

Figure 3. Perspective drawing of $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**4a**).

methyl groups. Both pyridine rings are planar within 0.031 (3) Å and form an angle of 58.0° with each other that is significantly larger than 47.7° in **2b** and 39.6° (average) in **3a**¹⁴ again because of the above reasons.

3. Hydrogen Bonding. In all three structures, the chloride ions and water molecules participate in extensive hydrogen-bonding networks. Typical separations are 3.1–3.3 Å for O...Cl and 2.7–2.9

Å for O...O. In addition, in most cases, the coordinated amine nitrogen atoms serve as hydrogen-bond donors to chloride ions. In **4b**, each amine nitrogen atom donates a near-linear hydrogen bond to a separate Cl ion: N2...Cl1 = 3.149 (3) Å, N–H...Cl = 167°; N3...Cl2 = 3.133 (3) Å, angle 167°. The same situation exists in **2b**, where the hydrogen-bond parameters are as follows: N2...Cl2 = 3.185 (6) Å, N–H...Cl = 152°; N3...Cl1 = 3.163 (6) Å, angle 166°. In the 2:1 complex **2a**, the stoichiometry does not allow for each amine nitrogen atom to form a hydrogen bond with chloride, and only one nitrogen atom of each ligand does this. Geometries: N3...Cl2 = 3.094 (4) Å, N–H...Cl = 152°; N6...Cl1 = 3.147 (4) Å, angle 174°. It is also of interest that for both independent molecules the N–H...Cl hydrogen bond is formed by the nitrogen atoms making the longer coordinate bond with Pd. The asymmetric hydrogen bonding probably causes the asymmetric chelation.

Conclusion. The terminal methyl groups cause slight distortions in the coordination environment around the central Pd(II) atom but do not cause any obstacle effect⁷ so as to change the overall geometry or stoichiometry of the complexes.

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Supplementary Material Available: Tables of bond distances, bond angles, coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for complexes $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2a**) (Tables S1–S5), $[\text{Pd}(\text{C}_{16}\text{H}_{22}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2b**) (Tables S6–S10), and $[\text{Pd}(\text{C}_{17}\text{H}_{24}\text{N}_4)]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**4a**) (Tables S11–S15) (62 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of a Diamagnetic Copper(II) Trichloroacetate Complex Containing a Nitroxyl Radical Ligand

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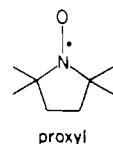
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From copper(II) trichloroacetate and the stable nitroxyl radical 2,2,4,4-tetramethylpyrrolinyl-1-oxy (proxyl) in the presence of water was isolated a stable adduct of stoichiometry $[\text{Cu}(\text{O}_2\text{CCCl}_3)_2(\text{proxyl})]_2 \cdot \text{H}_2\text{O}$. A crystal structure analysis has shown this adduct to have a novel binuclear structure. The two copper atoms are bridged by a pair of *syn,syn*-carboxylate groups and by the oxygen atom of a water molecule. The other two trichloroacetate ligands are monodentate, with the free oxygen participating in a hydrogen bond to the bridging water molecule. The nitroxyl ligands are bound via oxygen with short Cu–O distances of 1.928 (8) and 1.950 (9) Å. Magnetic susceptibility measurements show that this material is diamagnetic from 6 to 300 K. Crystal data: triclinic, $P\bar{1}$, $a = 11.804$ (3) Å, $b = 12.262$ (3) Å, $c = 15.675$ (3) Å, $\alpha = 84.39$ (16)°, $\beta = 83.65$ (16)°, $\gamma = 77.75$ (17)°. $Z = 2$.

Introduction

Recently, we reported the preparation and crystal structure of a novel dimeric copper(II) trichloroacetate adduct of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo).¹ This adduct, although its stoichiometry was of the well-known $[\text{Cu}(\text{O}_2\text{CR})_2\text{L}]_2$ type, possessed a number of unusual structural features. These included trigonal-bipyramidal copper atoms, short copper–nitroxyl bonds, and a long Cu–Cu distance. In an effort to prepare additional examples of this structure type, and as part of our continuing series of studies of metal complexes of nitroxyl radical ligands,^{2–6} we investigated the reaction of copper(II)

trichloroacetate with the five-membered ring nitroxyl 2,2,4,4-tetramethylpyrrolinyl-1-oxy (proxyl). We now report the prep-



aration and structure of a novel adduct obtained from this system. Like the previously reported trichloroacetate adduct, this material is binuclear and contains metal-coordinated nitroxyl groups; however, it proves to be an aqua complex and to have a new type of structure.

