt to understand more fully the magnetic interactions present in these clusters, we have measured the magnetic susceptibility of $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ as a function of temperature between 4.2 and 295°K. Herein we report the results of these measurements and discuss possible coupling mechanisms in these two complexes in relation to data available from other systems.

Experimental Section

$[(CH_3)_4N]_4[Cu_4OCl_{10}]$ was prepared using a slight modification of the previously reported technique.[2] A sample of $CuCl_2 \cdot 2H_2O$ was dehydrated by mild heating on a hot plate to give brown, powdery $CuCl_2$. A portion of the anhydrous salt (0.03 mol, 4.03 g) was dissolved in 225 ml of methanol to which was added an excess (0.015 mol, 1.2 g) of CuO. The mixture was refluxed for 24 hr. The solution was filtered to remove the excess CuO and then was reheated to boiling. Slightly less than a stoichiometric amount (0.038 mol, 4.15 g) of $[(CH_3)_4N]Cl$ was dissolved in the hot solution. After 48 hr, a crop of red, crystalline product was collected, washed with methanol, dried under nitrogen, and stored over P_2O_5 under vacuum (yield 0.44 g). *Anal.* Calcd: C, 20.86; H, 5.25; N, 6.08; Cl, 38.48. Found: C, 20.96; H, 5.22; N, 6.12; Cl, 38.78. The use of nonstoichiometric reactants was necessary to prevent a yellow-green impurity, probably $[(CH_3)_4N]_2CuCl_4$, from precipitating with the desired product.

Magnetic susceptibility measurements were made using a Faraday balance[4] for temperatures above 77°K and a Foner-type vibrating sample magnetometer[5] manufactured by Princeton Applied Research Corp. for the temperature range 4.2–59.1°K. Magnetometer measurements were made using a magnetic field strength of 10,000 G. Data were corrected for the magnetism of the sample holder assembly, for diamagnetism using Pascal's constants[6] (138×10^{-6} cgsu/g-atom of copper), and for TIP (60×10^{-6} cgsu/g-atom of copper). In the reported data, χ_M is calculated per gram-atom of copper, and $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Results

The data obtained from our measurements on $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ are shown in Tables I and II

TABLE I
MAGNETIC DATA FOR $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ MEASURED USING THE FARADAY BALANCE

Temp, °K	χ_M^{cor}, cgsu/g-atom of Cu	$1/\chi_M^{cor}$, g-atom of Cu/cgsu	μ, BM
295	0.001199	834	1.68
196	0.001596	627	1.58
77	0.002850	351	1.32

and Figure 2. The data clearly indicate the presence of an antiferromagnetic type of interaction with a Néel temperature of about 29°K. The effect of this coupling on the susceptibility can be expressed theoretically by eq 1, where χ_M is the susceptibility *per mole of tetramer.*

$$\chi_M = (N\beta^2 g^2/kT)[6 \exp(-4J/kT) + 10]/[2 \exp(-6J/kT) + 9 \exp(-4J/kT) + 5] \quad (1)$$

Susceptibilities calculated using (1) will be four times

(4) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

(5) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

(6) B. N. Figgis and J. Lewis in "Technique of Inorganic Chemistry," Vol. IV, H. B. Jonassen and A. Weissberger, Ed., Interscience, New York, N. Y., 1965, p 142.

TABLE II
MAGNETIC DATA FOR $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ MEASURED WITH THE VIBRATING SAMPLE MAGNETOMETER

Temp, °K	$10^6\chi_M^{cor}$, cgsu	Magnetic moment, BM	Temp, °K	$10^6\chi_M^{cor}$, cgsu	Magnetic moment, BM
59.1	3,274[a]	1.24	15.4	3,863	0.69
45.6	3,939	1.20	13.9	3,739	0.64
35.5	4,219	1.09	11.5	3,570	0.57
33.1	4,287	1.06	10.9	3,400	0.54
29.4	4,370	1.01	9.6	3,390	0.47
23.8	4,341	0.91	6	3,310	0.40
19.1	4,076	0.79	4.2	3,320	0.33
17.8	4,048	0.76			

[a] The magnetic susceptibilities are reported per copper ion *not* per mole of tetramer.

as large as the values for χ_M per mole of copper that are reported in Tables I and II. The use of a single coupling constant in this expression is justified by the structural symmetry of the $Cu_4OCl_{10}^{4-}$ unit.

The magnetic data below about 10°K do not conform to that expected for a system with a singlet ground state. The anomalous behavior may be explained by the presence of a small amount of paramagnetic impurity in our sample. This possibility is quite likely in light of the preparative problems with coprecipitation. Because of this impurity problem the low-temperature data were omitted from calculations to fit the experimental data to eq 1. The best parameters, which were obtained using a standard least-squares fitting program, were $J = -16 \pm 1$ cm^{-1} and $\langle g \rangle \simeq 2.0$.

This value of J obtained from the fitting process is the same as the value obtained from the Néel temperature using the relationship $J = -0.555T_N$ cm^{-1}/deg.[6,7]
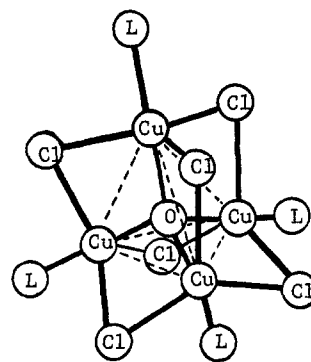

Figure 1.—The structure of $Cu_4OCl_6L_4^{n-}$.

The agreement of these two values of J is interesting because the Néel temperature relationship is usually discussed in terms of dimetallic copper complexes.

