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Magnetic Properties and Crystal Structure of an Acetate-Bridged Ferromagnetic Copper(II) Dimer

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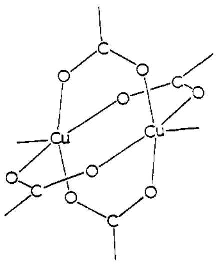
The synthesis, crystal structure, and magnetic properties are reported for an unusual acetate-bridged copper(II) dimer. In the complex $[Cu(L)CH_3COO]_2\cdot H_2O\cdot C_2H_5OH$, where LH = *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine, the two coppers are connected by a single atom bridge through the acetate oxygen. The dimer is not centrosymmetric, and therefore the two Cu–O–Cu bridges are dissimilar. The pathways consist of a large (antiferromagnetic) and a small (ferromagnetic) bridging angle. Although a net antiferromagnetism is predicted, a ferromagnetic interaction is observed from magnetic susceptibility measurements. The reasons for this are discussed. The $\Delta M_s = 2$ transition was observed in the EPR spectra at 77 and 4 K. Magnetic data are $g = 2.078$ and $J = 0.63$ cm^{-1}. Crystal data are as follows: space group $P2_1/n$, $Z = 4$, $a = 10.587$ (3) Å, $b = 16.972$ (8) Å, $c = 18.432$ (6) Å, $\beta = 97.37$ (2)°, $V = 3285$ Å^3, $R = 5.2\%$ after full-matrix least-squares refinement of 3472 intensities, collected by counter methods.

Introduction

Acetate bridging between transition-metal atoms is well-known in complexes such as copper(II) acetate hydrate (**1**),[2,3]



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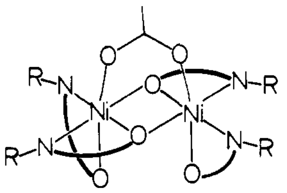

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its its analogues with other metal ions,[4-8] and the anion in $[Ni_2(N\text{-R-salicylaldimine})_4CH_3COO]^-C_5H_{10}NH_2^+$ (**2**).[9] The mode of bridging in **1** and **2** links adjacent metal atoms via the two different acetate oxygen atoms, to form a three-atom bridge. This bridging normally results in substantial antiferromagnetic interactions between the metal atoms if these have unpaired d electrons. We report here the magnetic and structural properties of a new complex containing a one-atom bridge via one of the oxygen atoms of an acetate ligand.

For one-atom bridges between paramagnetic transition-metal atoms, the magnetic interactions have been related to the magnitude of the bridging angle (ϕ)[10-27] and other structural features.[27-33] This has been especially studied for oxygen-bridged metal atoms such as Cu–O–Cu. Small ϕ angles near 96° should lead to strong ferromagnetic interactions, while larger values should make the interaction increasingly strongly antiferromagnetic.[14] An increasingly antiferromagnetic trend should also be produced by significantly smaller ϕ values, though these may be experimentally unattainable.[34] The title complex has both a large ("antiferromagnetic") and small ("ferromagnetic") bridging angle. The small angle is subtended by a less strongly bonded bridging oxygen, so that the ferromagnetic contribution should be less significant, yet the complex is ferromagnetic.

Experimental Section

Preparation of the Complex. Crystals of the complex $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2\cdot H_2O\cdot C_2H_5OH$, where *N*-Me$_2$EtOHSal represents the ligand *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine deprotonated at the phenolic oxygen atom, were obtained as a reaction intermediate in the synthesis of a tetranuclear copper(II) complex.[9] One of these crystals was selected for X-ray analysis.

Crystal Data for $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2\cdot H_2O\cdot C_2H_5OH$: $Cu_2O_{10}N_2C_{28}H_{42}$, mol wt 692, dark green crystal, space group $P2_1/n$, $Z = 4$, $a = 10.587$ (3) Å, $b = 16.972$ (8) Å, $c = 18.432$ (6) Å, $\beta = 97.37$ (2)°, $V = 3285$ Å^3, $\rho_{calcd} = 1.40$ g cm^{-3}, $\rho_{obsd} = 1.31$ g cm^{-3}, μ(Mo Kα) = 14.0 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (101) 0.13, (101) 0.13, (010) 0.31, (010) 0.31, (001) 0.21, (001) 0.21; maximum, minimum transmission coefficients 0.88, 0.53.