Experimental Section

Synthesis. Anhydrous copper(II) trichloroacetate was prepared by the method of Bateman and Conrad.⁷ The ligand proxyl was synthesized

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Table I. Crystal Data and Experimental Parameters

A. Crystal Data			
formula	Cu ₂ C ₂₄ H ₃₄ Cl ₁₂ N ₂ O ₁₁	<i>V</i> , Å ³	2197.1 (8)
fw	1079.07	<i>Z</i>	2
<i>a</i> , Å	11.804 (3)	<i>d</i> (obsd), g cm ⁻³	1.62 (2)
<i>b</i> , Å	12.262 (3)	<i>d</i> (calcd), g cm ⁻³	1.63
<i>c</i> , Å	15.675 (3)	space group	<i>P</i> 1
α , deg	84.39 (16)	μ (Mo K α), cm ⁻¹	17.9
β , deg	83.65 (16)	transmission factor range	0.76–0.83
γ , deg	77.75 (17)		
B. Experimental Parameters			
radiation	Mo K α ; λ (K α) = 0.710 73 Å; graphite monochromator		
temp, °C	23		
receiving aperture	circular, 4-mm diam, 20 cm from crystal		
scan rate, deg min ⁻¹	variable, 4–15		
scan range	–1.0° from K α_1 to +1.2° from K α_2		
bkgd counting	evaluated from 96-step peak profiles		
2 θ (max), deg	55		
no. of data colld	10 160 (<i>h</i> , $\pm k$, $\pm l$)		
no. of data with $F_o^2 > 3\sigma(F_o^2)$	4665		

from the corresponding hydroxylamine^{8–10} by air oxidation in aqueous methanol using a copper(II) acetate catalyst.¹¹ The crude nitroxyl was purified by column chromatography (silica gel, dichloromethane eluent) and subsequent fractional distillation (bp 54 °C (30 torr)).

The nitroxyl adduct of copper(II) trichloroacetate was prepared by adding an equimolar amount of proxyl to a pentane solution containing the anhydrous copper complex. The solution was refluxed for 1 h under nitrogen, filtered, and allowed to cool. Crystals suitable for X-ray study were obtained in good yield (ca. 60%) by recrystallization from hot petroleum ether. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd: C, 26.67; H, 3.15; N, 2.59; O, 15.21. Found: C, 27.28; H, 3.14; N, 2.57; O, 15.21.

X-ray Data Collection and Reduction. A regularly shaped deep green crystal of the title compound (tetragonal, 0.4 × 0.4 × 0.3 mm) was selected and mounted in a random orientation on a glass fiber. Initial centering, generation of possible cell vectors, and assignment of indices were carried out on a Syntex P2₁ diffractometer by procedures that have previously been described.^{12,13} Crystal density was determined by flotation in aqueous zinc bromide solution. Triclinic symmetry was suggested by interaxial angles and confirmed by a Delaunay reduction. Refined cell parameters were obtained by the use of 15 reflections with 30° < 2 θ < 35°. Crystal data and experimental parameters are summarized in Table I. Intensity data were collected by the 2 θ – θ scan technique in bisecting geometry, and three standard reflections were monitored after every 100 datum points. The data were corrected for standard decay (<10%), absorption, Lorentz, and polarization effects. Three reflections had intensities exceeding the valid range of the coincidence correction. These were recollected at a reduced filament current and adjusted accordingly during the processing.

Structure Solution and Refinement. The MULTAN package of direct-methods programs was used to solve the structure.¹⁴ Intensity statistics were consistent with the centrosymmetric space group *P*1̄. An *E* map based on 300 reflections with $E \geq 2.037$ yielded the location of two copper atoms and one nearly complete trichloroacetate ligand. Successive difference Fourier maps served to locate the remaining non-hydrogen atoms.¹⁵ During the course of least-squares refinement, it became evident that the CCl₃ groups were subject to a degree of disorder and/or

