

Nitroxyl Adducts of Copper(II) Trihaloacetates. Diamagnetic Copper(II) Complexes with a Novel Dimeric Structure

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A series of copper(II) trihaloacetate adducts of the cyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) and 2,2,5,5-tetramethylpyrrolinyl-1-oxy (proxyl) have been prepared. All products have the monoadduct stoichiometry $\text{Cu}(\text{O}_2\text{CCX}_3)_2\text{L}$ (L = tempo, X = F, Cl, Br; L = proxyl, X = Cl). Crystal structure analyses of the two trichloroacetate adducts have shown each to have a dimeric structure that is a novel variant of the classical copper(II) acetate monohydrate configuration. The coordination environment about each copper atom is trigonal bipyramidal, and the central portion of each molecule has approximate S_4 symmetry. Each of the four carboxylate groups bridges from an apical coordination site of one copper atom to an equatorial position on the other metal. The resulting Cu...Cu separations have very long values of 3.256 (2) Å (tempo adduct) and 3.197 (2) Å (proxyl adduct). The configurations of the metal-bound nitroxyls closely resemble those of analogous uncoordinated free radicals. It is likely that steric factors play a role in the adoption of this unusual structure. All of the nitroxyl adducts are diamagnetic from 6 to 300 K. Crystals of $[\text{Cu}(\text{O}_2\text{CCCl}_3)_2(\text{tempo})]_2$ are monoclinic, space group $P2_1/n$, with $a = 12.134$ (3) Å, $b = 22.465$ (5) Å, $c = 16.693$ (3) Å, $\beta = 100.43$ (2)°, and $Z = 4$. Crystals of $[\text{Cu}(\text{O}_2\text{CCCl}_3)_2(\text{proxyl})]_2$ are triclinic, space group $P\bar{1}$, with $a = 9.826$ (3) Å, $b = 13.216$ (4) Å, $c = 18.022$ (5) Å, $\alpha = 94.02$ (2)°, $\beta = 114.99$ (2)°, $\gamma = 100.45$ (2)°, and $Z = 2$.

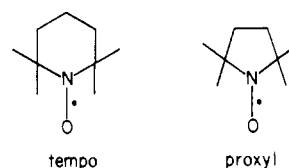
Introduction

Although stable nitroxyl radicals have been extensively exploited as spin labels in the study of biological systems,¹⁻⁴ their ability to function as ligands in transition-metal complexes has been much less thoroughly explored. The first complex believed to contain a covalent metal-nitroxyl interaction was reported in 1967,⁵ and a number of others were prepared (though in some cases not fully characterized) in the early 1970s.⁶⁻¹¹ Recently, interest in these complexes has been revived in our laboratory and elsewhere.

Metal nitroxyl complexes are of interest as one of a small number of types of systems that may be regarded as containing metal-coordinated free radical ligands. Notable other examples include metal complexes of semiquinones¹²⁻¹⁵ and of porphyrin radicals.^{16,17} In certain of these compounds, characterization of the coordinated ligand as a radical species is not definitive and other interpretations have been advocated. If the ligand does retain its radical character, there is the potential of interesting magnetic behavior, particularly in complexes with paramagnetic metal ions and/or with more than one radical ligand.

The nitroxyl function is not a good ligand and has been observed to bind to transition-metal ions only under rather special cir-

cumstances. In particular, enhancement of the Lewis acidity of the metal center by electron-withdrawing ligands seems to be required. Among the ligands employed for this purpose have been the hexafluoroacetylacetonate (F_6acac) ion,^{8,9,18-22} halides,^{5,7} and halocarboxylates.^{23,24} We have been carrying out exploratory studies in an effort to prepare new types of transition-metal-nitroxyl complexes. In this paper, we report the preparation and characterization of a series of dimeric adducts of the copper(II) trihaloacetates with the nitroxyls tempo and proxyl. A portion of this work has previously been communicated in preliminary form.²⁵



Experimental Section

Synthesis. The copper trihaloacetates were prepared by a modification of the procedure of Bateman and Conrad.²⁶ The hydrated bis(carboxylate) adducts were allowed to crystallize from aqueous solutions by slow evaporation and then dehydrated over P_2O_5 for several days. The crude product was purified by extraction into anhydrous diethyl ether, followed by filtration and solvent removal under vacuum. The ligand proxyl was prepared as previously described.^{21,27} Tempo was obtained from Aldrich Chemicals, Inc., and used as purchased.

The tempo adducts of copper(II) trifluoro-, trichloro-, and tribromoacetate were prepared by the addition of an equimolar amount of tempo to a pentane suspension of the appropriate anhydrous copper complex. The solutions were refluxed for 1 h under nitrogen, filtered, and then reduced in volume with use of a stream of dry nitrogen until crystals began to appear. By introducing a small amount of solvent sufficient to dissolve any formed crystals and cooling the mixture to -20 °C, it was

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possible to obtain in good yield crystals suitable for X-ray analysis. Because these complexes did not exhibit particularly good long-term stability, elemental analyses and magnetic measurements were conducted only on crystalline samples that had been freshly prepared. The trichloroacetate adduct appeared to be the most stable and the tribromoacetate least stable. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd for $C_{26}H_{36}N_2O_{10}Cl_{12}Cu_2$: C, 28.68; H, 3.31; N, 2.57. Found: C, 28.7; H, 3.3; N, 2.6. Calcd for $C_{26}H_{36}N_2O_{10}F_{12}Cu_2$: C, 35.03; H, 4.04; N, 3.14. Found: C, 36.2; H, 4.6; N, 3.4. Calcd for $C_{26}H_{36}N_2O_{10}Br_{12}Cu_2$: C, 19.24; H, 2.22; N, 1.73. Found: C, 21.3; H, 3.0; N, 2.0.

Initial attempts to prepare the proxyl adduct of copper(II) trichloroacetate by a similar procedure yielded a hydrated species;²⁷ the source of the water was found to be in the sample of proxyl employed. An anhydrous product could be obtained if the proxyl was dehydrated and subsequently stored in a desiccator over P_2O_5 . The dehydrated ligand was dissolved in petroleum ether, followed by the addition of an equimolar amount of anhydrous bis(trichloroacetato)copper(II). After being allowed to stand overnight, the green reaction mixture was filtered to remove any unreacted starting material. Dark green crystals suitable for X-ray analysis could be isolated from solution by slow evaporation in a desiccator containing P_2O_5 . Anal. Calcd for $C_{24}H_{32}N_2O_{10}Cl_{12}Cu_2$: C, 27.17; H, 3.04; N, 2.64; O, 15.08. Found: C, 27.28; H, 3.14; N, 2.57; O, 15.21.

X-ray Data Collection and Reduction. X-ray data for the tempo and proxyl adducts of copper(II) trichloroacetate were collected on a Syntex P₂ diffractometer. Initial centering, generation of possible unit cell vectors, and assignment of indices were carried out by procedures that have been described elsewhere.^{28,29} Refined unit cell parameters were obtained from least-squares refinement based upon the setting angles of 15 reflections with $30^\circ \leq 2\theta \leq 35^\circ$. Intensities of 3 standard reflections were measured after every 100 data. Reflections whose intensities exceeded the valid range of the coincidence correction were remeasured at a lower filament current. The data were corrected for standard decay, Lorentz, and polarization effects. All computations were carried out with a locally modified version of the UCLA Crystallographic Computing Package.³⁰ No absorption corrections were made. Crystal data and experimental parameters for both compounds are tabulated in Table I.

