All non-hydrogen atoms in **2** and **3** were refined anistropically. Only Hg and S atoms in **1** were refined anisotropically. The phenyl groups in **3** were refined as rigid bodies with fixed C–C distance of 1.395 Å and C–C–C angle of 120°. The positions of hydrogen atoms on the methyl group in **1** and on the phenyl group in **3** were calculated by using fixed C–H bond length, 0.96 Å. Their contributions were included in the structure factor calculations. The largest peaks, 1.68 and 0.98 e/Å³ in the final difference Fourier maps of **1** and **2**, are at 1.23 and 1.18 Å from the Hg atom, respectively. The largest peak in the final difference Fourier map of **3**, 2.4 e/Å³ is at 1.02 Å from the Hg atom. The data

for crystallographic analyses are given in Table I.

Supplementary Material Available: Tables S1–S6, listing crystallographic data, H atom parameters, and anisotropic temperature factors for **1–3** (4 pages); Tables S7 and S8, listing observed and calculated structure factors for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of Bis[(2,6-diacetylpyridine dioxime)chlorocopper(II)] Tetrachlorocuprate

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The synthesis, structure, and low-temperature magnetic susceptibility of a novel trinuclear copper(II) compound are described. The complex is a sandwich made of two Cu(DAPDH₂)Cl⁺ cations (the bread) and a CuCl₄²⁻ anion (the filling) where DAPDH₂ is the ligand 2,6-diacetylpyridine dioxime. The two Cu(DAPDH₂)Cl⁺ ions, related by a crystallographic C_2 axis passing through the Cu atom of the connecting CuCl₄²⁻ ion, are essentially parallel to each other. The Cu atom in Cu(DAPDH₂)Cl⁺ is bonded to the three nitrogen atoms of DAPDH₂ and to Cl⁻ to give a nearly planar local CuN₃Cl polyhedron. There are four distinct Cu–Cl distances in the compound: 2.193 Å in the Cu(DAPDH₂)Cl⁺ groups, 2.220 and 2.270 Å in the CuCl₄²⁻ ion, and 2.604 Å between Cu of Cu(DAPDH₂)Cl⁺ and the bridging chlorine. The compound crystallizes in orthorhombic group *Pccn*, with $a = 10.463$ (2) Å, $b = 12.514$ (12) Å, $c = 20.275$ (3) Å, $V = 2654$ (3) Å³, and $Z = 4$. The three Cu(II) centers are ferromagnetically coupled ($J = 3.0$ K).

Introduction

Many studies of electron spin interactions in magnetically concentrated compounds have focused on copper(II). The principal reasons for this are (1) the electronic configuration of the copper(II) ion, d⁹, effectively quenches the orbital contribution to the magnetic moment of the ion, thus allowing one to treat electron spin interactions as spin-only interactions; (2) the stereochemistry of copper complexes is extremely diverse; and (3) Cu(II) readily forms a rich variety of dimers and oligomers.

In magnetic studies of complex compounds, a heavy accent has been put on compounds with antiferromagnetically coupled metal atoms. The most thoroughly studied copper complexes are dimeric. Of them, "less than 5% ... are reported as ferromagnetically coupled and in some cases the result may be questioned".[1] A large number of magnetic studies on trimeric copper compounds have also been reported.[2] To the best of our knowledge, in all of them the copper ions are antiferromagnetically coupled. We report here on the structure, low-temperature magnetic susceptibility, and ESR spectrum of a novel trimeric copper complex in which the copper ions are ferromagnetically coupled. The trimer consists of a CuCl₄²⁻ anion sandwiched between two CuLCl⁺ cations, where L is the ligand 2,6-diacetylpyridine dioxime, hereafter DAPDH₂ (Figure 1).

Experimental Section

Preparations. Unless otherwise noted all chemical used were of reagent grade quality and were used as commercially obtained.

2,6-Diacetylpyridine Dioxime (DAPDH₂). This ligand was synthesized in the manner described by Vasilevsky et al.[3]

Bis[(2,6-diacetylpyridine dioxime)chlorocopper(II)] Tetrachlorocuprate ([Cu(DAPDH₂)Cl]₂CuCl₄). Method 1. Crystals suitable for X-ray and magnetic measurements were obtained by diffusion. To a mixture of 2,6-diacetylpyridine dioxime (0.39 g, 2.0 mmol) and tetraethylammonium chloride (1.9 g, 12.0 mmol) in 30 mL of acetonitrile was added tri-