Table II. Atomic Positional Parameters for Cu₂(O₂CCCl₃)₄(proxyl)₂·H₂O

atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0.5174 (1.3)	0.2084 (1.3)	0.8576 (1.0)
Cu(2)	0.6086 (1.4)	0.3165 (1.2)	0.6504 (0.8)
Cl(1)	0.3384 (8)	0.1452 (7)	0.5523 (4)
Cl(2)	0.4727 (8)	–0.0450 (6)	0.6343 (6)
Cl(3)	0.2678 (5)	0.0595 (6)	0.7208 (4)
Cl(4)	0.9708 (4)	0.0551 (5)	0.7370 (5)
Cl(5)	0.8688 (8)	–0.0454 (9)	0.8864 (6)
Cl(6)	0.8124 (7)	–0.0812 (5)	0.7242 (8)
Cl(7)	0.8449 (6)	0.6148 (5)	0.7587 (4)
Cl(8)	0.9128 (8)	0.5144 (11)	0.6039 (9)
Cl(9)	0.7310 (11)	0.6869 (8)	0.6149 (8)
Cl(10)	0.0744 (5)	0.4675 (7)	0.8896 (6)
Cl(11)	0.1155 (6)	0.2064 (8)	0.9004 (8)
Cl(12)	0.1499 (9)	0.3216 (10)	1.0134 (7)
O(1)	0.4714 (9)	0.1306 (8)	0.7646 (7)
O(2)	0.4895 (8)	0.2305 (8)	0.6411 (6)
O(3)	0.6685 (8)	0.1199 (8)	0.8519 (6)
O(4)	0.7325 (9)	0.1782 (8)	0.7168 (7)
O(5)	0.7077 (8)	0.4236 (7)	0.6397 (6)
O(6)	0.6485 (11)	0.5118 (10)	0.7623 (8)
O(7)	0.3541 (9)	0.2534 (9)	0.8913 (7)
O(8)	0.3027 (9)	0.3974 (11)	0.8008 (9)
O(9)	0.5402 (8)	0.2907 (8)	0.9526 (6)
O(10)	0.6523 (8)	0.2740 (8)	0.5342 (6)
O(11)	0.5227 (8)	0.3669 (7)	0.7611 (6)
N(1)	0.6157 (11)	0.2361 (10)	1.0061 (8)
N(2)	0.7304 (9)	0.2937 (9)	0.4767 (7)
C(1)	0.4549 (12)	0.1567 (11)	0.6910 (9)
C(2)	0.3806 (13)	0.0907 (13)	0.6511 (9)
C(3)	0.7376 (13)	0.1153 (12)	0.7832 (11)
C(4)	0.8452 (15)	0.0182 (13)	0.7854 (11)
C(5)	0.7119 (14)	0.4891 (12)	0.6926 (10)
C(6)	0.8020 (16)	0.5658 (14)	0.6711 (10)
C(7)	0.2857 (15)	0.3269 (17)	0.8594 (12)
C(8)	0.1572 (14)	0.3319 (16)	0.8941 (14)
C(9)	0.7082 (18)	0.3283 (17)	1.0061 (14)
C(10)	0.7570 (27)	0.2780 (28)	1.0851 (20)
C(11)	0.7090 (35)	0.1827 (25)	1.1237 (19)
C(12)	0.5998 (24)	0.1841 (17)	1.0854 (12)
C(13)	0.6563 (24)	0.4494 (17)	1.0087 (22)
C(14)	0.7921 (18)	0.3004 (19)	0.9242 (18)
C(15)	0.5887 (24)	0.0743 (17)	1.0605 (14)
C(16)	0.4958 (37)	0.2347 (33)	1.1363 (20)
C(17)	0.7038 (14)	0.3799 (14)	0.4050 (10)
C(18)	0.8241 (17)	0.3583 (21)	0.3500 (13)
C(19)	0.8812 (17)	0.2530 (28)	0.3720 (13)
C(20)	0.8431 (14)	0.2167 (13)	0.4638 (11)
C(21)	0.6088 (19)	0.3464 (19)	0.3605 (13)
C(22)	0.6678 (21)	0.5016 (15)	0.4351 (12)
C(23)	0.9266 (16)	0.2363 (18)	0.5349 (14)
C(24)	0.8237 (21)	0.0967 (15)	0.4775 (18)

high-amplitude thermal motion. Thermal parameters of many of the chlorine atoms were high, and difference Fourier maps showed evidence for alternative positions for those atoms. However, difference maps based on a model from which the chlorine atoms had been removed indicated that the refined chlorine positions were the principal (at least two-thirds) contributors to the difference electron density. Because no convincing overall disorder model emerged from these difference maps and because it was clear that the principal goals of the structure analysis were not being compromised, it was decided not to pursue the disorder problem further. This problem is clearly the reason for the larger than normal final *R* factor and the somewhat imprecise light-atom coordinates.

The final refinement model employed anisotropic thermal parameters for all non-hydrogen atoms and included the methylene hydrogens of the proxyl ligand at their calculated positions. This refinement converged to $R_1 = 0.109$ and $R_2 = 0.146$. A final difference map had 12 of its top 13 peaks within bonding distance of the trichloromethyl carbon atoms; the largest feature not interpretable as an alternative chlorine position was a peak of height 1.2 e/Å³ in the vicinity of one of the proxyl rings. In all structure factor calculations, atomic scattering factors were taken from ref 16.

