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Magnetic Interactions in Metal Complexes of Binucleating Ligands. 2. Synthesis and Properties of Binuclear Copper(II) Compounds Containing Exogenous Ligands That Bridge through Two Atoms. Crystal and Molecular Structure of a Binuclear μ-Pyrazolato-*N*,*N'*-Bridged Dicopper(II) Complex of 1,3-Bis(salicylideneamino)propan-2-ol

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The synthesis and characterization of a series of binuclear copper(II) complexes of binucleating ligands formed by the condensation of pyridine-2-carbaldehyde, salicylaldehyde, and acetylacetone with 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol are reported. All compounds have an endogenous bridging ligand alkoxide group and, in addition, have bridging exogenous ligands such as pyrazolate, 3,5-dimethylpyrazolate, and acetate ions that bridge through two atoms. The crystal and molecular structure of the μ-pyrazolate-bridged dicopper(II) complex of 1,3-bis(salicylideneamino)propan-2-ol of formula $C_{20}H_{20}CuN_4O_4$ having space group *Pbcn* and cell dimensions $a = 14.983$ (2) Å, $b = 8.276$ (5) Å, and $c = 31.163$ (4) Å was solved for 1033 non-zero structure factors ($I > 2.5\sigma(I)$). The crystal system is orthorhombic with $Z = 8$. Full-matrix least-squares refinement gave a final *R* factor of 0.0762. The ligand is binucleating, and the two copper(II) ions are bridged by the secondary alkoxo group and the pyrazolate moiety. Both copper(II) centers have essentially planar coordination of N_2O_2 donor sets. The compound contains an uncoordinated molecule of water. There are *no* significant intermolecular interactions between neighboring binuclear entities. The intramolecular Cu---Cu distance is 3.359 (4) Å. Magnetic susceptibilities for all the compounds in the solid state are measured over the temperature range 4.2–300 K. The magnetic behavior may be satisfactorily treated by the Bleaney–Bowers equation for a spin-coupled $S = 1/2$ system in which the singlet-triplet separation is $2J$. When the magnetic data for a series of previously reported analogues having single-atom bridges and the present two-atom-bridged species are compared, it is observed that $-J$ decreases in the order $OR^- \approx$ pyrazolate > acetate $\approx OH^- > Cl^-$. Structural data indicate that distortions from trigonal-planar toward pyramidal geometry of the endogenous alkoxo bridging ligand lead to a less negative value for *J*. In several compounds, this effect leads to net ferromagnetism.

Introduction

There is continuing interest in the properties of binuclear copper(II) complexes especially in understanding the factors that are responsible for the magnetic-exchange interactions that occur between coupled copper centers. Empirical structural/magnetic relationships (particularly involving μ-dihydroxo-bridged compounds) have shown some interesting correlations. For example, a linear relationship exists between the magnetic-exchange coupling constant, *J*, and the Cu–O–Cu bond angles involving the bridging hydroxo groups.[2] A somewhat more complex relationship has been derived for certain μ-dichloro-bridged copper(II) complexes.[3] The type (antiferromagnetic or ferromagnetic) and extent of magnetic exchange (interaction) between the coupled metal ($S = {}^1/_2$) centers are particularly sensitive to minor changes in bond angles at the bridging atoms and to the size of the dihedral angles between the planes containing the copper(II) ions.[4]

An increasing knowledge of the structural characteristics of the active center in the type 3 copper proteins[5-8] has encouraged an emphasis on the preparation of simple model compounds[9-21] containing two magnetically coupled copper(II) centers. One of these type 3 proteins which acts as an oxygen carrier in arthropods and mollusks is hemocyanin, which may exist in the colorless Cu(I) deoxy form and the blue Cu(II) oxy form, in which 1 mol of dioxygen is involved with the two Cu centers. EXAFS data on oxyhemocyanin indicate that each copper is four- or five-coordinate and the donor atoms are N or O. Two histidine imidazole N donors are bound to each copper,[7] and a symmetrically bridging peroxide ion occupies the exogenous site.[5] The nature of the endogenous bridging atom remains a subject of speculation. The EXAFS data indicate an atom of low atomic number that is probably oxygen.[7a] A phenoxide group from a tyrosine residue is a likely candidate. However, recent spectroscopic studies of