fluoroacetic acid dropwise until all the ligand dissolved. The solution was poured in a 30-mL beaker and several milliliters of acetonitrile was added so that the beaker was full. It was then placed in an 80-mL beaker. Solid cupric chloride dihydrate (1.02 g, 6.0 mmol) was placed in the annulus in the bottom of the 80-mL beaker, and acetonitrile was then slowly and carefully added to the 80-mL beaker until the lip of the smaller beaker was covered with approximately 0.5 cm of solvent. At this point, the mouth of the 80-mL beaker was covered with Parafilm, and the nested beakers were allowed to sit at room temperature. Over the course of several days dark green, long, prismatic crystals formed. The crystals were collected by filtration, washed with acetonitrile, and air dried. Yield: 0.695 g (88%). Anal. Calcd for C₁₈H₂₂N₆O₄Cl₆Cu₃: C, 27.39; H, 2.81; N, 10.65; Cl, 26.95; Cu, 24.15. Found: C, 27.46; H, 2.84; N, 10.47; Cl, 26.55; Cu, 24.4. Principal IR absorptions in a Nujol mull: 690 m, 740 w, 815 s, 835 m, 1058 vs. 1143 s, 1267 s, 1300 s, 1325 sh, 1585 s, 3350 s, br cm⁻¹.

Method 2. Trifluoroacetic acid was added dropwise to a suspension of DAPDH₂ (0.19 g, 1.0 mmol) in 20 mL of absolute methanol until the ligand dissolved. To this solution was then added a solution of CuCl₂·2H₂O (0.34 g, 3.0 mmol) and LiCl (0.15 g, 6.0 mmol). The walls of the beaker were scratched with a glass rod. Several hours later a green crystalline precipitate was filtered off, washed with several milliliters of absolute methanol, and air-dried. Yield: 90 mg. Slow evaporation of

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(3) Vasilevsky, I.; Stenkamp, R. E.; Lingafelter, E. C.; Rose, N. J. *J. Coord. Chem.* **1988**, 19, 171.

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‡ Department of Biological Structure, University of Washington.
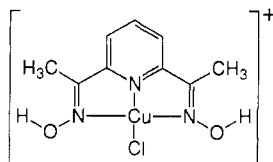§ Washington State University.

Figure 1. Schematic representation of the $Cu(DAPDH_2)Cl^+$ cation.

the remaining solution in air to a small volume yielded an additional 150 mg of the complex. Total yield: 0.24 g (61%). Anal. Found: C, 27.29; H, 2.81; N, 10.44; Cl, 26.76; Cu, 25.1. X-ray photos of a single crystal gave the same cell parameters as for crystals from the first method.

Structure Determination. Data Collection. A green prismatic crystal of bis[(2,6-diacetylpyridine dioxime)chlorocopper(II)] tetrachlorocuprate having approximate dimensions of $0.10 \times 0.55 \times 0.11$ mm was mounted on a glass fiber roughly along b. Preliminary photographic examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal–incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement, using the setting angles of 22 reflections in the range $5 < \theta < 10°$, measured by the computer-controlled diagonal-slit method of centering. The orthorhombic cell parameters and calculated volume are $a = 10.4630$ (17) Å, $b = 12.514$ (12) Å, $c = 20.275$ (4) Å, and $V = 2654$ (3) Å^3. With $Z = 4$ and a formula weight of 789.77, the calculated density is 1.98 g/cm^3. The systematic absences ($h0l, l$ odd; $0kl, l$ odd; $hk0, h + k$ odd) unambiguously determined the space group as *Pccn*. The data were collected at a temperature of 23 ± 2 °C by using ω–2θ scans. The scan rate was fixed at 2.1 deg/min (in ω). Data were collected in the $+h,+k,+l$ octant to a maximum θ of 25°. The scan range increased as a function of θ to allow for the separation of the $K\alpha$ doublet;[4] the scan range was calculated as $\Delta\omega = 0.45 + 0.344 \tan \theta$. Moving-crystal–moving-counter background counts were made by scanning an additional 25% above and below this range, yielding a ratio of peak counting time to background counting time of 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.2 mm, and the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.8 mm, and the crystal-to-detector distance was 21 cm. For intense reflections, an attenuator was automatically inserted in front of the detector; the attenuator factor was 20.9.

Data Reduction. A total of 2683 independent reflections were measured. Lorentz and polarization factors were applied. The linear absorption coefficient is 31.2 cm^{-1} for Mo $K\alpha$ radiation. An absorption correction was not applied since a set of ψ scans showed no significant changes in intensity. The crystal was stable during the data collection, and no linear decay was observed. After removal of systematic absences, 2336 reflections were left.