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Table III. Bond Distances (Å)

(a) Copper Coordination Spheres			
Cu(1)-O(1)	1.998 (10)	Cu(2)-O(2)	1.954 (9)
Cu(1)-O(3)	1.878 (9)	Cu(2)-O(4)	2.244 (10)
Cu(1)-O(7)	1.918 (10)	Cu(2)-O(5)	1.920 (8)
Cu(1)-O(9)	1.950 (9)	Cu(2)-O(10)	1.928 (9)
Cu(1)-O(11)	2.351 (9)	Cu(2)-O(11)	1.994 (9)
(b) Carboxylate Ligands ^a			
O(1)-C(1)	1.194 (15)	O(3)-C(3)	1.274 (17)
O(2)-C(1)	1.242 (15)	O(4)-C(3)	1.233 (16)
O(5)-C(5)	1.222 (17)	O(7)-C(7)	1.187 (20)
O(6)-C(5)	1.273 (17)	O(8)-C(7)	1.227 (20)
C(1)-C(2)	1.527 (18)	C(3)-C(4)	1.547 (21)
C(5)-C(6)	1.553 (19)	C(7)-C(8)	1.544 (21)
O(6)···O(11)	2.549 (13)	O(8)···O(11)	2.559 (14)
(c) Proxyl Ligands			
O(9)-N(1)	1.263 (14)	O(10)-N(2)	1.261 (12)
N(1)-C(9)	1.484 (20)	N(2)-C(17)	1.478 (19)
N(1)-C(12)	1.520 (22)	N(2)-C(20)	1.466 (18)
C(9)-C(10)	1.451 (32)	C(17)-C(18)	1.563 (23)
C(9)-C(13)	1.484 (28)	C(17)-C(21)	1.529 (23)
C(9)-C(14)	1.551 (31)	C(17)-C(22)	1.566 (23)
C(10)-C(11)	1.455 (37)	C(18)-C(19)	1.355 (28)
C(11)-C(12)	1.477 (25)	C(19)-C(20)	1.512 (25)
C(12)-C(15)	1.473 (24)	C(20)-C(23)	1.632 (25)
C(12)-C(16)	1.445 (38)	C(20)-C(24)	1.516 (24)

^a Distances within the CCl₃ groups are tabulated in supplementary Table III.

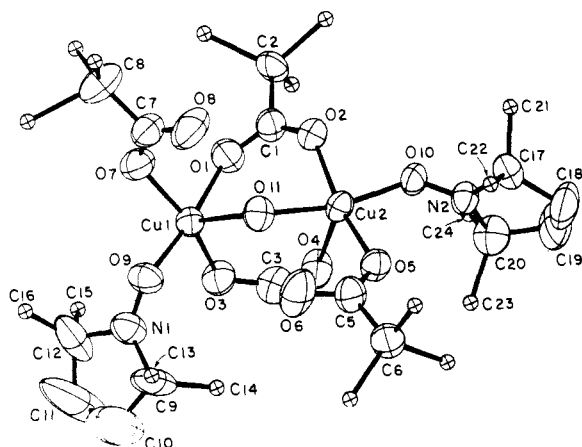


Figure 1. View of the molecular structure of [Cu(O₂CCl₃)₂-(proxyl)]₂·H₂O. For clarity, the CCl₃ group bound to C(3) has been omitted and thermal parameters of 1.0 Å² were assigned to chlorine and methyl carbon atoms. All other thermal ellipsoids are drawn at the 50% probability level.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured between 6 and 300 K by use of an SHE superconducting SQUID magnetometer at a field strength of 10 kG. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants. Effective magnetic moments per molecule were calculated from the relationship $\mu_{\text{eff}} = 2.828 \cdot [(\chi_m' - N\alpha)T]^{1/2}$ where $N\alpha$ was taken as 60×10^{-6} emu/copper atom.

Results

Crystal Structure. Final refined values of the atomic positional parameters are tabulated in Table II. Bond distances and angles, excluding those within the CCl₃ groups, are listed in Tables III and IV, respectively. Deposited as supplementary material are tables of observed and calculated structure factors, anisotropic thermal parameters, distances and angles within the CCl₃ groups, and least-squares planes.

Description of the Structure. The crystal structure of (μ -aqua)bis[(2,2,4,4-tetramethylpyrrolinyl-1-oxy)(μ -trichloroacetato-*O,O'*)(trichloroacetato)copper(II)] is comprised of discrete binuclear molecules. A view of the molecular structure is shown in Figure 1. A pair of bridging trichloroacetato ligands and the oxygen atom of a single water molecule link the two copper atoms.