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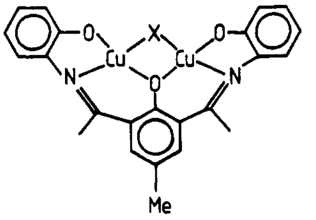
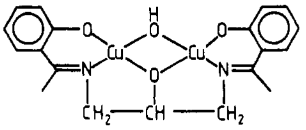
the native enzyme and model compounds have cast doubt on such a proposal.[7a,22,23] The presence of the amino acid residues serine and threonine in hemocyanin suggests the possible presence of an alkoxo bridging group, which is known to cause very strong antiferromagnetic coupling between bridged Cu(II) ions.[24] However, this is considered to be unlikely.[23] Very strong antiferromagnetic spin exchange between the two copper ($S = {}^1/_2$) centers is observed in oxyhemocyanin ($J \geq -500$ cm^{-1}, where the singlet–triplet separation for the spin-coupled $S = {}^1/_2$ system is $2J$ cm^{-1}).

Following the pioneering work of Robson[25] and Okawa[26] on the preparation of phenoxo-bridging pentadentate ligands and their metal complexes (**1**) numerous model binuclear copper(II) compounds that contain various ligands, X, in the exogenous bridging site have been reported. The relevance of such compounds as models for hemocyanin has been demonstrated by Karlin, who showed that a phenoxo-bridged complex of this type was capable of binding dioxygen as a peroxide ion in the exogenous site.[20]



1 (X = OR⁻, Cl⁻, pyrazolate etc.)

Although the occurrence of both antiferromagnetic and ferromagnetic exchange has been observed in a large number of binuclear copper(II) systems,[2e,27] no examples of ferromagnetic coupling have been reported for compounds of type **1**. However, we have recently shown[24] the occurrence of both antiferromagnetic and ferromagnetic coupling in compounds related to **1** but based on 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol backbones, which furnish pentadentate ligands of greater stereochemical flexibility. In these binuclear copper(II) compounds, which feature single-atom exogenous, and alkoxo endogenous, bridging atoms, it was shown that the type and extent of coupling were dependent on the nature of the bridging group, the nature of the counterion, the chain length of the ligand backbone, and the extent of saturation of the C–N linkages of the ligands. The first examples of ferromagnetic coupling were observed for compound **2** ($J = +17$ cm^{-1}) and compound **3** ($J = +80$ cm^{-1}).



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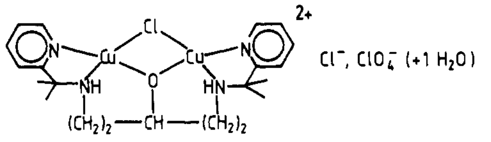
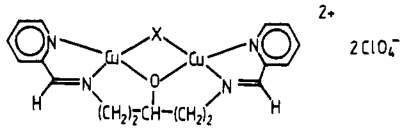
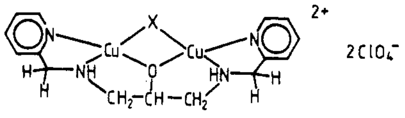


3

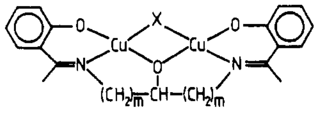
The present paper extends our study on the synthesis and properties (the extent of magnetic exchange between coupled binuclear copper(II) centers) of copper(II) compounds having, in addition to the flexible pentadentate ligands, a two-atom exogenous bridging ligand (e.g., pyrazolate, acetate). Compounds **4**–**7** were prepared and detailed magnetic studies to 4 K carried out. In addition, the crystal and molecular structure of **6a** is described. Some preliminary results on these systems have been reported.[24,28,29]