Crystal dimensions and space group data were obtained by standard

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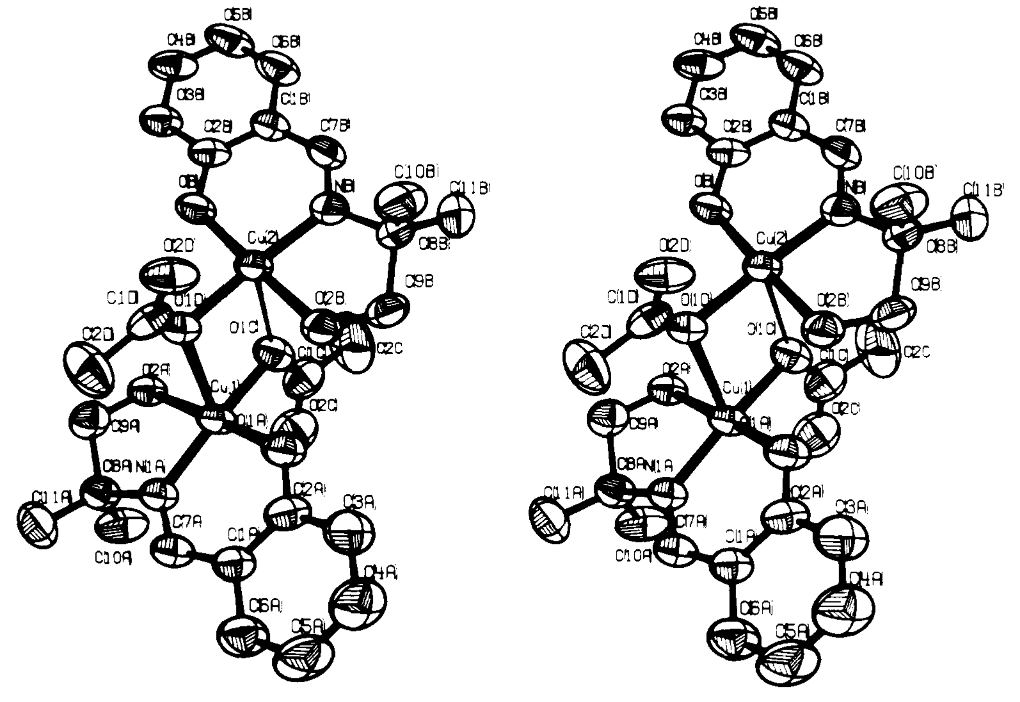

Figure 1.

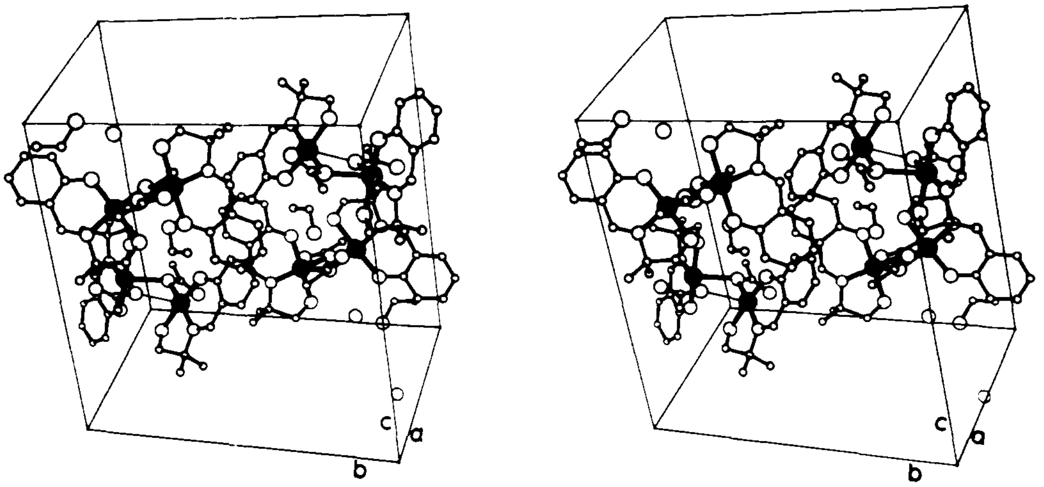

Figure 2.

methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used with Mo Kα radiation, as previously described,[35] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 44°$. Scan widths were calculated as ($A + B \tan\theta$), where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.35°, respectively.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 3994 independent intensities, there were 3472 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[36] These data were used in the final refinement of the structural parameters.

Structure Determination. The positions of the two independent copper atoms were determined from three-dimensional Patterson functions calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the other nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[35] Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference syntheses permitted location of the hydrogen atoms which were included in the refinement for three cycles of least-squares refinement and then held fixed. The methyl carbon of the ethanol molecule is disordered over two positions with 53 and 47% occupancy (C(2) and C(2′), respectively). The model converged with $R = 5.2\%$ and $R_w = 6.7\%$, with changes in parameters in the last cycle being 0.20 or less. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 6.0\%$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors are available.[36] The principal programs used are as previously described.[35]

Magnetic Measurements. Low-temperature magnetic susceptibilities (4–200 K) were determined with use of a superconducting SQUID susceptometer. Calibration and measuring techniques are described elsewhere.[38,39]