Structure Solution and Refinement. In the beginning, the structure was thought to have one Cu atom per molecule, and only the Cu atom of the complex cation was located by interpretation of the Patterson function. The second Cu atom and the remaining atoms were located in succeeding Fourier maps. Hydrogen atom positions on the pyridine ring and methyl carbons were calculated, and hydrogen atoms on oxime oxygens were found in a difference Fourier map. All hydrogen atoms were added to the structure factor calculations, and their positions and isotropic thermal parameters were not refined. The structure was refined by full-matrix least-squares techniques to minimize $\sum w(|F_o| - |F_c|)^2$ and with $w = 4F_o^2/\sigma^2(F^2)$. The standard deviation, σ_{F^2}, was defined by $\sigma_{F^2} = [S(C + R^2B) + (qF_o^2)^2]^{1/2}/(Lp)$, where S is the scan rate, C is the total integrated peak count, $R = 2$ is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor, and the parameter $q = 0.03$ is a factor introduced to downweight intense reflections. Scattering factors were taken from Cromer and Mann[5] for non-hydrogen atoms and from Stewart et al.[6] for hydrogen. Anomalous dispersion effects were included;[7] the values for f' and f'' were those of Cromer.[8] In the final cycles of refinement, only the 1981 reflections of intensity greater than 2σ were used, and 13 reflections with abnormally large residuals were deleted. The last cycle of refinement, with 168 parameters, converged (largest parameter shift 0.02σ) to $R =$

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(8) Cromer, D. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table I. Crystallographic Data for $[Cu(DAPDH_2)Cl]_2CuCl_4$

chem formula:	space group: orthorhombic, *Pccn* (No. 56)
$Cu_3Cl_6O_4N_6C_{18}H_{22}$	$T = 23$ (2) °C
fw = 789.77	$\lambda = 0.7107$ Å (Mo $K\alpha$)
$a = 10.463$ (2) Å	$\rho_{calcd} = 1.98$ g/cm^3
$b = 12.514$ (12) Å	$\mu = 31.2$ cm^{-1}
$c = 20.275$ (3) Å	$R = 0.054$
$V = 2654$ (3) Å^3	$R_w = 0.069$
$Z = 4$	

Table II. Positional Parameters, Estimated Standard Deviations, and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Cu(DAPDH_2)Cl]_2CuCl_4$

atom	x	y	z	U, Å^2
Cu(1)	0.29057 (8)	0.08534 (7)	0.40420 (4)	0.0283
Cu(2)	0.250000	−0.250000	0.33744 (6)	0.0270
Cl(1)	0.49762 (17)	0.10822 (18)	0.41356 (13)	0.0458
Cl(2)	0.30685 (20)	−0.12162 (14)	0.41097 (10)	0.0374
Cl(3)	0.14195 (18)	−0.14973 (16)	0.26646 (11)	0.0393
N(1)	0.2645 (6)	0.1064 (5)	0.3054 (3)	0.0317
N(2)	0.1091 (5)	0.1114 (4)	0.3982 (3)	0.0259
N(3)	0.2420 (7)	0.1030 (5)	0.5013 (3)	0.0323
O(1)	0.3568 (6)	0.1065 (6)	0.2567 (3)	0.0511
O(2)	0.3222 (7)	0.1031 (6)	0.5541 (3)	0.0518
C(1)	0.1123 (9)	0.1176 (8)	0.2141 (4)	0.0435
C(2)	0.1490 (8)	0.1109 (6)	0.2851 (4)	0.0324
C(3)	0.0560 (7)	0.1135 (5)	0.3391 (4)	0.0285
C(4)	−0.0768 (7)	0.1233 (6)	0.3330 (4)	0.0348
C(5)	−0.1460 (7)	0.1318 (6)	0.3898 (5)	0.0376
C(6)	−0.0916 (8)	0.1352 (7)	0.4506 (5)	0.0408
C(7)	0.0421 (7)	0.1215 (6)	0.4537 (4)	0.0306
C(8)	0.1223 (7)	0.1226 (6)	0.5132 (4)	0.0305
C(9)	0.0680 (9)	0.1458 (8)	0.5805 (4)	0.0457

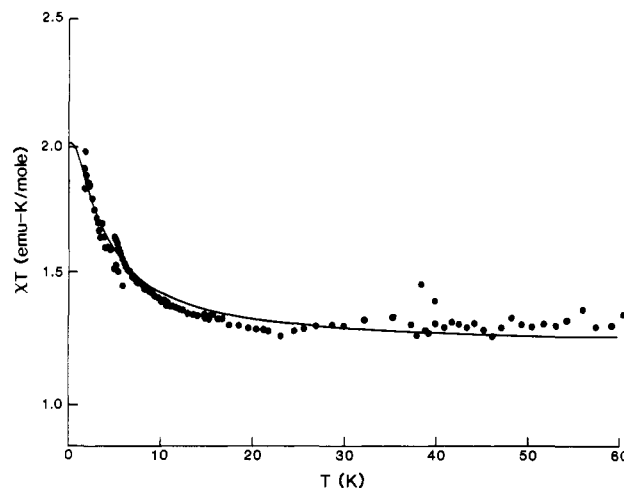**Figure 2.** Experimental (circles) and theoretical (solid line) dependence of χT vs T for $[Cu(DAPDH_2)Cl]_2CuCl_4$.