Data for the tempo adduct were collected from a regularly shaped deep green crystal of approximate dimensions $0.3 \times 0.3 \times 0.4$ mm mounted on a glass fiber and protected with a thin coating of epoxy cement. The monoclinic crystal symmetry was confirmed by axial rotation photographs. The standard reflections declined in intensity by about 10% during data collection.

Data for the proxyl complex were collected from a well-formed dark green crystal of dimensions $0.3 \times 0.4 \times 0.4$ mm mounted inside a glass capillary. Triclinic symmetry was confirmed by a Delaunay reduction. The standard reflections showed no significant decay.

Structure Solution and Refinement. Both crystal structures were solved by a combination of direct methods and difference Fourier techniques. In each case, direct methods (MULTAN 78)³¹ yielded atomic coordinates for the copper atoms, their coordination spheres, and a number of additional atoms. Successive difference Fourier syntheses served to locate the remaining non-hydrogen atoms. Structure refinement was carried out by full-matrix least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms. In both structures, there was evidence for a degree of disorder and/or high amplitude thermal motion of the CCl_3 groups. Difference Fourier maps gave some evidence for alternative chlorine atom positions but did not yield a second well-resolved and internally consistent set of chlorine atoms for any of the CCl_3 groups. These maps clearly indicated that the refined positions accounted for the majority ($>2/3$) of the electron density associated with the chlorine atoms. Consequently, no provision for disorder was introduced into the refinement. The difficulty of accurately modeling the CCl_3 groups is clearly the reason for the higher than usual final R values but does not seriously affect the chemically significant features of the structures. In all structure factor calculations, atomic scattering factors were taken from ref 32.

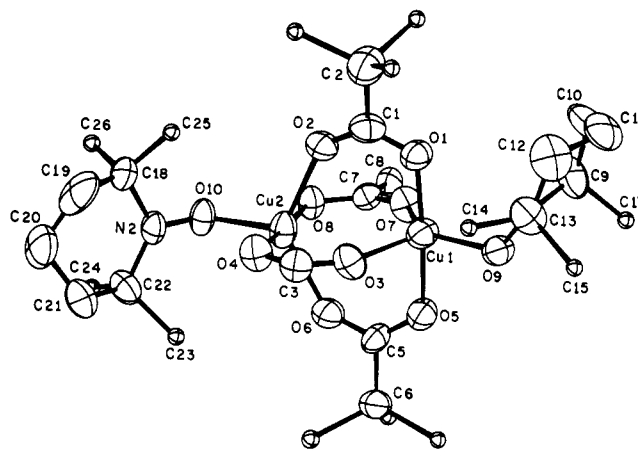


Figure 1. View of the molecular structure of $[Cu(O_2CCCl_3)_2(tempo)]_2$. For clarity, hydrogen atoms, the CCl_3 group bound to C(3), and the Cl atoms bound to C(8) have been omitted. Also, thermal parameters of the remaining chlorine atoms and of the tempo methyl groups have been artificially reduced.

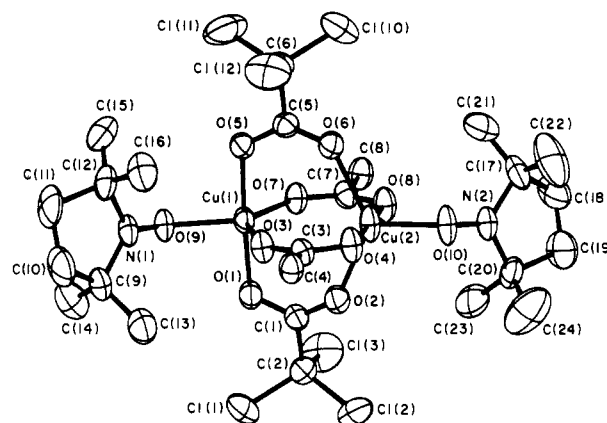


Figure 2. View of the molecular structure of $[Cu(O_2CCCl_3)_2(proxyl)]_2$. For clarity, hydrogen atoms and the Cl atoms bound to C(4) and C(8) have been omitted.

For the tempo adduct, refinement converged to final conventional R values of $R_1 = 0.090$ and $R_2 = 0.119$. The final refinement model included all hydrogen atoms in fixed, idealized positions (tetrahedral angles, $C-H = 0.95$ Å) with the exception of those of the methyl groups. The largest feature of a final difference Fourier map not interpretable as an alternative chlorine position was a peak of height $1.2 e/\text{Å}^3$ in the vicinity of one of the tempo ligands.

The final R factors for the proxyl complex were $R_1 = 0.070$ and $R_2 = 0.100$. All hydrogen atoms were included in fixed, idealized positions in the final refinement. The largest positive peak not in the vicinity of the CCl_3 groups on a final difference map was one of the height $1.1 e/\text{Å}^3$ near one of the proxyl ligands.

Magnetic Susceptibility Measurements. The magnetic susceptibilities of all complexes reported were measured between 6 and 300 K by use of an SHE superconducting SQUID magnetometer operating at a fixed field strength of 10 kG. The data were corrected for magnetization of the sample holder and for ligand diamagnetism, with the latter correction estimated by use of Pascal's constants.

Results

Synthesis. Four new nitroxyl adducts of stoichiometry $Cu(O_2CCX_3)_2L$ have been prepared and characterized. For $L = tempo$, adducts were prepared with $X = F, Cl, \text{ and } Br$; in addition the proxyl adduct was prepared for $X = Cl$. The presence of a halogen substituent appears necessary for nitroxyl adduct formation, as no analogous product could be obtained with unsubstituted copper(II) acetate.

Crystal Structure. Final atomic positional parameters for the tempo and proxyl adducts of copper(II) trichloroacetate are tabulated in Tables II and III. Bond distances and angles are listed in Tables IV–VII. Deposited as supplementary material are tables of observed and calculated structure factors, anisotropic

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Table I. Crystal Data and Experimental Parameters

	L = tempo	L = proxyl
(a) Crystal Data		
formula	Cu ₂ C ₂₆ H ₃₆ Cl ₁₂ N ₂ O ₁₀	Cu ₂ C ₂₄ H ₃₂ Cl ₁₂ N ₂ O ₁₀
fw	1089.1	1061.1
a, Å	12.134 (3)	9.826 (3)
b, Å	22.465 (5)	13.216 (4)
c, Å	16.693 (3)	18.022 (5)
α, deg	90	94.02 (2)
β, deg	100.43 (2)	114.99 (2)
γ, deg	90	100.45 (2)
V, Å ³	4475 (2)	2057 (1)
Z	4	2
d(obsd), g cm ⁻³	1.62 (2)	
d(calcd), g cm ⁻³	1.65	1.71
space group	P2 ₁ /n	P1̄
μ(Mo Kα), cm ⁻¹	17.8	19.0
(b) Experimental Parameters		
radiation	Mo Kα; λ = 0.71073 Å; graphite monochromator	a
temp, °C	23	22
receiving aperture	circular, 4 mm diam, 24 cm from cryst	a
scan rate, deg min ⁻¹	4-16	6-18
scan range, deg	-1.0 from Kα ₁ to +1.2 from Kα ₂	-1.1 from Kα ₁ to +1.2 from Kα ₂
bkgds	evaluated from 96-step peak profile	a
2θ(max), deg	50	55
data collected	8561	9501
data with F _o ² > 3σ(F _o ²)	4100	6198

^a As for L = tempo.

thermal parameters, and distances and angles within the CCl₃ groups.