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.02191 (6)	0.43131 (3)	0.18981 (3)	5.04 (3)	2.63 (2)	3.52 (3)	−0.64 (2)	0.49 (2)	−0.08 (2)
Cu(2)	0.00041 (5)	0.24280 (3)	0.25647 (3)	4.79 (3)	2.64 (2)	3.64 (3)	−0.34 (2)	0.94 (2)	0.04 (2)
O(1A)	−0.0083 (3)	0.4552 (2)	0.2882 (2)	6.9 (2)	3.3 (1)	4.2 (1)	−1.1 (1)	1.8 (1)	−0.3 (1)
O(1B)	0.0400 (3)	0.1726 (2)	0.1831 (2)	6.5 (2)	3.6 (1)	4.5 (2)	−1.3 (1)	2.0 (1)	−0.7 (1)
O(1C)	−0.1213 (3)	0.3579 (2)	0.1794 (2)	5.2 (2)	3.8 (2)	5.5 (2)	−0.9 (1)	0.4 (1)	−0.1 (1)
O(1D)	0.1374 (3)	0.3131 (2)	0.2360 (2)	4.6 (1)	2.7 (1)	4.0 (1)	−0.2 (1)	0.2 (1)	0.4 (1)
O(2A)	0.0693 (3)	0.4042 (2)	0.0913 (2)	5.9 (2)	3.2 (1)	3.4 (1)	−0.7 (1)	0.5 (1)	−0.2 (1)
O(2B)	−0.0412 (3)	0.3129 (2)	0.3377 (2)	6.2 (2)	3.6 (2)	4.4 (2)	−0.1 (1)	1.8 (1)	0.1 (1)
O(2D)	0.2457 (4)	0.2454 (2)	0.3256 (2)	8.0 (2)	3.7 (2)	5.0 (2)	0.4 (2)	−0.7 (2)	0.9 (1)
O(2C)	−0.2119 (4)	0.4665 (3)	0.1349 (3)	7.4 (2)	7.1 (2)	7.3 (2)	1.8 (2)	0.3 (2)	0.2 (2)
O(1)	−0.4181 (4)	0.2427 (2)	−0.4430 (2)	8.5 (2)	3.7 (2)	5.3 (2)	0.5 (2)	1.0 (2)	0.5 (1)
N(A)	0.1463 (4)	0.5143 (2)	0.1858 (2)	4.7 (2)	3.1 (2)	3.2 (2)	−0.4 (1)	0.4 (1)	−0.2 (1)
N(B)	−0.1323 (4)	0.1776 (2)	0.2881 (2)	4.7 (2)	3.0 (2)	4.7 (2)	0.0 (1)	1.2 (2)	0.8 (2)
C(1A)	0.1166 (5)	0.5741 (3)	0.3021 (3)	5.3 (2)	3.0 (2)	3.5 (2)	−0.1 (2)	0.4 (2)	−0.3 (2)
C(2A)	0.0343 (5)	0.5190 (3)	0.3271 (3)	5.9 (2)	3.4 (2)	3.4 (2)	0.1 (2)	0.7 (2)	−0.2 (2)
C(3A)	−0.0061 (7)	0.5315 (4)	0.3951 (3)	9.4 (3)	5.8 (3)	4.7 (3)	−1.4 (3)	2.6 (2)	−0.3 (3)
C(4A)	0.0326 (7)	0.5957 (4)	0.4363 (3)	10.9 (4)	6.0 (3)	4.5 (3)	−1.0 (3)	2.8 (3)	−1.2 (3)
C(5A)	0.1136 (7)	0.6504 (4)	0.4128 (3)	10.5 (4)	5.8 (3)	4.8 (3)	−1.0 (3)	1.6 (3)	−2.6 (2)
C(6A)	0.1549 (6)	0.6399 (3)	0.3457 (3)	7.6 (3)	4.5 (3)	4.7 (3)	−1.3 (2)	1.2 (2)	−1.0 (2)
C(7A)	0.1695 (5)	0.5682 (3)	0.2331 (3)	5.2 (2)	2.8 (2)	4.1 (2)	−0.4 (2)	0.2 (2)	−0.0 (2)
C(8A)	0.2009 (5)	0.5192 (3)	0.1148 (3)	5.9 (2)	3.8 (2)	3.5 (2)	−1.2 (2)	1.1 (2)	−0.4 (2)
C(9A)	0.1932 (5)	0.4356 (3)	0.0839 (3)	6.3 (3)	4.4 (3)	4.0 (2)	−0.4 (2)	1.3 (2)	−0.9 (2)
C(10A)	0.1113 (7)	0.5743 (3)	0.0646 (3)	10.2 (4)	3.9 (3)	4.1 (3)	−0.0 (3)	0.1 (3)	0.9 (2)
C(11A)	0.3398 (2)	0.5469 (8)	0.1236 (7)	6.4 (2)	7.2 (6)	7.1 (5)	−2.8 (1)	2.6 (2)	−1.9 (2)
C(1B)	−0.1116 (5)	0.0713 (3)	0.2033 (3)	5.4 (2)	3.0 (2)	4.3 (2)	−0.7 (2)	0.4 (2)	0.3 (2)
C(2B)	−0.0121 (5)	0.1025 (3)	0.1672 (3)	5.3 (2)	2.7 (2)	3.7 (2)	−0.6 (2)	0.3 (2)	0.1 (2)
C(3B)	0.0359 (6)	0.0579 (3)	0.1136 (3)	7.8 (3)	3.5 (2)	4.3 (2)	−0.9 (2)	1.5 (2)	−0.5 (2)
C(4B)	−0.0151 (7)	−0.0153 (3)	0.0942 (3)	10.2 (4)	3.3 (2)	4.2 (2)	−0.4 (3)	1.2 (3)	−1.0 (2)
C(5B)	−0.1123 (2)	−0.0454 (7)	0.1268 (7)	10.0 (2)	3.9 (8)	5.6 (5)	−3.0 (1)	1.6 (3)	−1.1 (1)
C(6B)	−0.1599 (2)	−0.0038 (7)	0.1798 (7)	6.7 (2)	3.9 (7)	6.9 (4)	−1.9 (1)	1.2 (2)	−0.4 (1)
C(7B)	−0.1659 (5)	0.1091 (3)	0.2609 (3)	4.0 (2)	3.2 (2)	5.4 (3)	−0.6 (2)	1.0 (2)	1.0 (2)
C(8B)	−0.1886 (5)	0.2081 (3)	0.3525 (3)	6.4 (2)	3.2 (2)	5.7 (3)	0.3 (2)	2.8 (2)	0.1 (2)
C(9B)	−0.1701 (6)	0.2967 (3)	0.3504 (3)	7.0 (3)	3.6 (2)	5.8 (3)	1.0 (2)	2.2 (2)	0.2 (2)
C(10B)	−0.1139 (7)	0.1726 (4)	0.4212 (3)	12.2 (4)	4.4 (3)	4.9 (3)	1.9 (3)	3.6 (3)	1.3 (2)
C(11B)	−0.3323 (6)	0.1916 (4)	0.3485 (4)	6.3 (3)	6.6 (4)	12.0 (5)	−0.5 (3)	5.0 (3)	−0.2 (4)
C(1D)[b]	0.2401 (5)	0.2981 (3)	0.2789 (3)	4.9 (2)	3.4 (2)	4.2 (2)	0.6 (2)	0.2 (2)	−0.9 (2)
C(2D)[b]	0.3546 (6)	0.3485 (4)	0.2691 (4)	4.8 (3)	7.9 (4)	9.6 (4)	−2.1 (3)	−0.6 (3)	2.2 (4)
C(1C)[c]	−0.2184 (6)	0.3971 (4)	0.1524 (3)	5.9 (3)	5.8 (3)	5.3 (3)	−0.4 (2)	0.8 (2)	−1.0 (3)
C(2C)[c]	−0.3483 (7)	0.3566 (7)	0.1431 (6)	5.8 (3)	15.8 (7)	11.8 (6)	−3.8 (4)	−0.4 (4)	0.4 (6)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(1)	−0.214 (1)	0.1741 (7)	−0.0082 (6)	12.3 (3)	H(92A)	0.205 (5)	0.439 (3)	0.034 (3)	6 (1)
C(2)	−0.255 (2)	0.2289 (15)	0.0220 (14)	14.4 (7)	H(3B)	0.110 (4)	0.072 (3)	0.090 (3)	4 (1)
C(2′)	−0.268 (2)	0.1056 (17)	−0.0433 (16)	13.7 (8)	H(4B)	0.016 (4)	−0.045 (3)	0.062 (2)	5 (1)
O(2)	−0.1119 (5)	0.2065 (4)	−0.0445 (3)	9.1 (1)	H(5B)	−0.141 (5)	−0.095 (3)	0.113 (3)	7 (1)
H(3A)	−0.075 (4)	0.496 (3)	0.412 (2)	5 (1)	H(6B)	−0.228 (5)	−0.022 (3)	0.202 (3)	7 (1)
H(4A)	−0.000 (5)	0.605 (3)	0.479 (3)	7 (1)	H(7B)	−0.231 (4)	0.081 (2)	0.285 (2)	4 (1)
H(5A)	0.150 (5)	0.697 (3)	0.444 (3)	6 (1)	H(91B)	−0.186 (4)	0.324 (3)	0.397 (3)	5 (1)
H(6A)	0.215 (4)	0.675 (3)	0.329 (3)	5 (1)	H(92B)	−0.228 (4)	0.317 (3)	0.313 (2)	4 (1)
H(7A)	0.226 (4)	0.611 (3)	0.227 (2)	4 (1)	H(1)	0.019 (4)	0.259 (3)	0.052 (2)	4 (1)
H(91A)	0.262 (4)	0.401 (3)	0.110 (2)	5 (1)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$. [b] Occupancy 0.67. [c] Occupancy 0.33.