$\sum ||F_o| - |F_c||/\sum |F_o| = 0.054$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.069$, and goodness-of-fit $(\sum w(|F_o| - |F_c|)^2/(n - p))^{1/2} = 1.94$. The highest peak (1.2 e/Å^3) in the final difference Fourier map is Cu(2). All calculations were performed on a VAX/780 computer using XRAY76,[9] except for placing the hydrogen atoms, for which purpose the program CALCAT was used.[10] The results of the crystallographic experiment are summarized in Table I.

Magnetic Measurements. Magnetic data were measured at Montana State University with a PAR vibrating sample magnetometer on a 0.108-g powdered sample in a field of 2000 Oe over the temperature range 1.76–79 K. The results are presented as a plot of $\chi_M T$ vs T in Figure 2. EPR data of a single crystal were measured at Washington State University on a Varian E3 spectrometer operated at 9.488 GHz. A single broad line was observed in all orientations with no indication of hyperfine or zero-field splittings. Resonance fields yielded $g_a = 2.154$,

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Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) in [Cu(DAPDH₂)Cl]₂CuCl₄[a]

N(3)–Cu(1)	2.044 (6)	N(2)–Cu(1)	1.930 (6)
N(1)–Cu(1)	2.040 (7)	Cl(1)–Cu(1)	2.1931 (20)
Cl(2)–Cu(1)	2.6042 (12)	Cl(2)–Cu(2)	2.2730 (20)
Cl(3)–Cu(2)	2.2201 (21)	Cl(1)–Cl(3)	3.983 (2)
C(6)–Cl(1)	3.445 (9)		
N(2)–Cu(1)–Cl(2)	103.66 (17)	N(1)–Cu(1)–Cl(2)	100.93 (19)
Cl(1)–Cu(1)–N(1)	105.54 (20)	Cl(1)–Cu(1)–Cl(2)	93.51 (8)
N(1)–Cu(1)–N(3)	153.94 (27)	N(1)–Cu(1)–N(2)	77.58 (26)
N(2)–Cu(1)–Cl(1)	162.70 (18)	Cl(1)–Cu(1)–N(3)	98.52 (21)
N(2)–Cu(1)–N(3)	78.32 (27)	Cl(2)–Cu(1)–N(3)	94.23 (19)
Cl(2)–Cu(2)–Cl(2′)	98.04 (24)	Cl(3)–Cu(2)–Cl(3′)	99.20 (16)
Cl(2′)–Cu(2)–Cl(3′)	99.05 (25)	Cl(2)–Cu(2)–Cl(3′)	133.85 (11)
Cu(2)–Cl(2)–Cu(1)	130.84 (9)	Cu(1)–N(1)–C(2)	116.6 (5)
Cu(1)–N(1)–O(1)	127.5 (5)		

[a] A prime denotes atoms related by the symmetry operation $-x + \frac{1}{2}, -y - \frac{1}{2}, z$.
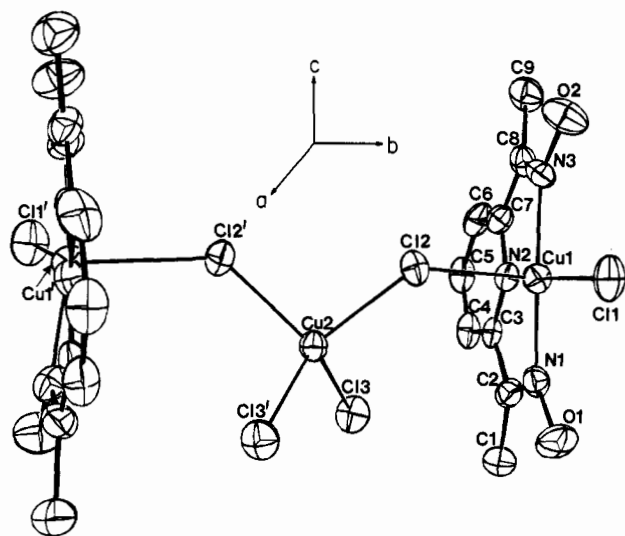
**Figure 3.** ORTEP view of the [Cu(DAPDH₂)Cl]₂CuCl₄ trimer showing 50% probability thermal ellipsoids.

g_b = 2.175, g_c = 2.041. Line widths varied from 130 (**H** ‖ c) to 280 (**H** ‖ a) Oe.