Table IV. Bond Angles (deg)

(a) Copper Coordination Spheres			
O(1)-Cu(1)-O(3)	92.4 (4)	O(2)-Cu(2)-O(4)	96.7 (4)
O(1)-Cu(1)-O(7)	86.6 (4)	O(2)-Cu(2)-O(5)	166.9 (4)
O(1)-Cu(1)-O(9)	172.4 (4)	O(2)-Cu(2)-O(10)	80.8 (4)
O(1)-Cu(1)-O(11)	89.7 (4)	O(2)-Cu(2)-O(11)	88.2 (4)
O(3)-Cu(1)-O(7)	159.2 (4)	O(4)-Cu(2)-O(5)	95.8 (4)
O(3)-Cu(1)-O(9)	94.8 (4)	O(4)-Cu(2)-O(10)	97.9 (4)
O(3)-Cu(1)-O(11)	107.1 (4)	O(4)-Cu(2)-O(11)	92.9 (4)
O(7)-Cu(1)-O(9)	85.8 (4)	O(5)-Cu(2)-O(10)	93.6 (4)
O(7)-Cu(1)-O(11)	93.7 (4)	O(5)-Cu(2)-O(11)	95.1 (4)
O(9)-Cu(1)-O(11)	90.6 (4)	O(10)-Cu(2)-O(11)	165.4 (4)
(b) Carboxylate Ligands			
Cu(1)-O(1)-C(1)	131.0 (10)	Cu(1)-O(3)-C(3)	122.8 (10)
Cu(2)-O(2)-C(1)	133.7 (9)	Cu(2)-O(4)-C(3)	140.8 (10)
O(1)-C(1)-O(2)	129.4 (13)	O(3)-C(3)-O(4)	129.5 (14)
O(1)-C(1)-C(2)	116.2 (12)	O(3)-C(3)-C(4)	114.7 (14)
O(2)-C(1)-C(2)	114.5 (13)	O(4)-C(3)-C(4)	115.8 (14)
Cu(1)-O(7)-C(7)	128.1 (10)	Cu(2)-O(5)-C(5)	126.2 (9)
O(7)-C(7)-O(8)	128.9 (16)	O(5)-C(5)-O(6)	130.7 (14)
O(7)-C(7)-C(8)	115.4 (16)	O(5)-C(5)-C(6)	117.1 (13)
O(8)-C(7)-C(8)	115.6 (18)	O(6)-C(5)-C(6)	112.0 (14)
(c) Proxyl Ligands			
Cu(1)-O(9)-N(1)	128.2 (8)	Cu(2)-O(10)-N(2)	133.8 (8)
O(9)-N(1)-C(9)	120.2 (12)	O(10)-N(2)-C(17)	121.3 (11)
O(9)-N(1)-C(12)	122.1 (14)	O(10)-N(2)-C(20)	122.4 (11)
C(9)-N(1)-C(12)	116.0 (14)	C(17)-N(2)-C(20)	114.6 (11)
N(1)-C(9)-C(10)	99.0 (18)	N(2)-C(17)-C(18)	99.3 (13)
N(1)-C(9)-C(13)	110.4 (18)	N(2)-C(17)-C(21)	105.7 (13)
N(1)-C(9)-C(14)	106.1 (14)	N(2)-C(17)-C(22)	113.1 (12)
C(13)-C(9)-C(14)	113.2 (21)	C(21)-C(17)-C(22)	112.8 (16)
C(9)-C(10)-C(11)	114.0 (20)	C(17)-C(18)-C(19)	108.3 (16)
C(10)-C(11)-C(12)	108.6 (22)	C(18)-C(19)-C(20)	110.6 (16)
N(1)-C(12)-C(11)	99.3 (19)	N(2)-C(20)-C(19)	100.5 (13)
N(1)-C(12)-C(15)	110.6 (15)	N(2)-C(20)-C(23)	108.6 (12)
N(1)-C(12)-C(16)	107.6 (21)	N(2)-C(20)-C(24)	108.6 (14)
C(11)-C(12)-C(15)	114.2 (24)	C(19)-C(20)-C(23)	114.5 (16)
C(11)-C(12)-C(16)	114.1 (25)	C(19)-C(20)-C(24)	114.8 (18)
C(15)-C(12)-C(16)	110.4 (25)	C(23)-C(20)-C(24)	109.2 (16)
(d) Bridging Water Molecule			
Cu(1)-O(11)-Cu(2)	108.4 (4)	Cu(2)-O(11)-O(6)	90.3 (4)
Cu(1)-O(11)-O(6)	127.5 (5)	Cu(2)-O(11)-O(8)	126.8 (5)
Cu(1)-O(11)-O(8)	81.0 (4)	O(6)-O(11)-O(8)	126.0 (5)

^a Angles within the CCl₃ groups are tabulated in supplementary Table III.

In addition, each metal ion is bound to a monodentate trichloroacetato group and to the oxygen atom of a proxyl radical. The two uncoordinated carboxylate oxygen atoms are involved in short contacts, presumably indicative of hydrogen bonds, to the bridging oxygen atom. The Cu...Cu distance is 3.529 Å.