Description of the Structure. Although differing in some details (see below), the molecular structures of the tempo and proxyl adducts of copper(II) trichloroacetate are qualitatively similar in most respects. Views of the structures of the two adducts are shown in Figures 1 and 2.

The dimers have the same stoichiometry and atomic connectivity as are found in the well-known dimeric copper(II) acetate monohydrate structure.³³ Specifically, each dimer has penta-coordinate metal ions, four syn,syn bridging carboxylate groups, and two terminal, O-bound nitroxyl ligands. However, the geometry of the central portion of the molecule differs qualitatively from the usual square-pyramidal configuration. The arrangement of oxygen atoms about the two copper ions is best described as distorted trigonal bipyramidal. This interpretation is clearly illustrated in Figures 1 and 2 and is confirmed by the bond angle values listed in Tables VI and VII. In each molecule, the mean deviation of the O-Cu-O angles from their ideal values of 90, 180, or 120° is less than 5°. Within each molecule, the axial vectors of the two copper coordination polyhedra are approximately perpendicular to each other. As a consequence, the central portion of the molecule has approximate S₄ symmetry and each trichloroacetate ligand bridges from an axial coordination site on one copper atom to an equatorial position on the other. This bridging arrangement gives rise to Cu...Cu distances substantially longer than those of ca. 2.6 Å associated with the copper(II) acetate structure;³⁴ the Cu-Cu separations in the tempo and proxyl adducts are 3.256 (2) and 3.197 (2) Å, respectively.

Bond distance patterns for the four copper atoms in the two dimeric adducts show close similarities. The axial Cu-O bonds are very short, ranging in length from 1.896 (9) to 1.928 (4) Å. Slightly longer, but still on the short side, are the equatorial

Table II. Atomic Positional Parameters for the tempo Adduct

atom	x	y	z
Cu(1)	0.21878 (14)	0.18832 (6)	0.77805 (10)
Cu(2)	-0.00446 (13)	0.10682 (8)	0.72527 (10)
Cl(1)	0.0714 (6)	0.3223 (3)	0.5629 (4)
Cl(2)	-0.1464 (4)	0.2956 (2)	0.5973 (4)
Cl(3)	0.0077 (5)	0.3642 (2)	0.7083 (4)
Cl(4)	0.0026 (9)	0.2463 (5)	0.9884 (6)
Cl(5)	-0.1534 (15)	0.1527 (5)	0.9591 (8)
Cl(6)	-0.1669 (17)	0.2415 (11)	0.8895 (11)
Cl(7)	0.3805 (5)	0.0580 (2)	0.9834 (3)
Cl(8)	0.1681 (5)	-0.0024 (4)	0.9544 (4)
Cl(9)	0.3288 (6)	-0.0251 (2)	0.8610 (4)
Cl(10)	0.1242 (3)	0.0298 (2)	0.4918 (2)
Cl(11)	0.3247 (3)	0.0306 (2)	0.6117 (3)
Cl(12)	0.2673 (4)	0.1325 (2)	0.5094 (3)
O(1)	0.1449 (7)	0.2558 (4)	0.7220 (5)
O(2)	-0.0084 (7)	0.2020 (4)	0.6758 (5)
O(3)	0.0824 (8)	0.1905 (4)	0.8576 (5)
O(4)	-0.0694 (8)	0.1364 (4)	0.8124 (5)
O(5)	0.2809 (7)	0.1229 (4)	0.8436 (6)
O(6)	0.1286 (7)	0.0666 (4)	0.8082 (5)
O(7)	0.2094 (7)	0.1395 (4)	0.6730 (5)
O(8)	0.0602 (7)	0.0801 (4)	0.6348 (5)
O(9)	0.3439 (7)	0.2341 (4)	0.8363 (6)
O(10)	-0.1362 (7)	0.0609 (4)	0.6768 (5)
N(1)	0.3622 (9)	0.2885 (5)	0.8205 (7)
N(2)	-0.2261 (8)	0.0567 (5)	0.7082 (6)
C(1)	0.0469 (13)	0.2481 (6)	0.6834 (9)
C(2)	-0.0053 (13)	0.3040 (7)	0.6402 (11)
C(3)	-0.0110 (13)	0.1718 (7)	0.8609 (8)
C(4)	-0.0660 (13)	0.1939 (9)	0.9299 (12)
C(5)	0.2214 (11)	0.0781 (6)	0.8488 (8)
C(6)	0.2681 (11)	0.0315 (6)	0.9115 (8)
C(7)	0.1558 (10)	0.1015 (5)	0.6291 (7)
C(8)	0.2129 (10)	0.0744 (6)	0.5624 (7)
C(9)	0.4341 (13)	0.3002 (6)	0.7577 (10)
C(10)	0.4142 (16)	0.3614 (8)	0.7281 (10)
C(11)	0.4165 (15)	0.4083 (7)	0.7932 (11)
C(12)	0.3294 (15)	0.3929 (7)	0.8416 (11)
C(13)	0.3364 (14)	0.3330 (7)	0.8807 (8)
C(14)	0.2294 (15)	0.3169 (8)	0.9054 (10)
C(15)	0.4402 (18)	0.3300 (10)	0.9549 (10)
C(16)	0.3956 (18)	0.2541 (8)	0.6849 (11)
C(17)	0.5564 (14)	0.2858 (9)	0.7974 (14)
C(18)	-0.3223 (11)	0.0955 (7)	0.6696 (9)
C(19)	-0.4070 (12)	0.1003 (10)	0.7267 (11)
C(20)	-0.4318 (14)	0.0420 (11)	0.7646 (12)
C(21)	-0.3251 (13)	0.0162 (7)	0.8113 (10)
C(22)	-0.2347 (11)	0.0058 (6)	0.7625 (8)
C(23)	-0.1195 (12)	-0.0039 (7)	0.8199 (10)
C(24)	-0.2651 (16)	-0.0515 (7)	0.7055 (12)
C(25)	-0.2775 (13)	0.1582 (8)	0.6544 (12)
C(26)	-0.3711 (14)	0.0637 (8)	0.5894 (9)

Cu-O(nitroxyl) bonds, which range from 1.942 (8) to 1.970 (4) Å. The remaining two equatorial bonds are longer for each copper atom, though details vary. In the tempo adduct, each metal atom has one long (ca. 2.3 Å) equatorial Cu-O bond and one that is shorter (2.055 (9) Å for Cu(1) and 2.129 (8) Å for Cu(2)). In the proxyl adduct, Cu(1) shows this pattern (Cu-O distances of 2.292 (4) and 2.045 (4) Å) but the two long equatorial distances for Cu(2) are nearly equal (2.159 (5) and 2.163 (5) Å).