Results and Discussion

Structure Discussion. The results of the structure determination are summarized in Tables II (positional parameters) and III (selected bond distances and angles) and Figures 3 and 4. The structure consists of two Cu(DAPDH₂)Cl⁺ cations bridged by Cl(2), Cu(2), and Cl(2′) of the CuCl₄²⁻ ion (Figure 3), which is highly distorted, with Cl(2)–Cu(2)–Cl(3′) = 133.9° and Cl(2)–Cu(2)–Cl(3) = 99°. A useful comparison is a CuCl₄²⁻ anion with a configuration midway between square planar and tetrahedral, where the corresponding angles are 145° and 99.5°. The bridging angle, Cu(1)–Cl(2)–Cu(2), is 130.8° in the trimer.

At 2.193 (2) Å the Cu(1)–Cl(1) distance in the cation is the shortest copper–chlorine distance in the trimer. It is comparable with 2.211 (4) Å for the Cu–Cl bond in [Cu(Hsbh)Cl], which is also pseudo square planar (Hsbh⁻ is salicylaldehyde benzoylhydrazonate, a tridentate ligand).[11] The Cu(1)–Cl(2) bond (2.604 (1) Å), which is the longest copper–chlorine distance in the trimer, is reasonable for semicoordination where a rather wide range of bond distances is known.[12] The other bridging bond (Cu(2)–Cl(2) = 2.273 (2) Å) is longer than the terminal bond (Cu(2)–Cl(3) = 2.220 (2) Å).

The pyridine ring of the DAPDH₂ ligand is essentially planar. The maximum deviation from the plane defined by all six atoms of the ring is 0.023 Å for C(6). The deviations from the Cu-
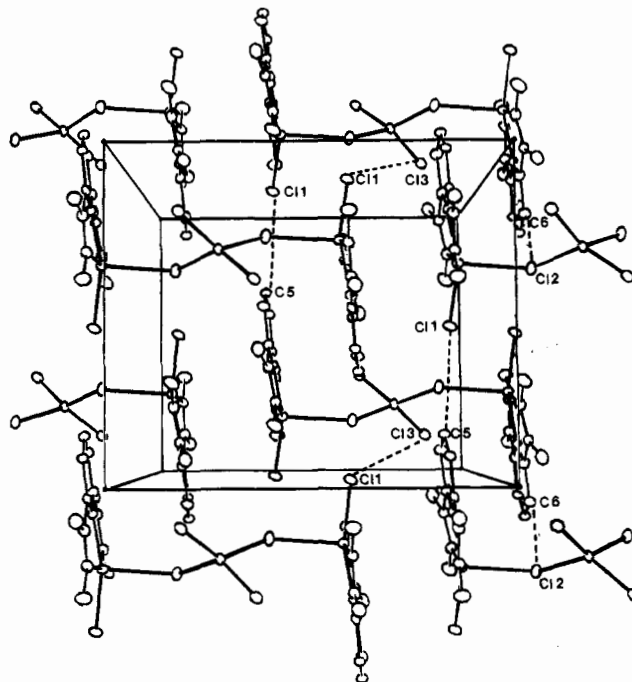
Figure 4. Crystal packing of the trimer molecules showing some important intertrimer interactions.

(1)–N(1)–N(2)–N(3)–Cl(1) plane are +0.23 Å (Cu(1), toward Cl(2)), –0.09 Å (Cl(1) and N(2)), and –0.02 Å (N(1) and N(2)). Altogether, the cation is reminiscent of a shallow bowl with its bottom oriented toward the bridge. The Cu(1)–Cl(2) bond is nearly perpendicular to the plane of the cation and almost parallel to the b axis of the unit cell. Rotation about the C_2 axis passing through Cu(2) results in a configuration in which the planes of the two cations are almost parallel (Figures 3 and 4).

The packing of the trimer molecules is shown in Figure 4. The most interesting features are the weak interactions H(6)–Cl(2) (at 2.634 (2) Å) and Cl(1)–H(5) (at 2.808 (2) Å). Both are short compared to 3.0 Å, the sum of the van der Waals radii of chlorine and hydrogen.[13] These "apparently attractive" interactions are most likely a factor in the parallel packing of the trimers. A rather short contact distance between Cl(1) and Cl(3) (3.983 (2) Å) may also be important in intertrimer magnetic exchange (vide infra). Finally C(6), the carbon atom with the largest deviation from the plane within the pyridine group is also only 3.445 (9) Å from Cl(1) of an adjacent molecule.