The coordination environment about each copper(II) ion is distorted square pyramidal; however, the five ligands about each metal are distributed differently among the apical and basal sites. In the coordination sphere of Cu(1), the water oxygen atom, O(11), occupies the apical site at a distance of 2.351 (9) Å from the metal. The remaining four oxygen atoms—three from the carboxylates and one from the nitroxyl ligand—fill the basal positions, with Cu-O distances ranging from 1.878 (9) to 1.998 (10) Å. A trichloroacetato oxygen atom, O(4), is the axial ligand for Cu(2) with a Cu-O distance of 2.244 (10) Å. Distances to the four basal atoms range from 1.920 (8) to 1.994 (9) Å. Bond angles are consistent with expectations for square-pyramidal coordination, with substantially greater distortions from the ideal geometry about Cu(1). A line drawing of the central portion of the structure, with the two square-pyramidal coordination polyhedra sketched in, is shown in Figure 2.

Because of the different coordination environments about the two copper atoms, the two bridging carboxylate groups are inequivalent and the overall structure is unsymmetrical. Both of the M-O-C-O-M groupings are nonplanar, but each is distorted in a different way. The O(1)-C(1)-C(2)-O(2) group is twisted, so that the two Cu atoms are displaced by 0.35 and 0.52 Å on opposite sides of the OCCO plane. In contrast, the O(3)-C-

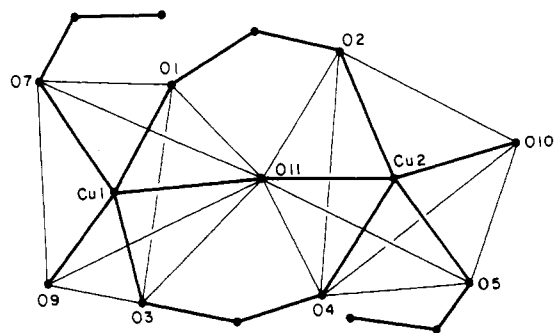


Figure 2. Line drawing of the central portion of the structure, with square-pyramidal coordination polyhedra outlined with lighter lines.

(3)–C(4)–O(4) plane is tilted, with the metal atoms on the *same* side of the OCCO plane at distances of 0.27 and 0.38 Å. In a symmetrical carboxylate bridge, the Cu–O–C–O–Cu grouping would be planar. The two monodentate trichloroacetate groups display no unusual structural features.

The geometry of binding to the two proxyl ligands to copper is similar to that previously observed in two copper(II) complexes of the six-membered nitroxyl radical tempo.^{1,2} The Cu–O distances are rather short at 1.928 (8) and 1.950 (9) Å. The Cu–O–N angles of 128.2 (8) and 133.8 (8)° are somewhat larger than those of approximately 124° in the two tempo complexes. Also typical of values observed for other nitroxyl complexes are the dihedral angles of 74.6 and 86.9° between the Cu–O–N plane and the plane defined by the three atoms bound to N.

Important structural parameters of the coordinated proxyl radicals include the N–O distances (N(1)–O(9) = 1.263 (14) Å and N(2)–O(10) = 1.261 (12) Å) and the out-of-plane displacements of the two nitrogen atoms (0.108 Å for N(1) and 0.105 Å for N(2)). These values are well within the ranges previously observed for free and coordinated nitroxyl radicals,^{17,18} though the nitrogen atoms in uncoordinated proxyl derivatives have more nearly planar geometries.^{19–23} In view of the low precision of the coordinates of the ring carbon atoms we will not discuss further details of the five membered ring conformation, except to note that thermal ellipsoids of the atoms of one ring (bound to Cu(1)) suggest averaging over more than one conformer.

The bridging oxygen atom, O(11), is involved in short contacts of 2.549 (12) and 2.559 (14) Å to the free carboxylate oxygen atoms O(6) and O(8). These contacts are well within the range of distances normally taken to be indicative of O–H...O hydrogen bonds. The geometry about O(11) is distorted tetrahedral, with bond angles Cu(1)–O(11)–Cu(2) = 108.4 (4)° and O(6)–O(11)–O(8) = 126.0 (5)°. Difference maps yielded no convincing evidence for the location of hydrogen atoms.

Magnetic Susceptibility Data. A table of magnetic susceptibility measurements is included with the supplementary material. The complex is essentially diamagnetic over the entire temperature range investigated, 6–300 K. The effective magnetic moment per Cu²⁺ ion varies only from 0.15 to 0.23 μ_B over this temperature range. The low-temperature susceptibilities are consistent with the presence of a small amount (<1%) of paramagnetic impurity, a common occurrence in Cu²⁺ complexes with singlet ground states. The small, nearly constant susceptibility values above 170 K are probably a result of uncertainty in the corrections for

diamagnetism and/or temperature-independent paramagnetism.