The nitroxyl ligands bind to copper in a fashion very similar to that which has been found in the tempo adduct of Cu(F₆acac)₂²⁰ and in a hydrated dinuclear proxyl adduct of bis(trichloroacetato)copper(II).²⁷ In particular, all of these complexes display short (≤1.97 Å) Cu-O(nitroxyl) distances and near-perpendicular Cu-O-N and N-C-C planes. As has previously been observed in other complexes,^{20,27} the Cu-O-N angles are slightly greater in the proxyl adduct (126.0 (4) and 132.5 (4)°) than in the tempo complex (123.5 (7) and 123.9 (7)°).

The most significant difference between the structures of the two adducts involves the orientation of the coordinated nitroxyls with respect to the copper coordination polyhedra. In the tempo adduct, both Cu-O-N planes are approximately perpendicular (dihedral angles of 83.8 and 88.8°) to the plane defined by the

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Table III. Atomic Positional Parameters for the proxyl Adduct

atom	x	y	z
Cu(1)	0.6512 (0.9)	0.2877 (0.6)	0.8285 (0.4)
Cu(2)	0.3349 (0.9)	0.2295 (0.7)	0.6615 (0.4)
Cl(1)	0.6385 (3)	0.6482 (2)	0.8667 (1)
Cl(2)	0.3588 (3)	0.5983 (2)	0.7162 (2)
Cl(3)	0.6443 (3)	0.5981 (2)	0.7106 (2)
Cl(4)	0.5953 (2)	0.3405 (2)	0.5006 (1)
Cl(5)	0.8718 (2)	0.4001 (2)	0.6535 (1)
Cl(6)	0.7383 (4)	0.1835 (2)	0.5790 (2)
Cl(7)	0.0152 (4)	0.2233 (4)	0.7998 (3)
Cl(8)	0.2770 (4)	0.2289 (5)	0.9479 (2)
Cl(9)	0.1419 (6)	0.0513 (3)	0.8345 (3)
Cl(10)	0.4771 (4)	-0.1042 (2)	0.6551 (2)
Cl(11)	0.7392 (3)	-0.0529 (2)	0.8133 (2)
Cl(12)	0.4349 (4)	-0.0902 (2)	0.8020 (2)
N(1)	0.8076 (6)	0.3012 (4)	0.0122 (3)
N(2)	0.1266 (6)	0.2113 (4)	0.4870 (3)
O(1)	0.6392 (5)	0.4318 (3)	0.8325 (3)
O(2)	0.4121 (5)	0.3915 (3)	0.7192 (3)
O(3)	0.4288 (5)	0.2430 (4)	0.8436 (3)
O(4)	0.2164 (5)	0.2000 (4)	0.7220 (2)
O(5)	0.6531 (5)	0.1424 (3)	0.8191 (3)
O(6)	0.4370 (6)	0.0989 (3)	0.6991 (3)
O(7)	0.6824 (5)	0.2977 (3)	0.7238 (2)
O(8)	0.4609 (5)	0.2647 (4)	0.6058 (3)
O(9)	0.8110 (5)	0.3186 (3)	0.9446 (2)
O(10)	0.1419 (5)	0.1934 (4)	0.5584 (2)
C(1)	0.5259 (7)	0.4528 (5)	0.7744 (4)
C(2)	0.5394 (8)	0.5686 (5)	0.7688 (4)
C(3)	0.2885 (7)	0.2139 (5)	0.7992 (4)
C(4)	0.1834 (8)	0.1854 (6)	0.8429 (4)
C(5)	0.5453 (7)	0.0806 (5)	0.7566 (4)
C(6)	0.5545 (8)	-0.0360 (5)	0.7574 (5)
C(7)	0.6035 (7)	0.2877 (5)	0.6473 (4)
C(8)	0.6994 (8)	0.3044 (6)	0.5978 (4)
C(9)	0.8115 (9)	0.3875 (6)	0.0718 (4)
C(10)	0.8076 (12)	0.3232 (8)	0.1411 (5)
C(11)	0.8853 (12)	0.2357 (8)	0.1359 (5)
C(12)	0.8223 (9)	0.1990 (6)	0.0423 (4)
C(13)	0.6662 (11)	0.4285 (8)	0.0314 (5)
C(14)	0.9587 (12)	0.4700 (8)	0.0984 (6)
C(15)	0.9319 (11)	0.1551 (7)	0.0188 (6)
C(16)	0.6621 (10)	0.1262 (6)	0.0044 (5)
C(17)	0.1180 (10)	0.1300 (6)	0.4229 (4)
C(18)	0.1222 (12)	0.1965 (7)	0.3585 (5)
C(19)	0.0604 (14)	0.2848 (8)	0.3667 (5)
C(20)	0.0904 (9)	0.3079 (6)	0.4575 (4)
C(21)	0.2487 (14)	0.0783 (7)	0.4568 (6)
C(22)	-0.0408 (14)	0.0520 (9)	0.3903 (7)
C(23)	0.2220 (13)	0.3991 (7)	0.5087 (6)
C(24)	-0.0544 (7)	0.3231 (11)	0.4630 (9)

three equatorial oxygen atoms. In the proxyl adduct, one nitroxyl (bound to Cu(2)) has a similar orientation (dihedral angle 77.4°), but for the other proxyl the Cu-O-N plane is nearly parallel (dihedral angle 12.7°) to the equatorial plane. These differences are evident in Figures 1-3.

Within the coordinated nitroxyl radicals, the most significant structural feature is the N-O distance, which ranges from 1.257 (6) to 1.296 (12) Å. These values are similar to those observed in uncoordinated nitroxyls^{35,36} and in other nitroxyl complexes.^{19-22,24,27} Also in agreement with previous observations is the slightly greater displacement in the tempo ligand of the N atom from the plane defined by its three bonded atoms (0.110 and 0.121 Å), as compared to that in the proxyl ligand (0.062 and 0.070 Å). Other structural features of the coordinated nitroxyls are much as expected.