Electronic spin resonance spectra were recorded on a Varian E-109 EPR spectrometer operating at X-band (9.506 GHz) frequency.

Results and Discussion

Final positional and thermal parameters for the complex are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows a stereoview of the molecule. The complex consists of well-separated binuclear complex molecules, but unlike many such complexes the molecule has no center of symmetry: the environments of the two copper atoms in the complex are different. Each copper is bonded to a tridentate Schiff base ligand, and a fourth coordination site, to make an approximate plane, is furnished by one atom of an oxygen of an acetate anion. Each complete fragment so formed is linked via a bond to the in-plane coordinated acetate oxygen atom of the other. One of these bonds is significantly stronger (2.446 (2) Å) than the other (2.651 (1) Å). The mode of acetate bridging differs from the normal: many copper(II) complexes are known in which a different acetate oxygen is bonded to each of two different copper atoms. Here, however, the second oxygen of each carboxylate ligand is at a weakly linking distance of only one copper atom (Cu(1)–O(2C) = 2.621 (2) Å, Cu(2)–O(2D) = 2.742 (1) Å) and is not involved in any bridging. The unsymmetrical nature of the complex is presumably due to the hydrogen bonding between lattice solvent molecules and the bridging oxygen atom O(2D), and it seems likely that in solution the complex would be symmetrical.