This structure provides only the second example of an isolated trimeric copper(II) complex bridged primarily by halide ions. A Cu₃Cl₁₄⁸⁻ ion exists in (N-(2-aminoethyl)piperazinium)₄Cu₅Cl₂₂, which consists of a square planar CuCl₄²⁻ ion sandwiched between two square pyramidal CuCl₅³⁻ ions.[14] Unfortunately, the structure is complicated by the presence of two isolated CuCl₄²⁻ anions. The trimers in (adeninium)₂Cu₃Cl₈·4H₂O are linked to form infinite chains[15] whereas the planar, bibridged trimers Cu₃X₆L₂ form infinite stacks.[2a] The role of the tetrahedral copper chlorides as ligands semicoordinating to other copper(II) complexes is also relatively rare, but not unknown. The dimeric compound Cu₂-[(3,6-bis(3,5-dimethyl-1-pyrazolyl)pyridazine)(OH)Cl₂] has been shown to bind a tetrahedrally distorted CuCl₃(H₂O)⁻ anion.[16]

Magnetic Susceptibility and ESR. The magnetic susceptibility data indicate ferromagnetic coupling at low temperatures given that χT increases as T decreases (Figure 2). For an isolated symmetric trimer, one can easily obtain the following expression

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(15) de Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2400.

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for the magnetic susceptibility, assuming the absence of interaction between the two terminal Cu(1) ions:[2a]

$$\chi = \frac{N_{av}g^2\beta^2[10 + \exp(-J/kT) + \exp(-3J/kT)]}{3kT[2 + \exp(-J/kT) + \exp(-3J/kT)]}$$

The magnetic data were fit to this expression, yielding $J/k = 3.0$ (1) K with g fixed at the value of 2.08 derived from Curie–Weiss analysis of data taken at higher temperatures. While the fit to the data (solid line in Figure 2) is quite good, the existence of strong correlations between g and J in ferromagnetic systems means that the actual uncertainty in J/k is definitely somewhat larger than 0.1, probably on the order of ±0.5 K. The presence of the definite, but weak, ferromagnetic coupling is consistent with the structure of the trimer. For each of the two Cu(1) ions the unpaired electron is in a predominantly $d_{x^2-y^2}$ orbital lying in the equatorial plane (in Figure 4 the molecular z axis of the cation is parallel to the b axis of the unit cell). That orbital is a major contributor to σ-antibonding orbitals lying in the equatorial plane of the cation, and therefore, very little delocalization onto the Cu(2)Cl$_4^{2-}$ occurs through the σ-pathway. For Cu(2) it is not immediately clear where the unpaired electron is located because a crossover of the energies of the $d_{x^2-y^2}$ (b_{1g}) and d_{xy} (b_{2g}) occurs at a conformation intermediate between square planar and tetrahedral.

A thorough theoretical and experimental study of isolated CuCl$_4^{2-}$ ions for both D_{4h} and the tetrahedrally distorted square-planar configuration, D_{2d}, has been recently done by Solomon and co-workers.[17] According to the results of their Xα calculations (which are in excellent agreement with the reported experimental results) an electron in the HOMO, b_{1g} ($d_{x^2-y^2}$), of a D_{4h} CuCl$_4^{2-}$ anion is 1.5 eV above the next lower level, which is the b_{2g} (d_{xy}) orbital. They modeled D_{2d} CuCl$_4^{2-}$ with Cs$_2$CuCl$_4$ in which the smaller Cl–Cu–Cl angles are 100.7° and the larger are 129.2° and found the HOMO, b_2 (d_{xy}), is 0.5 and 0.8 eV above the next two levels which are e (d_{xz},d_{yz}) and b_1 ($d_{x^2-y^2}$), respectively. Given that the Cl–Cu–Cl angles (of CuCl$_4^{2-}$) in the trimer are 133.9 and 99°, we might surmise that the energies of electrons in its d_{xy} and $d_{x^2-y^2}$ orbitals will be closer than the 0.8 eV cited above. Clearly, however, detailed calculations are necessary to take into account the bridging chlorine atoms and the differing Cu–Cl distances.

In the absence of a detailed picture of the electronic nature of the CuCl$_4^{2-}$ ion in the trimer, it is instructive to briefly consider two alternative possible CuCl$_4^{2-}$ structures, square planar and square-planar-distorted tetrahedral. The square-planar case is illustrated in Figure 5a where the $d_{x^2-y^2}$ orbital is the HOMO of the CuCl$_4^{2-}$ ion. According to Kahn's formalism,[18] the magnetic orbitals on Cu(1) and Cu(2) are accidently orthogonal, which must lead to ferromagnetic coupling.