The long Cu-Cu separation in these dimers is reflected in the bond angles involving the bridging carboxylate ligands. The largest effect occurs for the Cu-O-C angles involving the equatorial

Table IV. Bond Distances for the tempo Adduct (Å)^a

(a) Copper Coordination Spheres			
Cu(1)-O(1)	1.917 (8)	Cu(2)-O(2)	2.289 (9)
Cl(1)-O(3)	2.302 (9)	Cu(2)-O(4)	1.896 (9)
Cu(1)-O(5)	1.905 (8)	Cu(2)-O(6)	2.129 (8)
Cu(1)-O(7)	2.055 (9)	Cu(2)-O(8)	1.920 (8)
Cu(1)-O(9)	1.942 (8)	Cu(2)-O(10)	1.950 (8)
Cu(1)...Cu(2)	3.256 (2)		
(b) Carboxylate Groups			
C(1)-O(1)	1.258 (16)	C(5)-O(5)	1.252 (14)
C(1)-O(2)	1.228 (15)	C(5)-O(6)	1.232 (13)
C(1)-C(2)	1.529 (19)	C(5)-C(6)	1.514 (17)
C(3)-O(3)	1.220 (15)	C(7)-O(7)	1.231 (13)
C(3)-O(4)	1.258 (15)	C(7)-O(8)	1.275 (13)
C(3)-C(4)	1.515 (20)	C(7)-C(8)	1.539 (16)
(c) tempo Ligands			
N(1)-O(9)	1.278 (12)	N(2)-O(10)	1.296 (12)
N(1)-C(9)	1.503 (18)	N(2)-C(18)	1.506 (16)
N(1)-C(13)	1.490 (17)	N(2)-C(22)	1.475 (16)
C(9)-C(10)	1.466 (21)	C(18)-C(19)	1.526 (21)
C(9)-C(16)	1.599 (21)	C(18)-C(25)	1.547 (21)
C(9)-C(17)	1.546 (23)	C(18)-C(26)	1.539 (20)
C(10)-C(11)	1.511 (23)	C(19)-C(20)	1.508 (26)
C(11)-C(12)	1.482 (23)	C(20)-C(21)	1.501 (23)
C(12)-C(13)	1.492 (22)	C(21)-C(22)	1.499 (19)
C(13)-C(14)	1.476 (21)	C(22)-C(23)	1.561 (19)
C(13)-C(15)	1.599 (22)	C(22)-C(24)	1.602 (21)

^aBond distances involving the CCl₃ groups are tabulated with the supplementary material.

Table V. Bond Distances for the proxyl Adduct (Å)^a

(a) Copper Coordination Sphere			
Cu(1)-O(1)	1.928 (4)	Cu(2)-O(2)	2.163 (5)
Cu(1)-O(3)	2.292 (4)	Cu(2)-O(4)	1.915 (4)
Cu(1)-O(5)	1.919 (4)	Cu(2)-O(6)	2.159 (5)
Cu(1)-O(7)	2.045 (4)	Cu(2)-O(8)	1.914 (4)
Cu(1)-O(9)	1.970 (4)	Cu(2)-O(10)	1.961 (4)
Cu(1)...Cu(2)	3.197 (2)		
(b) Carboxylate Groups			
C(1)-O(1)	1.257 (7)	C(5)-O(5)	1.268 (7)
C(1)-O(2)	1.230 (7)	C(5)-O(6)	1.209 (8)
C(1)-C(2)	1.527 (9)	C(5)-C(6)	1.560 (9)
C(3)-O(3)	1.234 (7)	C(7)-O(7)	1.247 (7)
C(3)-O(4)	1.246 (7)	C(7)-O(8)	1.242 (8)
C(3)-C(4)	1.554 (9)	C(7)-C(8)	1.547 (9)
(c) proxyl Ligands			
O(9)-N(1)	1.268 (6)	O(10)-N(2)	1.257 (6)
N(1)-C(9)	1.495 (9)	N(2)-C(17)	1.486 (9)
N(1)-C(12)	1.499 (9)	N(2)-C(20)	1.463 (9)
C(9)-C(10)	1.568 (11)	C(17)-C(18)	1.514 (10)
C(9)-C(13)	1.523 (12)	C(17)-C(21)	1.484 (13)
C(9)-C(14)	1.510 (12)	C(17)-C(22)	1.549 (12)
C(10)-C(11)	1.514 (14)	C(18)-C(19)	1.436 (13)
C(11)-C(12)	1.537 (10)	C(19)-C(20)	1.533 (10)
C(12)-C(15)	1.500 (12)	C(20)-C(23)	1.498 (12)
C(12)-C(16)	1.523 (11)	C(20)-C(24)	1.515 (12)

^aDistances within the trichloroacetate groups are tabulated with the supplementary material.

oxygen atoms, which gave an average value of 140.8°, substantially larger than the typical value of ca. 123° found in the classical copper(II) acetate structure.³⁴ The corresponding angles for the axial oxygen atoms are actually smaller than those in the usual dimeric structure, with a mean value of 117.6°. The O-C-O angles (mean value 128.3°) are slightly greater than the typical values of about 125° observed in copper(II) acetate. The O-C bond distances do not deviate significantly from their expected values.

Magnetic Results. Over the temperature range examined (6-300 K), all of the dimeric nitroxyl adducts are diamagnetic. Small paramagnetic susceptibilities at low temperatures are presumably a consequence of the presence of small amounts of

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Table VI. Bond Angles for the tempo Adduct (deg)^a

(a) Copper Coordination Spheres			
O(1)-Cu(1)-O(3)	86.8 (4)	O(2)-Cu(2)-O(4)	88.0 (4)
O(1)-Cu(1)-O(5)	172.9 (4)	O(2)-Cu(2)-O(6)	126.5 (3)
O(1)-Cu(1)-O(7)	93.3 (4)	O(2)-Cu(2)-O(8)	89.6 (4)
O(1)-Cu(1)-O(9)	94.6 (4)	O(2)-Cu(2)-O(10)	112.5 (4)
O(3)-Cu(1)-O(5)	86.3 (4)	O(4)-Cu(2)-O(6)	91.2 (4)
O(3)-Cu(1)-O(7)	124.8 (4)	O(4)-Cu(2)-O(8)	177.6 (4)
O(3)-Cu(1)-O(9)	106.1 (4)	O(4)-Cu(2)-O(10)	94.6 (4)
O(5)-Cu(1)-O(7)	91.9 (4)	O(6)-Cu(2)-O(8)	90.5 (3)
O(5)-Cu(1)-O(9)	85.9 (4)	O(6)-Cu(2)-O(10)	120.9 (4)
O(7)-Cu(1)-O(9)	128.9 (4)	O(8)-Cu(2)-O(10)	86.0 (3)
(b) Carboxylate Groups			
Cu(1)-O(1)-C(1)	117.1 (8)	Cu(1)-O(5)-C(5)	119.2 (8)
Cu(2)-O(2)-C(1)	140.8 (9)	Cu(2)-O(6)-C(5)	141.2 (9)
Cu(1)-O(3)-C(3)	142.1 (8)	Cu(1)-O(7)-C(7)	145.1 (8)
Cu(2)-O(4)-C(3)	116.9 (9)	Cu(2)-O(8)-C(7)	116.6 (8)
O(1)-C(1)-O(2)	128.2 (12)	O(5)-C(5)-O(6)	127.7 (12)
O(1)-C(1)-C(2)	113.6 (13)	O(5)-C(5)-C(6)	117.1 (1)
O(2)-C(1)-C(2)	118.2 (13)	O(6)-C(5)-C(6)	115.2 (12)
O(3)-C(3)-O(4)	127.5 (12)	O(7)-C(7)-O(8)	127.3 (11)
O(3)-C(3)-C(4)	117.6 (13)	O(7)-C(7)-C(8)	116.5 (11)
O(4)-C(3)-C(4)	114.9 (13)	O(8)-C(7)-C(8)	116.1 (11)
(c) tempo Ligands			
Cu(1)-O(9)-N(1)	123.5 (7)	Cu(2)-O(10)-N(2)	123.9 (7)
O(9)-N(1)-C(9)	117.1 (11)	O(10)-N(2)-C(18)	115.4 (10)
O(9)-N(1)-C(13)	115.9 (11)	O(10)-N(2)-C(22)	117.6 (10)
C(9)-N(1)-C(13)	125.0 (11)	C(18)-N(2)-C(22)	125.2 (10)
N(1)-C(9)-C(10)	108.5 (13)	N(2)-C(18)-C(19)	109.3 (12)
N(1)-C(9)-C(16)	106.9 (11)	N(2)-C(18)-C(25)	109.2 (10)
N(1)-C(9)-C(17)	107.4 (14)	N(2)-C(18)-C(26)	104.4 (12)
C(10)-C(9)-C(16)	110.1 (14)	C(19)-C(18)-C(25)	109.6 (15)
C(10)-C(9)-C(17)	115.2 (14)	C(19)-C(18)-C(26)	112.3 (12)
C(16)-C(9)-C(17)	108.4 (14)	C(25)-C(18)-C(26)	111.8 (13)
C(9)-C(10)-C(11)	115.6 (14)	C(18)-C(19)-C(20)	114.2 (15)
C(10)-C(11)-C(12)	107.8 (13)	C(19)-C(20)-C(21)	109.5 (13)
C(11)-C(12)-C(13)	117.4 (14)	C(20)-C(21)-C(22)	115.2 (14)
N(1)-C(13)-C(12)	108.1 (12)	N(2)-C(22)-C(21)	110.7 (12)
N(1)-C(13)-C(14)	109.1 (12)	N(2)-C(22)-C(23)	109.3 (10)
N(1)-C(13)-C(15)	105.2 (14)	N(2)-C(22)-C(24)	107.0 (12)
C(12)-C(13)-C(14)	111.1 (16)	C(21)-C(22)-C(23)	110.5 (12)
C(12)-C(13)-C(15)	110.6 (14)	C(21)-C(22)-C(24)	109.6 (12)
C(14)-C(13)-C(15)	112.5 (14)	C(23)-C(22)-C(24)	109.7 (13)