The ligand environments of the two copper atoms are similar in general form, though different in detail. The copper atoms are strongly bonded to four ligand atoms in a nearly planar

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Table II. Bond Lengths and Selected Molecular Distances (Å) for $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$

	Distances[a]		
Cu(1)–O(1A)	1.925 (1)	N(B)–C(8B)	1.486 (3)
Cu(1)–O(1C)	1.952 (1)	C(1A)–C(2A)	1.396 (4)
Cu(1)–O(2A)	1.998 (1)	C(1A)–C(6A)	1.404 (4)
Cu(1)–N(A)	1.937 (2)	C(1A)–C(7A)	1.457 (4)
Cu(1)–O(1D)	2.446 (2)	C(2A)–C(3A)	1.392 (4)
Cu(1)–O(2C)	2.621 (2)	C(3A)–C(4A)	1.360 (4)
Cu(1)–Cu(2)	3.445 (1)	C(4A)–C(5A)	1.371 (4)
Cu(2)–O(1B)	1.888 (1)	C(5A)–C(6A)	1.377 (4)
Cu(2)–O(1D)	1.952 (1)	C(8A)–C(9A)	1.527 (5)
Cu(2)–O(2B)	2.006 (1)	C(8A)–C(10A)	1.550 (5)
Cu(2)–N(B)	1.937 (2)	C(8A)–C(11A)	1.532 (4)
Cu(2)–O(1C)	2.651 (1)	C(1B)–C(2B)	1.418 (4)
Cu(2)–O(2D)	2.742 (2)	C(1B)–C(6B)	1.420 (4)
O(1A)–C(2A)	1.344 (3)	C(1B)–C(7B)	1.424 (4)
O(1B)–C(2B)	1.329 (3)	C(2B)–C(3B)	1.392 (4)
O(1C)–C(1C)	1.271 (3)	C(3B)–C(4B)	1.383 (4)
O(1D)–C(1D)	1.285 (3)	C(4B)–C(5B)	1.355 (4)
O(2A)–C(9A)	1.439 (3)	C(5B)–C(6B)	1.354 (4)
O(2B)–C(9B)	1.440 (3)	C(8B)–C(9B)	1.518 (5)
O(2C)–C(1C)	1.226 (2)	C(8B)–C(10B)	1.528 (5)
O(2D)–C(1D)	1.237 (3)	C(8B)–C(11B)	1.540 (4)
N(A)–C(7A)	1.266 (3)	C(1C)–C(2C)	1.527 (4)
N(A)–C(8A)	1.500 (3)	C(1D)–C(2D)	1.513 (4)
N(B)–C(7B)	1.297 (3)	O(2)–C(1)	1.45 (2)
C(1)–C(2)	1.20 (8)	C(1)–C(2′)	1.41 (7)
	Closest Intermolecular Contacts		
O···O(2A)	2.581^{b,c}	O(2)···O(2D)	2.784^{b,c}
O···O(2)	2.732^{b,c}	O(2A)···C(10A)	3.261^{d}
O···O(1B)	2.817^{b,c}		

[a] ⟨C–H⟩ = 0.96 Å. [b] H-bonding contacts. [c] $x - 1/2, 1/2 - y, z - 1/2$. [d] $-x, 1 - y, -z$.

arrangement. A weak fifth bond links each metal atom to a bridging carboxylate oxygen, with a still weaker sixth bond to the nonbridging carboxylate oxygen. Consequently, each copper atom is displaced out of the principal ligand plane toward the bridging oxygen by 0.04 Å.

Because of the asymmetry between the halves of the molecule, the fifth and sixth bonds to Cu(2) are considerably weaker than to Cu(1). The two principal ligand planes are tilted at an angle of 19.6° to each other. The metal–ligand–metal bridging angles are unequal. The angle at O(1C), Cu(1)–O(1C)–Cu(2), is 95.7°, which is in the region of expected ferromagnetic coupling; the other bridging angle, Cu(1)–O(1D)–Cu(2), is in the region of expected antiferromagnetic coupling, with a value of 102.6°. The larger angle corresponds to the more strongly linked superexchange pathway.

The present complex constitutes a reaction intermediate along the synthetic pathway to an alkoxy-bridged complex of type **3**, investigated previously.[28,29,32,40,41] The final product in this case would probably be tetrameric,[42] formed by linkages between the normal dimeric units obtained with such ligands. The reaction normally proceeds via this intermediate to completion fairly rapidly, so that the intermediate is only evident from the color changes in the solution. It can be isolated in solid form, however, by the use of a considerable excess of copper acetate with a slight excess of the amine. Effectively this constitutes a deficiency of salicylaldehyde and consequently of the tridentate Schiff base ligand.

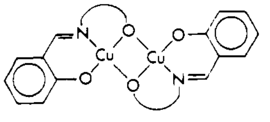

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Table III. Bond Angles (Deg) for $[Cu(N\text{-}Me_2EtOSal)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$