Discussion

The title compound was prepared in the course of studies of the interactions of nitroxyl radicals with the copper(II) trihaloacetates. On the basis of its elemental analysis, it was initially formulated as an anhydrous adduct, analogous to the previously reported [Cu(O₂CCCl₃)₂tempo]₂.¹ Once it was recognized to be an aqua complex, the source of the water was found to be in the initial sample of proxyl employed in the preparation. The presence of water in this starting material was confirmed by its infrared spectrum. Subsequent experiments in which rigorously dried proxyl was employed yielded an anhydrous product. This material is part of a larger series of compounds and will be discussed elsewhere.⁶

Because hydrogen atoms were not located in the crystallographic study, the identification of the bridging atom as the oxygen atom of a water molecule must rest on indirect evidence. The preparative results discussed above show that the presence of water in the starting material is necessary for the isolation of this product. The geometry about O(11) is consistent with expectations for a water molecule participating in hydrogen bonds to O(6) and O(8). The structural results clearly imply the presence of divalent copper, neutral nitroxyl radicals, and carboxylate ions. Charge balance then requires the monatomically bridging ligand to be neutral. Taken together, the evidence is persuasive.

Although the overall molecular structure is novel, the arrangement of metal ions, carboxylate ligands, and the bridging water molecule (including the details of the intramolecular hydrogen bonding) is identical with that found in a series of seven dinuclear *N,N,N',N'*-tetramethylethylenediamine complexes of Ni(II).^{24,25} The major structural features that distinguish the copper complex from these nickel systems are a somewhat shorter metal–metal distance, five-coordinate rather than six-coordinate metal ions, and a lower overall degree of symmetry. The adoption of this structure type by a whole series of nickel complexes and in the present case suggests that it may be a stable arrangement in other dinuclear carboxylates having a water/metal ratio of 1:2.

The combination of two *syn,syn*-carboxylate bridges and a monatomic oxygen bridge in a dinuclear metal complex is of some significance, having recently been shown to be present in the binuclear active centers of the iron proteins methemerythrin and azidomethemerythrin.²⁶ In the protein, the monatomic bridge is an oxo ligand rather than a water oxygen atom, but the structural details are quite similar. In fact, the Cu–Cu distance we observe is virtually the same as the Fe–Fe distances of 3.21 and 3.25 Å. Small-molecule models for this diiron core have recently been reported.^{27,28}

This is the first reported metal complex of the five-membered ring nitroxyl radical proxyl. As noted above, the geometry of binding of the proxyl to copper is qualitatively similar to that observed for the six-membered ring radical tempo in two copper(II) complexes.^{1,2} The fact that the structure of the coordinated proxyl is virtually the same as that of closely related noncoordinated radicals indicates that the ligand is best described as a nitroxyl radical and has not undergone formal oxidation or reduction. Particularly pertinent parameters are the N–O distance and the near-planarity of the nitrogen atom, both of which would be expected to be sensitive to oxidation or reduction.

Of the five structurally characterized complexes containing a nitroxyl group bound to copper(II), three have short (<2.0 Å) Cu–O(nitroxyl) bonds^{1,2} and two have much longer (>2.4 Å) Cu–O interactions.^{29,30} The three complexes with short bonds

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have three very different structures, but all have five-coordinate copper ions and similar metal-nitroxyl binding configurations. It is likely that steric requirements of the ligand methyl groups are an important factor in determining the binding geometry and the coordination environment about copper. More surprising is the fact that the nitroxyl ligands, which are generally reluctant to form metal complexes, form such short, and apparently stable, Cu-O bonds. In the present case, as in the two previous complexes with short Cu-nitroxyl bonds, the sterically bulky nitroxyl ligands prefer the coordination sites associated with short Cu-O bond distances. Also interesting is the fact that in the presence of coordinated water the nitroxyl radical remains bound to copper and two carboxylate ligands become monodentate. Results like these suggest that, under appropriate conditions, the nitroxyl function may be a better ligand than has been appreciated.

The magnetic properties of this complex were of potential interest because of the formal presence of four $S = 1/2$ para-

magnetic centers per molecule. However, with the exception of a small (<1%) amount of paramagnetic impurity, the complex is diamagnetic from 6 to 300 K. This magnetic behavior is most reasonably explained by the presumption of strong coupling between copper and nitroxyl free spins. It is not clear whether this coupling is a consequence of use of the odd metal and ligand electrons to form the Cu-O bond or whether it is simply a result of antiferromagnetic coupling strong enough to give rise to diamagnetism at room temperature. Studies of other, simpler, systems now in progress may shed some light on this point.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, distances and angles within the CCl_3 groups, least-squares planes, and magnetic susceptibility data (27 pages). Ordering information is given on any current masthead page.