^a Bond angles involving the CCl₃ groups are tabulated with the supplementary material.

paramagnetic impurities, a common occurrence in dimeric copper(II) complexes with singlet ground states. Impurity concentrations no greater than 1% would account for the observed susceptibilities.

Discussion

The four nitroxyl complexes prepared and characterized in this study, together with analogous systems recently reported by Sharrock and Melnik,³⁷ demonstrate that the formation of nitroxyl adducts by the copper(II) trihalocarboxylates is quite general. The presence of one or more halogen substituents appears to be necessary, as no nitroxyl-containing product could be obtained when unsubstituted copper(II) acetate was employed. The monoadduct stoichiometries of the adducts, together with their diamagnetism, strongly suggest that all are dimeric.

Although trigonal-bipyramidal Cu(II) is not unknown, we are aware of only one other dimeric carboxylate adduct in which the copper ions adopt this configuration.³⁸ In that complex, the pyridine monoadduct of copper(II) phenylacetate, the copper coordination polyhedra are oriented similarly to those we observe and somewhat similar bond distance patterns are found. The angular distortions from ideal trigonal-bipyramidal symmetry are, however, considerably greater than those we find. All other

Table VII. Bond Angles for the proxyl Adduct (deg)^a

(a) Copper Coordination Sphere			
O(1)-Cu(1)-O(3)	102.1 (2)	O(2)-Cu(2)-O(4)	90.7 (2)
O(1)-Cu(1)-O(5)	176.9 (2)	O(2)-Cu(2)-O(6)	130.2 (2)
O(1)-Cu(1)-O(7)	88.2 (2)	O(2)-Cu(2)-O(8)	86.7 (2)
O(1)-Cu(1)-O(9)	90.2 (2)	O(2)-Cu(2)-O(10)	115.9 (2)
O(3)-Cu(1)-O(5)	88.0 (2)	O(4)-Cu(2)-O(6)	90.4 (2)
O(3)-Cu(1)-O(7)	130.3 (2)	O(4)-Cu(2)-O(8)	177.0 (2)
O(3)-Cu(1)-O(9)	102.1 (2)	O(4)-Cu(2)-O(10)	88.8 (2)
O(5)-Cu(1)-O(7)	90.5 (2)	O(6)-Cu(2)-O(8)	90.2 (2)
O(5)-Cu(1)-O(9)	92.8 (2)	O(6)-Cu(2)-O(10)	114.0 (2)
O(7)-Cu(1)-O(9)	127.6 (2)	O(8)-Cu(2)-O(10)	93.7 (2)
(b) Carboxylate Groups			
Cu(1)-O(1)-C(1)	116.8 (4)	Cu(1)-O(5)-C(5)	118.1 (4)
Cu(2)-O(2)-C(1)	140.5 (4)	Cu(2)-O(6)-C(5)	138.7 (4)
Cu(1)-O(3)-C(3)	138.4 (4)	Cu(1)-O(7)-C(7)	139.2 (4)
Cu(2)-O(4)-C(3)	117.2 (4)	Cu(2)-O(8)-C(7)	118.6 (4)
O(1)-C(1)-O(2)	128.0 (6)	O(5)-C(5)-O(6)	129.4 (6)
O(1)-C(1)-C(2)	115.0 (5)	O(5)-C(5)-C(6)	113.7 (6)
O(2)-C(1)-C(2)	116.8 (6)	O(6)-C(5)-C(6)	116.9 (6)
O(3)-C(3)-O(4)	129.0 (6)	O(7)-C(7)-O(8)	129.5 (6)
O(3)-C(3)-C(4)	117.3 (5)	O(7)-C(7)-C(8)	114.3 (6)
O(4)-C(3)-C(4)	113.6 (5)	O(8)-C(7)-C(8)	116.2 (5)
(c) proxyl Ligands			
Cu(1)-O(9)-N(1)	132.5 (4)	Cu(2)-O(10)-N(2)	126.0 (4)
O(9)-N(1)-C(9)	120.7 (5)	O(10)-N(2)-C(17)	122.6 (6)
O(9)-N(1)-C(12)	122.5 (6)	O(10)-N(2)-C(20)	121.9 (6)
N(1)-C(9)-C(10)	98.5 (6)	N(2)-C(17)-C(18)	99.7 (6)
N(1)-C(9)-C(13)	109.2 (6)	N(2)-C(17)-C(21)	111.3 (6)
N(1)-C(9)-C(14)	108.7 (7)	N(2)-C(17)-C(22)	107.4 (8)
C(10)-C(9)-C(13)	111.6 (7)	C(18)-C(17)-C(21)	114.4 (8)
C(10)-C(9)-C(14)	114.4 (7)	C(18)-C(17)-C(22)	110.8 (8)
C(13)-C(9)-C(14)	113.3 (8)	C(21)-C(17)-C(22)	112.4 (9)
C(9)-C(10)-C(11)	105.6 (11)	O(17)-C(18)-C(19)	108.9 (7)
C(10)-C(11)-C(12)	104.0 (7)	C(18)-C(19)-C(20)	107.3 (7)
N(1)-C(12)-C(11)	99.6 (6)	N(2)-C(20)-C(19)	101.7 (6)
N(1)-C(12)-C(15)	109.5 (6)	N(2)-C(20)-C(23)	110.3 (6)
N(1)-C(12)-C(16)	108.2 (6)	N(2)-C(20)-C(24)	109.7 (8)
C(11)-C(12)-C(15)	113.9 (7)	C(19)-C(20)-C(23)	114.6 (8)
C(11)-C(12)-C(16)	112.9 (7)	C(19)-C(20)-C(24)	110.6 (8)
C(15)-C(12)-C(16)	111.9 (7)	C(23)-C(20)-C(24)	109.7 (9)