Cu(1)–O(1C)–Cu(2)	95.7 (1)	C(1A)–C(2A)–C(3A)	118.1 (2)
Cu(1)–O(1D)–Cu(2)	102.6 (1)	C(2A)–C(3A)–C(4A)	121.3 (2)
O(1A)–Cu(1)–O(1C)	90.4 (1)	C(3A)–C(4A)–C(5A)	121.5 (2)
O(1A)–Cu(1)–O(1D)	88.9 (1)	C(4A)–C(5A)–C(6A)	118.6 (2)
O(1A)–Cu(1)–O(2A)	174.9 (1)	C(1A)–C(6A)–C(5A)	121.0 (2)
O(1A)–Cu(1)–N(A)	94.5 (1)	N(A)–C(7A)–C(1A)	126.0 (2)
O(1A)–Cu(1)–O(2C)	93.0 (1)	N(A)–C(8A)–C(9A)	105.4 (2)
O(1C)–Cu(1)–O(1D)	81.8 (1)	N(A)–C(8A)–C(10A)	106.2 (2)
O(1C)–Cu(1)–O(2A)	92.6 (1)	N(A)–C(8A)–C(11A)	113.3 (2)
O(1C)–Cu(1)–N(A)	169.6 (2)	C(9A)–C(8A)–C(10A)	109.8 (2)
O(1C)–Cu(1)–O(2C)	54.9 (1)	C(9A)–C(8A)–C(11A)	109.2 (2)
O(1D)–Cu(1)–O(2A)	87.4 (1)	C(10A)–C(8A)–C(11A)	112.6 (2)
O(1D)–Cu(1)–N(A)	107.3 (1)	O(2A)–C(9A)–C(8A)	108.3 (2)
O(1D)–Cu(1)–O(2C)	136.6 (1)	C(2B)–C(1B)–C(6B)	116.9 (2)
O(2A)–Cu(1)–N(A)	83.2 (1)	C(2B)–C(1B)–C(7B)	125.2 (2)
O(2A)–Cu(1)–O(2C)	92.1 (1)	C(6B)–C(1B)–C(7B)	117.9 (2)
N(A)–Cu(1)–O(2C)	115.6 (1)	O(1B)–C(2B)–C(1B)	122.9 (2)
O(1B)–Cu(2)–O(1D)	90.5 (1)	O(1B)–C(2B)–C(3B)	117.7 (2)
O(1B)–Cu(2)–O(2B)	177.2 (2)	C(1B)–C(2B)–C(3B)	119.4 (2)
O(1B)–Cu(2)–N(B)	95.3 (1)	C(2B)–C(3B)–C(4B)	120.4 (2)
O(1D)–Cu(2)–O(2B)	91.3 (1)	C(3B)–C(4B)–C(5B)	121.2 (2)
O(1D)–Cu(2)–N(B)	173.5 (2)	C(4B)–C(5B)–C(6B)	119.8 (2)
O(2B)–Cu(2)–N(B)	82.9 (1)	C(1B)–C(6B)–C(5B)	122.4 (2)
Cu(1)–O(1A)–C(2A)	125.9 (1)	N(B)–C(7B)–C(1B)	125.2 (2)
Cu(2)–O(1B)–C(2B)	126.8 (1)	N(B)–C(8B)–C(9B)	105.0 (2)
Cu(1)–O(1C)–C(1C)	106.5 (1)	N(B)–C(8B)–C(10B)	107.8 (2)
Cu(2)–O(1D)–C(1D)	110.6 (1)	N(B)–C(8B)–C(11B)	113.2 (2)
Cu(1)–O(2A)–C(9A)	109.8 (1)	C(9B)–C(8B)–C(10B)	110.9 (2)
Cu(2)–O(2B)–C(9B)	108.1 (1)	C(9B)–C(8B)–C(11B)	108.0 (2)
Cu(1)–N(A)–C(7A)	124.9 (1)	C(10B)–C(8B)–C(11B)	111.8 (2)
Cu(1)–N(A)–C(8A)	114.4 (1)	O(2B)–C(9B)–C(8B)	108.8 (2)
C(7A)–N(A)–C(8A)	119.9 (2)	O(1C)–C(1C)–O(2C)	122.4 (2)
Cu(2)–N(B)–C(7B)	124.7 (1)	O(1C)–C(1C)–C(2C)	118.7 (2)
Cu(2)–N(B)–C(8B)	115.0 (1)	O(2C)–C(1C)–C(2C)	118.9 (2)
C(7B)–N(B)–C(8B)	120.2 (2)	O(1D)–C(1D)–O(2D)	122.2 (2)
C(2A)–C(1A)–C(6A)	119.5 (2)	O(1D)–C(1D)–C(2D)	116.2 (2)
C(2A)–C(1A)–C(7A)	124.5 (2)	O(2D)–C(1D)–C(2D)	121.6 (2)
C(6A)–C(1A)–C(7A)	116.0 (2)	O(2)–C(1)–C(2)	105.0 (3)
O(1A)–C(2A)–C(1A)	123.1 (2)	O(2)–C(1)–C(2′)	112.4 (3)
O(1A)–C(2A)–C(3A)	118.8 (2)		

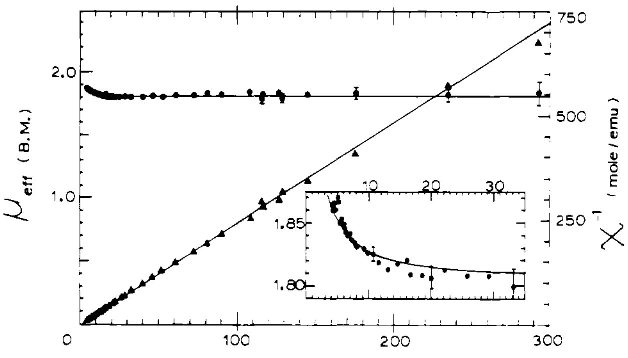

Figure 3.