The distorted tetrahedron is illustrated in Figure 5b. Here the d_{xy} orbital is the HOMO for the CuCl$_4^{2-}$ ion. Now a nonzero overlap of the π-antibonding orbitals on the Cu(2) ion and the $d_{x^2-y^2}$ orbital on the Cu(1) ion is possible (dashed line in Figure 5b). This would result in an antiferromagnetic exchange pathway. The data at our disposal at this point suggest that the $d_{x^2-y^2}$ orbital is the HOMO. However, the small absolute value of J indicates that the total ferromagnetic coupling may be weakened by other orbital interactions. These interactions may involve, for instance, the π-system of the DAPDH$_2$ ligand ring and the Cl(3) atoms. The Cl(3)–C(1) distance is 3.291 (2) Å, which is smaller than

a, D$_4$h
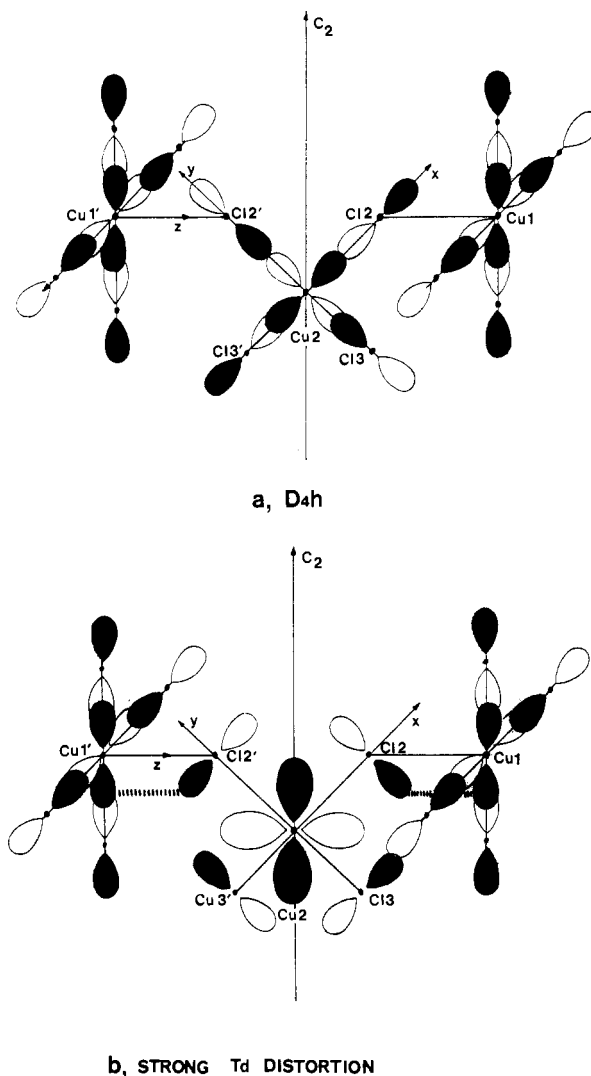

b, STRONG Td DISTORTION

Figure 5. Magnetic orbitals on Cu atoms in the trimer assuming (a) idealized D_{4h} symmetry or (b) strong tetrahedral distortion.

the sum, 3.5 Å, of the van der Waals radii of chlorine and carbon.[13]

It is interesting to note that the phenomenological correlation between the ratio of ϕ/R_0 and the value of J introduced by Hatfield,[19] where ϕ is the copper–(bridging ligand)–copper angle and R_0 is the length of the semicoordinate bond, predicts a value ~-4 cm^{-1} for the trimer. The absolute value is approximately correct, but the sign is reversed. This correlation does give a reasonable prediction for an adenine-bridged trimer.[20]

The presence of a single, structureless EPR signal indicates that some weak exchange coupling also occurs between trimers. The short intertrimer contact Cl(1)–Cl(3) is likely to be responsible for this interaction. The EPR g values are in accord with the structure of the trimer (Figure 3). The EPR **g** tensor will be, to first order, given by an average of the **g** tensors for the three individual copper atoms. For Cu(1), and its symmetry related equivalents, its pseudo-4-fold axis lies nearly parallel to the b axis. Thus, $g_b^{(1)} = g_{\parallel}^{sp}$ and $g_a^{(1)} = g_c^{(1)} = g_{\perp}^{sp}$ for a square-pyramidal conformation. For Cu(2), the pseudo-S_4 axis is approximately parallel to the a axis. Thus $g_a^{(2)} = g_{\parallel}^{dt}$ and $g_b^{(2)} = g_c^{(2)} = g_{\perp}^{dt}$ for the distorted-tetrahedral environment. With $g_{\parallel} \gg g_{\perp} > 2$, $g_{\parallel}^{dt} > g_{\parallel}^{sp}$, and $g_\alpha = \frac{1}{3}(2g_\alpha^{sp} + g_\alpha^{dt})$ for $\alpha = a, b, c$, we expect to find $g_b > g_a \gg g_c$, in accord with the observed values of $g_b = 2.175$, $g_a = 2.154$, and $g_c = 2.041$.