^a Bond angles involving the CCl₃ groups are tabulated with the supplementary material.

dimeric copper(II) carboxylate monoadducts have the well-known copper(II) acetate structure with square-pyramidal coordination about copper. The present results document the extreme flexibility of the tetrakis(carboxylato)dimeral framework that is characteristic of this structure type.^{34,39}

In the consideration of possible reasons for the adoption of this unusual copper coordination geometry, the obvious factor that comes to mind is steric crowding between the nitroxyl methyl groups and the carboxylate oxygen atoms. Examination of intramolecular contacts shows that there is indeed significant crowding. The sum of the van der Waals radii of a methyl group and an oxygen atom is 3.4 Å,⁴⁰ all contacts close to or shorter than this value are shown in Figure 3, which illustrates the three different geometries of nitroxyl coordination found in the two adducts.

The two nitroxyl ligands in the tempo adduct show very similar patterns of nonbonded contacts, one of which is illustrated in Figure 3a. Two methyl groups are involved, each of which has a short interaction with one of the equatorial carboxylate oxygens and both of which have a close contact with the same axial oxygen atom, O(4). The latter interactions are actually somewhat shorter (3.22 (2) and 3.34 (2) Å vs. 3.44 (2) and 3.37 (2) Å). A qualitatively similar pattern is found for the nitroxyl ligand bound to Cu(2) in the proxyl adduct (Figure 3c), but with one much longer

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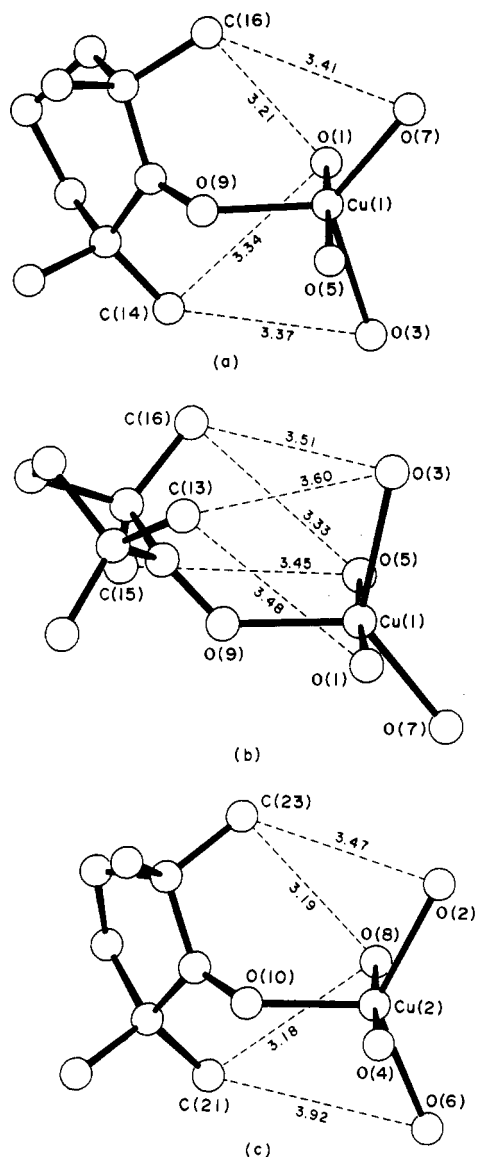


Figure 3. Intramolecular contacts between methyl group carbon atoms and carboxylate oxygen atoms: (a) Cu(1) of the tempo adduct; (b) Cu(1) of the proxyl adduct; (c) Cu(2) of the proxyl adduct. The pattern of contacts for Cu(2) of the tempo adduct closely resembles that shown in (a).

C–O(equatorial) contact of 3.923 (12) Å. The C–O(axial) distances of 3.178 (10) and 3.194 (10) Å are actually shorter than those in the tempo adduct. Finally, the other proxyl ligand (Figure 3b) is in a quite different environment, with three methyl carbons involved in close C–O contacts, but with only one of these contacts <3.4 Å. The overall pattern that emerges from consideration of nonbonded interactions is one of a high degree of steric crowding, which may well play a deciding role in determining the copper coordination geometry. However, the situation is sufficiently complex that no single type of contact can be identified as critical.

The shortest bonds in each of the four copper coordination polyhedra are those to the axial oxygen atoms. This is consistent with the usual pattern for d^9 metal ions in a trigonal-bipyramidal environment.^{41–43} Almost as short as the axial Cu–O bonds are the equatorial Cu–O(nitroxyl) distances. Comparably short distances have been observed in two other copper(II) complexes of nitroxyl ligands,^{20,27} though in three other cases much longer Cu–O(nitroxyl) bonds are found.^{19,44,45} The equatorial Cu–O-

(carboxylate) distances are all longer, and in some cases much longer, than the comparable distances in the conventional bridged dimer structure.³⁴

These adducts are clearly best regarded as Cu(II) complexes of free radical ligands, rather than as species in which the nitroxyl has undergone formal oxidation or reduction. The structural details of the tempo and proxyl ligands are virtually identical with those of analogous noncoordinated radicals. Particularly pertinent are the N–O distances of ca. 1.27 Å and the magnitude of the deviations of the N atoms from planarity, both of which are characteristic of nitroxyl radicals.^{35,36} Also, the structural results clearly imply the presence of divalent copper and uninegative carboxylates, both consistent with description of the nitroxyls as coordinated free radicals.

The geometry of the metal–nitroxyl binding in this and related complexes is not easily explicable on the basis of simple localized bonding models. In the usual description of the electronic structure of nitroxyl radicals, the odd electron is considered to occupy an orbital of π^* symmetry with respect to the N–O bond. The oxygen lone pairs would then be found in the nodal plane of this π system. Binding to copper via one of these lone pairs would require the Cu–O–N and C–N–C planes to be approximately parallel (with a small deviation arising from the nonplanarity of N). This is at variance with the observed dihedral angles between these planes, which range from 79.3 to 85.6°. An alternative bonding model, consistent with the observed dihedral angles and with the diamagnetism of these adducts, is one in which the Cu–O bond is a result of pairing of the copper and nitroxyl odd electrons. One might infer that such a bonding description would predict a shortening of the N–O bond distance as a consequence of the formal transfer of an electron from an N–O π^* orbital to the Cu–O bond; however, there is no basis upon which to estimate the expected magnitude of such an effect. In any event, no such shortening is observed in these or other metal–nitroxyl complexes.