Discussion

It is very difficult to relate the magnetic susceptibility data above 60°K for the present system to those reported[3] for $Cu_4OCl_6(TPPO)_4$. While our high-temperature data for $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ are restricted to three points, there is no evidence of an increase in the magnetic moment of this complex as the temperature is lowered. Assuming that no experimental error has been made, it is likely that the differences in the magnetic behavior result from differences in the effects of ligand L (Figure 1) on the spin–spin coupling through

(7) J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Phys. Lett.*, **7**, 374 (1970).
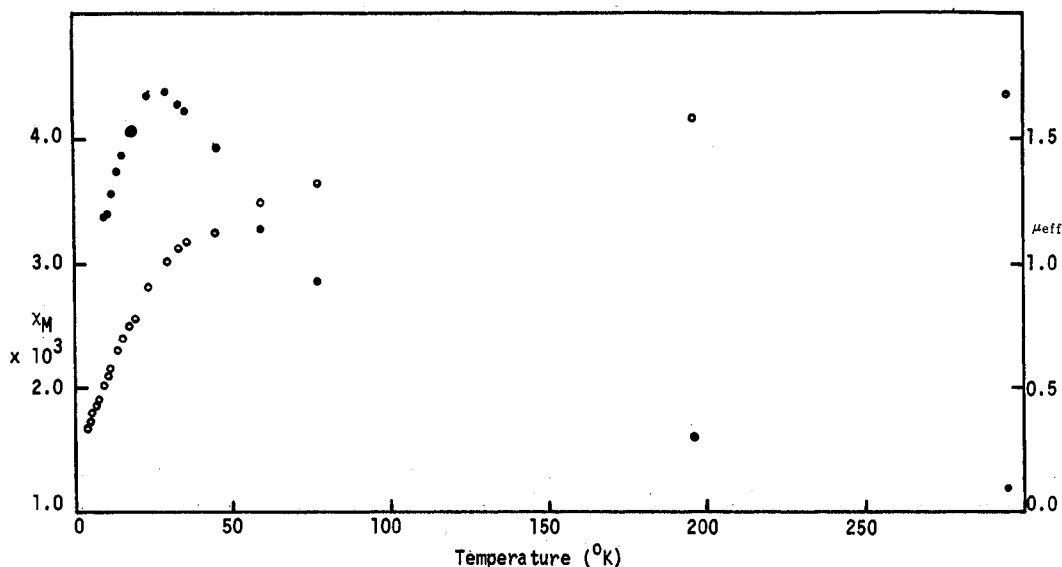
Figure 2.—The magnetic data of $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ shown as a function of temperature: ●, χ_M^{cor}; O, μ_{eff}.

the Cu–O–Cu bridges. Ferromagnetic coupling has been identified in other systems containing Cu–O–Cu bridges similar to those in the $Cu_4OCl_{10}^{4-}$ unit,[8] but similar Cu–Cl–Cu bridged complexes have exhibited antiferromagnetic interactions.[7] Thus it is more likely that the oxygen bridges are involved in any ferromagnetic coupling present in $Cu_4OCl_6L_4$. It is difficult to evaluate the effect of replacing TPPO with Cl^- on the spin–spin coupling through the oxygen bridges, but the effect of this coupling per copper pair is expected to be relatively small because the complex contains only a single bridging oxygen.

It has been suggested[9] that the relative magnitudes of the coupling constants of similar multimetallic compounds may be compared in terms of the number of bridging units between pairs of metal ions with little concern for structural details. Although, strictly speaking, there is only one chloride bridge per pair of copper ions, there are three such links. While there are limitations, this approach does seem to be a workable approximation and may be used to compare the J value of the present system with that of the $Cu_2Cl_8^{4-}$ anion in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$.[7,10] The structural details of the two systems are quite similar; in each case the copper ions are in a trigonal-bipyramidal environment with Cu–Cl–Cu bridges to neighboring metals. The chloride bridges both involve approximately right angles (81° in $Cu_4OCl_{10}^{4-}$, 95° in $Cu_2Cl_8^{2-}$) with similar bond lengths, although the dimer does

contain one Cu–Cl bond considerably shorter than the other (2.3 and 2.7 Å) while the Cu–Cl bonds in the tetramer are more constant ($\sim$2.4 Å). The units do differ in that the bridging chloride is axial to one copper and equatorial to the other in the dimer but is equatorial to both metals in the tetramer.

In the present approximation, we will disregard these similarities and differences and the presence of fractional Cu–O–Cu bridges in the tetramer and will consider only the number of Cu–Cl–Cu bridges. In the tetramer, each copper ion is linked to another by three chloride bridges; while in the dimer there are only two links per copper. Thus the J value of the dimer is expected to be two-thirds that of the tetramer or ~ -10.6 cm^{-1}. Since one of the bonds of the dimer bridge is longer than those of the tetramer, coupling would be expected to be less in the dimer than predicted from the tetramer. Thus one might expect J for the dimer to be < -10.6 cm^{-1}; the experimental value[7] is ~ -8.6 cm^{-1}. Other systems are under study to determine the limits of this method of approximation.

The general mechanisms of spin–spin coupling in the $Cu_4OCl_{10}^{4-}$ anion are those found in any 90° cation–anion–cation system and have been fully reviewed elsewhere.[7,11]

(8) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, Jr., *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

(9) J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1456 (1969).

(10) D. J. Hodgson, P. K. Hale, J. A. Barnes, and W. E. Hatfield, *Chem. Commun.*, 786 (1970).

(11) J. A. Barnes and W. E. Hatfield, to be submitted for publication.