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Synthesis and Structural Characterization of Three New Trinuclear Group VI Clusters

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$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot3THF$ (**1**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot2MeOH$ (**2**) were prepared by reacting $Mo_3S_7Cl_4$ with the corresponding phosphine ligands at room temperature in THF. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.651$ (2) Å, $b = 20.227$ (4) Å, $c = 27.720$ (6) Å, $\beta = 96.25$ (2)°, $V = 7051$ (5) Å^3, and $Z = 4$. Compound **2** crystallizes in the monoclinic space group Pc with $a = 20.341$ (4) Å, $b = 13.307$ (3) Å, $c = 24.567$ (5) Å, $\beta = 141.08$ (2)°, $V = 4179$ (4) Å^3, and $Z = 4$. Both **1** and **2** belong to the B_1, M_3X_{13} structure family. In addition, we report the sealed-tube synthesis of $W_3S_7Br_4$ (**3**) from stoichiometric quantities of the elements. Crystallographic parameters for **3** are as follows: monoclinic space group $P2_1/c$; $a = 9.488$ (2), $b = 12.303$ (3), $c = 14.143$ (3) Å; $\beta = 121.62$ (2)°; $V = 1406$ (1) Å^3; $Z = 4$. Compound **3** is a B_2 type of trinuclear cluster and is isomorphous with $Mo_3S_7Cl_4$.

Introduction

Over the past three decades several routes to trinuclear transition-metal clusters have been discovered. The molecular clusters are typically prepared in solution by (1) reaction of a mononuclear starting material in the presence of a donating ligand and an appropriate amount (if any) of oxidizing/reducing agent[1–5] or (2) a ligand-exchange reaction that preserves the structural integrity of the M_3 core.[6–10] Several other less general methods have also been described.[11,12]

Fedorov et al. recently reported a promising new route to substituted molecular trimolybdenum chloro sulfido clusters from polymeric starting materials.[13] They prepared $Mo_3S_7X_4\cdot2PPh_3$ (X = Cl, Br) by boiling $Mo_3S_7X_4(Mo_3S_7X_4 = (Mo_3S\text{-}(S_2)_3X_2X_{4/2})_\infty)$ with PPh_3 in MeCN. In 1987, Saito prepared $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_n(MeOH)^{5-n}$ ($n = 3$, 4) by reacting $Mo_3S_7Cl_4$ with triethylphosphine in THF at room temperature.[14] We have extended this approach by preparing $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot3THF$ (**1**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3\text{-}(dmpe)_3]Cl\cdot2MeOH$ (**2**) by similar routes. We report here the

syntheses and crystal structures of **1** and **2**.

Preparation of trinuclear solid-state, polymeric structures is typically carried out by reacting stoichiometric amounts of the starting materials at high temperatures.[15] Trimeric clusters have been prepared by reacting simple metal compounds that are in the required oxidation states[16,17] by comproportionation reactions[18] and by redox reactions.[19] A variety of trinuclear oxide/chalcogenide/halide clusters have been produced. However, until the present the only trinuclear chalcogenide halides had molybdenum as the transition element and these were the only compounds that yielded molecular clusters.[13] We anticipate that the tungsten congeners should provide an entry into the chemistry of analogous molecular tungsten clusters. We report here the synthesis and crystal structure of $W_3S_7Br_4$ (**3**), a complex that should be a useful synthon for the preparation of substituted molecular tritungsten bromo sulfido clusters.

Experimental Section

Materials and Methods. All manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agents. Chemicals were obtained from the following sources: phosphines, S_2Cl_2, and tungsten (100-mesh powder), Strem; sulfur, precipitated grade, Fischer; molybdenum (200-mesh powder), Alfa. All chemicals were used without further purification. The preparations of $Mo_3S_7Cl_4$ and $W_3S_7Br_4$ were carried out in Pyrex tubes with the following dimensions: 15 cm (length) × $2^1/_2$ cm (o.d.), wall thickness 4 mm.

Preparation of $Mo_3S_7Cl_4$. Molybdenum powder (1.00 g, 10.4 mmol), sulfur (0.34 g, 10.4 mmol), and S_2Cl_2 (0.94 g, 6.9 mmol) were placed in a tube. The contents was degassed by three freeze–pump–thaw cycles and then sealed under a vacuum of 2×10^{-4} Torr. The tube was placed in an oven that was slowly warmed to 425 °C (over ca. 8 h) and kept there for 48 h. The oven was then turned off, and the tube was cooled to room temperature over a period of 12 h. A homogeneous mass of red crystals was formed. The product was washed with dichloromethane and dried under vacuum. The isolated yield was 1.92 g, 85% based on Mo.

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