The observed diamagnetism of these two dimers is consistent with the magnetic properties of the two other copper–nitroxyl complexes which have been shown to have short (~ 1.95 Å) Cu–O(nitroxyl) bonds.^{8,20,27} In all four of these molecules, the geometry of the metal–nitroxyl linkage is appropriate to permit direct overlap between copper and nitroxyl magnetic orbitals. In the present case, one of these interactions (Figure 3b) would involve overlap of the nitroxyl π^* orbital with the “belt” of the copper d_{z^2} orbital, while for the other three coppers (Figure 3a,c) the extended lobes of the d_{z^2} orbital would be involved. The magnitude of the splitting resulting from this interaction must be at least great enough to prevent significant population of any spin-free states at 300 K. Beyond this constraint, there is no firm evidence on the strength of the spin coupling interaction.

There is another group of copper–nitroxyl complexes, which have structures and magnetic properties distinctly different from those reported here. The most thoroughly studied of these is Cu(F₆acac)₂(tempol) (tempol = 4-OH-tempo), which has a linear-chain structure with tetragonal six-coordinate copper(II) ions and a long axial Cu–O(nitroxyl) distance of 2.439 (6) Å.¹⁹ Magnetically, this material behaves as an alternating linear chain, with ferromagnetic and antiferromagnetic interactions, both much weaker than those in systems with short Cu–O bonds.^{46,47} A qualitatively similar situation is found in a copper(II) complex of a nitroxyl keto ester.⁴⁴ The qualitative differences in magnetic properties of these two types of copper–nitroxyl complexes can be understood on the basis of simple orbital overlap considerations.²⁰

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magnetometer, which was purchased with the aid of a grant from the National Science Foundation.

Registry No. [Cu(O₂CCF₃)₂(tempo)]₂, 100021-75-8; [Cu(O₂CCCl₃)₂(tempo)]₂, 100021-76-9; [Cu(O₂CCBr₃)₂(tempo)]₂, 100045-

26-9; [Cu(O₂CCl₃)₂(proxyl)]₂, 100021-77-0.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, distances and angles within the CCl₃ groups, and hydrogen atom coordinates (53 pages). Ordering information is given on any current masthead page.

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Binding of Pt(NH₃)₃²⁺ to Nucleic Acid Bases

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The ab initio SCF energies for Pt(NH₃)₃²⁺ binding to guanine, adenine, cytosine, and thymine are calculated. A relativistic effective potential is used to represent the core electrons of Pt, and compact effective potentials are also used to replace the core electrons in carbon, nitrogen, and oxygen to simplify the calculation of these large molecules. In order to analyze the bonding, SCF calculations were also done for H₂O, NH₃, imidazole, pyrimidine, 2- and 4-pyrimidone, and several deprotonated anions. The binding is calculated to have a large electrostatic component, but there is a significant contribution from polarization of the base. The valence-all-electron binding energies can be reproduced by an SCF energy for a system where the Pt(NH₃)₃²⁺ complex is replaced by an effective point charge, Z_{eff}. The binding order for all the sites on the nucleic acid bases was calculated by this means after checking the accuracy with all-valence-electron calculations on binding to the N7 and O6 sites on guanine. Force constants were calculated for one-dimensional energy curves between Pt(NH₃)₃²⁺ and selected bases. Valence-all-electron SCF calculations were used to show that chelate bonding of the N7 and O6 sites of guanine to either Pt(NH₃)₂²⁺ or Pt(NH₃)₃²⁺ is unlikely to compete with intrastrand binding of the N7 sites on neighboring guanines.

Introduction

The interest in platinum amines binding to the purine and pyrimidine bases has been inspired by the antitumor properties of these complexes.¹ One of the main goals of such studies is to determine the binding site preferences of the *cis*-Pt(NH₃)₂²⁺ (PDA) moiety. At this time neither the PDA-base bond energies nor even a stability order of binding to different base sites is experimentally available,² although a number of monofunctional binding sites have been identified in model systems. Binding is observed to the neutral bases guanine (G), adenine (A), cytosine (C),³ and thymine (T),⁴ as well as to the deprotonated anions.^{3,5} The N7 site on guanine, G(N7), has been identified as a preferred site.⁶ An intramolecular chelate of the N7 and O6 sites of guanine with PDA has also been proposed,^{7,8} although the binding to G(O6) may be through a hydrogen bond.⁹

Quantum-mechanical calculations of the bond energies for Pt-base binding permit an analysis of the type of bonding and competition among the available sites. Binding of PDA to two heterocyclic bases would result in a large and expensive calculation. Since at least three nitrogen sites are bound to Pt in all cases considered, the binding of a single base to Pt(NH₃)₃²⁺ (PTA) was considered a suitable model. This paper will report the details of the electronic structure and interaction energies of the PTA complex interacting with a number of model bases and the nucleic acid bases G, C, A, and T. In addition, the possibility of PDA chelate binding to guanine is examined. An ab initio calculation of the binding of metal cations such as Zn²⁺ to nucleic acid bases has shown that the preferred binding sites can be correctly identified in the free bases.¹⁰

Relativistic effective potentials (REP)¹¹ are used to simplify the calculations by eliminating the core electrons. The REP also allow the incorporation of relativistic effects on the valence electrons,¹² which are important in a heavy element like Pt. In addition, the valence-electron basis set for carbon and nitrogen can be compact but still reasonably accurate since they are nodeless.¹³ Interaction energy curves for the binding of H₂O, NH₃, imidazole, pyrimidine, 1,2- and 1,4-pyrimidone, guanine, cytosine, adenine, thymine, and several deprotonated species like

Table I. Binding of Pt(NH₃)₃²⁺ to Bases

base	R _e , Å	D _e , kcal/mol				ω _e , cm ⁻¹
		SCF		ΔE(pol)		
		VAL ^a	EFF ^b			
NH ₃	2.07 ₅	72				
H ₂ O	2.06 ₀	56.5			560	
OH ⁻	1.90 ₉	297			870	
imidazole (ImH)	1.98 ₇	100.5	101.5	33.1	387	
Im ⁻	1.94 ₀	262			430	
pyrimidine	2.00 ₉	83	85.0	32.8	351	
2-pyrimidone (O)	2.00	84		22.6		
2-pyrimidone (N)	2.00	99.5				
4-pyrimidone (O) (4-PyH)	2.01 ₅	77	77.3	23.5	303	
4-Py ⁻	1.91 ₂	237			372	
guanine (N7)	2.00	114	117	37.1		
guanine (O6)	2.00	93	95	25.1		
guanine (N3)	2.00		74			
adenine (N1)	2.00		87			
adenine (N3)	2.00		88			
adenine (N7)	2.00		81			
cytosine (N3)	2.00		104			
cytosine (O2)	2.00		101			
thymine (O2)	2.00		70			
thymine (O4)	2.00		73			

^a Obtained by using all valence electrons. ^b Obtained by using an effective point charge (*q* = 1.25) to replace Pt(NH₃)₃²⁺.

OH⁻ to the PTA square-planar complex are obtained in self-consistent-field (SCF) molecular orbital calculations with the

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