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The Clusters $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$: Preparations, Properties, and Structural Relationship of Near-Cubic $\text{Co}_8(\mu_4\text{-S})_6$ Cores to the Clusters in Synthetic Pentlandite

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In a search for Co-S-SR clusters, $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ was found to react with NaSH in acetone to give the octanuclear cluster $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ (**1**), isolated as its $n\text{-Pr}_4\text{N}^+$ salt. Reduction of **1** in acetonitrile with sodium acenaphthylenide in THF afforded $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ (**2**), which was obtained as its Et_4N^+ salt. $(n\text{-Pr}_4\text{N})_4(\text{1})$ crystallizes in monoclinic space group $P2_1/c$ with $a = 23.912$ (4) Å, $b = 27.466$ (6) Å, $c = 17.173$ (6) Å, $\beta = 90.86$ (2)°, $Z = 4$, and two centrosymmetric, independent anions. $(\text{Et}_4\text{N})_5(\text{2})$ crystallizes in triclinic space group $P\bar{1}$ with $a = 14.126$ (6) Å, $b = 14.150$ (2) Å, $c = 14.470$ (2) Å, $\alpha = 113.37$ (1)°, $\beta = 97.73$ (3)°, $\gamma = 72.74$ (2)°, $Z = 1$, and a centrosymmetric anion. Both clusters contain near-cubic $\text{Co}_8(\mu_4\text{-S})_6$ cores, composed of a concentric Co_8 cube and S_6 octahedron, which are only slightly distorted. Each cobalt atom is in an approximately tetrahedral site with one terminal PhS^- ligand. Mean values of corresponding metric features of the two anions **1** and **2** are insignificantly different except for the tendency of Co-SPh distances in **2** to exceed those in **1** by ~ 0.04 Å. This result suggests that the odd electron in **2** has structurally detectable Co character. Electronic properties reveal spin-coupled clusters, $S = 0$ (**1**) and $1/2$ (**2**) ground states, contact-shifted ^1H NMR spectra, and in solution equivalent Co sites and complete delocalization of the odd electron in **2**. The core units have the same topology as the recognizable Co_8S_6 clusters in the synthetic pentlandite Co_8S_8 , in which the clusters are extensively bridged by sulfide. However, the $[\text{Co}_8\text{S}_6]^{4+}$ cores of **1** and **2** are not isoelectronic with the pentlandite clusters, which have the apparent $[\text{Co}_8\text{S}_6]^{2+}$ oxidation level, and volumes of the Co_8 and S_6 components are substantially smaller (81-84%) than those of the synthetic clusters. Despite differences in oxidation levels and detailed structural features, the formation of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ is a favorable indicator of the ability to synthesize small solubilized fractions of nonmolecular inorganic solids, particularly those containing recognizable metal-sulfur clusters.

Introduction

Evidence, albeit not extensive, is accumulating that bears favorably on the prospect of the synthesis of portions of nonmolecular inorganic solids in the form of small solubilized fractions. This matter has been most extensively pursued in the course of examination of possible analogies between metal clusters, especially carbonyls, and metal surfaces under conditions of chemisorption and catalysis.^{2,3} An entirely different domain for investigation is provided by solids other than metals. In this respect, metal sulfide minerals and synthetic phases⁴⁻⁶ offer a dazzling variety of structures and properties not yet encountered in discrete molecules. In the broadest terms, these materials, which sometimes contain other elements, can be classified as (i) infinite polymers containing no recognizable M-S clusters or (ii) extended lattices

containing recognizable M-S clusters that are discrete except for the bridging interactions connecting them.

With regard to type i compounds, $(\text{C}_3\text{H}_5)_6\text{Ni}_6(\mu_4\text{-S})_3$ contains a fraction of the framework of one form of NiS ,⁷ $[\text{Fe}_3\text{S}_4(\text{SR})_4]^{3-8}$ has the same $\text{Fe}_3(\mu\text{-S})_4$ group that repeats in the linear polymers M^1FeS_2 ,^{6,9} and $(\text{MeCp})_2\text{V}_2\text{S}_4$ ¹⁰ may possess a $\text{V}_2(\eta^4\text{-}\mu\text{-S}_2)_2$ group similar to that in patronite¹¹ (VS_4), also a linear polymer. The $\text{Nb}_2(\mu\text{-S})(\eta^4\text{-}\mu\text{-S}_2)$ core of $\text{Nb}_2\text{S}_3\text{Br}_4(\text{tbt})_4$ ¹² resembles a portion of the NbS_3 structure.¹³ The cages $[\text{M}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ ($\text{M} = \text{Zn(II), Cd(II)}$)¹⁴ have been proposed as congruent representations

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