The complex $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2$ resembles the bidentate Schiff base complexes **4**[26,30,31,33,43-46] in having

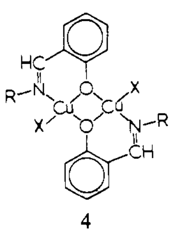

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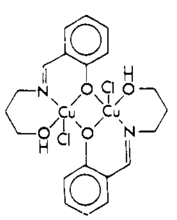
Table IV. Magnetic Moments (μ_{eff}, μ_B) as a Function of Temperature (K) ($J = 0.63$ cm^{-1}, $g = 2.078$, TIP = 6×10^{-5} cgs emu)

T, K	4.32	4.44	4.57	4.81	5.12	5.29	5.54	5.78	6.01	6.27	6.51	6.80
μ_{eff}	1.866	1.865	1.866	1.860	1.871	1.867	1.851	1.853	1.849	1.846	1.842	1.840
T, K	7.08	7.34	7.63	7.93	8.22	9.02	9.82	10.7	11.6	13.2	14.6	16.1
μ_{eff}	1.841	1.836	1.835	1.832	1.831	1.831	1.825	1.822	1.819	1.813	1.817	1.820
T, K	16.9	18.5	20.1	22.2	25.9	29.3	33.3	40.0	46.4	52.8	61.1	72.5
μ_{eff}	1.809	1.809	1.807	1.813	1.809	1.809	1.798	1.800	1.803	1.807	1.813	1.814
T, K	80.8	90.2	108.8	117.3	126.5	145.0	116.0	129.0	175.5	235.0	293.5	
μ_{eff}	1.837	1.823	1.852	1.833	1.843	1.835	1.775	1.797	1.846	1.832	1.859	

the same general formula $[Cu(SB)X]_2$, where SB represents a Schiff base ligand of the salicylaldimine type and X can be Cl^-, Br^-, NO_3^-, a β-diketonate, and now acetate. A major difference from the common form, **4**, of the binuclear complexes is that $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2$ contains no bridges at the phenolic oxygen of the salicylaldimine ligand. The properties and reactivity of the complex is similar to complex **5**[47] and its nitrate analogue which, on removal of HCl or HNO_3, rearrange to form complex **6**. The difference again is that the phenolic oxygen bridging of **5** is replaced by acetate bridging in $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2$.[40,41]



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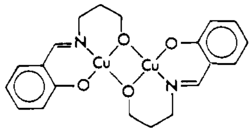

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Magnetic Properties. EPR spectra of polycrystalline material were recorded at X-band frequency and at several temperatures. A broad featureless transition was observed with a g value of about 2.15. In addition, a low-field resonance corresponding to the $\Delta M_s = 2$ transition was observed. This transition is characteristic of magnetically coupled binuclear copper(II) complexes and is in agreement with the crystal structure. Spectra recorded at 77 and 4 K are illustrated in Figure 4. At very low temperatures, there is a large increase in the intensity of the $\Delta M = 2$ region of the spectrum relative to the $\Delta M_s = 1$ region. The overall increase in intensity and especially the increase in the low-field spectrum relative to the $g = 2$ spectrum is consistent with ferromagnetically coupled dimeric centers. The observation of the $\Delta M_s = 2$ line indicates that interdimer coupling is not important compared with the intradimer exchange interaction.

Magnetic susceptibility measurements were undertaken to further elucidate the nature of the magnetic coupling observed in the EPR experiment. Magnetic susceptibilities of polycrystalline $[Cu(N\text{-}Me_2EtOHSal)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$ were measured in the 4–300 K temperature region. The magnetic moment was observed to rise with decreasing temperature, and data were therefore interpreted in terms of the ferromagnetic binuclear coupling model as previously described.[48] The data are given in Table IV and graphically in Figure 3. The rise in magnetic moment is small but unambiguous and is indicative of a small ferromagnetic coupling constant of 0.63 cm^{-1}.

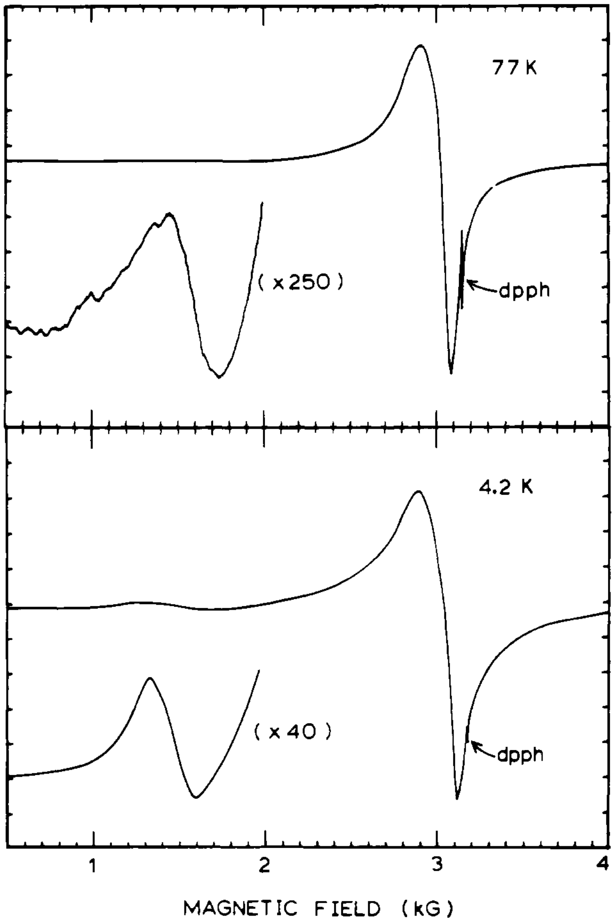

Figure 4.

In addition to the unusual bridging geometry of the acetate ion, this compound is noteworthy for its apparent violation of the empirical bond angle rules which predict the sign of magnetic exchange. Empirical tabulation of the hydroxide-bridged dimers indicate an angular dependence which marks a crossover from antiferromagnetic to ferromagnetic coupling at a Cu–O–Cu bridging angle of about 97.6°.[25] Studies of chlorine-bridged dimeric systems (Cu–Cl–Cu) have shown that, while the crossover bridging angle is different from the hydroxide bridged group, it is even smaller at 95.1°; the same angle vs. coupling constant trend seems to be obeyed.[49] However, this trend is very tentative,[49] and some workers find no trend at all.[50] Anderson predicts the antiferromagnetic coupling will predominate over the ferromagnetic coupling

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when both are present.[10] In the title complex, the 102.6° Cu–O–Cu bridge angle corresponds to an antiferromagnetic interaction, and this interaction would be expected to predominate over the ferromagnetic interaction of the smaller Cu–O–Cu angle of 95.7°. This is especially so since the ferromagnetic pathway corresponds to somewhat weaker Cu–O linkages. This surprising result may be as much due to unreasonable expectations as to the numerical data. There are a number of factors to be considered in accounting for these observations.

(1) The experimentally observed J vs. ϕ trend applies strictly for a set of hydroxy-bridged Cu(II) complexes. It has also been shown that distortion from planar toward tetrahedral decreases the magnitude of $-J$, in four-coordinated Cu complexes, while noncoplanarity of the principal ligand planes produces a similar result,[51] as do a number of other structural features.[27–33] Thus, the J vs. ϕ trend should not be overinterpreted.

(2) When both p and s orbital contributions to the bridging bonds are taken ito consideration,[52] the magnitude of the calculated ferromagnetic interaction should peak at a Cu–O–Cu angle of about 96°. Thus the ferromagnetic component may be unusually large, here, given the 95.7° bridging angle, and in this special case the ferromagnetic interaction may slightly dominate a less effective antiferromagnetic path.

(3) The J vs. ϕ correlation applies to Cu–(OH)–Cu linkages. The acetate bridges are markedly different from OH, and thus a large substituent effect at the bridging O atoms could make the generalizations about the J vs. ϕ trend less applicable here. Such large substituent effects are already known in other complexes both due to the nature of the R group on O–R and the angle it makes with the metal bridging framework.[52]

Thus despite a large amount of work done on the correlation between structure and magnetism in binuclear complexes, there can be surprises when antiferent bridging groups are placed together. In this case a presumably ferromagnetic and a presumably antiferromagnetic bridging group are seen together. Work is in progress on the synthesis of other analogues which will provide additional data on the new category of copper dimers.[53]

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Registry No. $[Cu(NMe_2EtOHSal)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$, 76430-68-7.

Supplementary Material Available: A table of coefficients of least-squares planes and a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Solution and Solid-State Studies of Cobaloxime Complexes Containing Alkylated 6-Aminopurine Ligands. Molecular and Crystal Structure of the Complex with N(7)-Bound 3-Benzyladenine and Dimethyl Phosphonate as the Axial Ligands

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In order to ascertain the effect on complex stability of long bonds from a metal to an endocyclic nitrogen center of a nucleic acid base, we have examined the formation of complexes containing good trans-directing ligands. Conditions leading to isolable complexes of formula $LCo(DH)_2X$ (where L = 3- or 9-alkylated adenine; X = alkyl or $P(O)(OCH_3)_2$; DH = monoanion of dimethylglyoxime) have been found. In Me_2SO-d_6 solutions the complex is in equilibrium with the 6-aminopurine base and the solvato complex. The equilibrium was quantified for L = 3-alkyladenine by measuring the areas of the ^1H NMR signals of the oxime methyl groups. The measured stability constants are about 300–500 times smaller than those found earlier for $LCo(acac)_2NO_2$ (where acac = monoanion of acetylacetone). A complete structural characterization of $(3\text{-benzyladenine})Co(DH)_2(P(O)(OCH_3)_2) \cdot EtOH \cdot H_2O$ was undertaken. The complex crystallizes from chloroform (containing 0.75% EtOH and 2 drops of H_2O/100 mL) in the monoclinic system, space group $P2_1/c$, with cell data $a = 14.674$ (5) Å, $b = 13.607$ (3) Å, $c = 16.735$ (9) Å, $\beta = 111.23$ (3)°, $Z = 4$, and $V = 3114.7$ Å^3. The structure was solved by standard heavy-atom methods and has been refined to a final R value of 0.093. Both O···H···O protons in the equatorial plane appear to be localized on one of the two dimethylglyoxime ligands, yielding a neutral and a dianionic ligand. This less usual arrangement for cobaloximes is probably due to the presence of interligand hydrogen bonding involving the 6-amino group of the axial 3-benzyladenine base and the dianionic equatorial dimethylglyoxime ligand. The complex has a long Co–N(7) distance of 2.101 (7) Å and a relatively short Co–P distance of 2.229 (3) Å. The observed length of the Co–N(7) bond most likely arises from a combination of the σ-donor power of the trans dimethyl phosphonate ligand and of steric interactions between the 6-amino group and the equatorial dimethylglyoxime system. The relative instability of the dimethylglyoxime vs. the acetylacetonate complexes is proposed to result from these same two considerations.

Introduction

For some time now, we have been investigating how the exocyclic functional groups on purine and pyrimidine ligands influence metal binding of these heterocyclic compounds.[1] It is now clear that these exocyclic groups influence both binding site selection and complex stability via nonbonded repulsive and hydrogen-bonding attractive interactions with other ligands in the coordination environment. The nature of the other attached ligands (e.g., size and hydrogen-bonding affinity) can

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