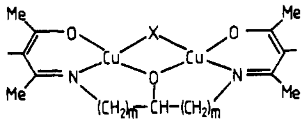
4a X = pyrazolate
4b X = acetate



5a X = pyrazolate
5b X = acetate



6a m = 1, X = pyrazolate
6b m = 1, X = acetate
6c m = 2, X = pyrazolate



7a m = 1, X = pyrazolate
7b m = 1, X = acetate
7c m = 1, X = 3,5-dimethylpyrazolate
7d m = 2, X = pyrazolate

Experimental Section

Synthesis of Complexes. Compound 4a. An aqueous solution (7 cm^3) of the hydroxy-bridged analogue of **4a**[24] (0.065 g, 0.001 mol) and pyrazole (0.07 g, 0.001 mol) was allowed to stand at room temperature for 48 h. The blue-green crystals that formed were separated by filtration, washed with water and ethanol, and dried under suction; yield 0.04 g. Anal. Calcd for $C_{20}H_{22}N_6O_9Cl_2Cu_2$: C, 34.89; H, 3.22; N, 12.21; Cu, 18.46. Found: C, 34.76; H, 3.18; N, 12.52; Cu, 18.95.

Compound 4b. The ligand[24] (0.3 g, 0.001 mol) in ethanol (15 cm^3) was added to cupric acetate monohydrate (0.4 g, 0.002 mol) in ethanol (30 cm^3). The solution was heated on a water bath for 0.5 h and then allowed to stand overnight at room temperature. Sodium perchlorate (0.7 g, 0.0057 mol) in ethanol (20 cm^3) was added, and after evaporation at room temperature for 2 days to a volume of 20 cm^3, a green crystalline material formed. The solid was collected by filtration, washed with

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ethanol, and air-dried. This product was recrystallized from methanol/ethanol to give a green crystalline solid; yield 0.46 g. Anal. Calcd for $C_{19}H_{22}N_4O_{11}Cl_2Cu_2$: C, 33.54; H, 3.26; N, 8.23; Cu, 18.68. Found: C, 33.27; H, 3.32; N, 8.41; Cu, 19.18.

Compound 5a. Pyridine-2-carbaldehyde (10.7 g, 0.1 mol) in methanol (20 cm^3) was added to 1,3-diaminopropan-2-ol (4.5 g, 0.05 mol) dissolved in methanol (20 cm^3). The solution was allowed to stand overnight, and after the volume was increased to ca. 100 cm^3 with methanol, it was warmed on a water bath while sodium borohydride (2.8 g, 0.1 mol) was added in small quantities. The mixture was then refluxed for 0.75 h and evaporated to dryness on a rotary evaporator. The resulting solid was dissolved in chloroform (100 cm^3), and the chloroform solution was washed three times with water (15 cm^3). The chloroform layer was separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated in vacuo to yield the ligand as a yellow-brown oil (14 g). The ligand was dissolved in ethanol (50 cm^3) and this solution used in the preparation of the copper complexes. The ligand solution (4.6 cm^3, 0.0047 mol) was added to ethanol (40 cm^3) containing cupric nitrate trihydrate (2.4 g, 0.01 mol). The mixture was warmed and mixed with pyrazole (0.34 g, 0.005 mol) and potassium hydroxide (0.28 g, 0.005 mol) in ethanol (20 cm^3). Sodium perchlorate (4 g, 0.032 mol) in water (10 cm^3) was added to give a blue precipitate, which was collected by filtration and washed with water, ethanol, and acetone. The product was recrystallized from hot water (100 cm^3) to give blue crystals; yield 0.5 g. Anal. Calcd for $C_{18}H_{22}N_6O_9Cl_2Cu_2$: C, 32.54; H, 3.34; N, 12.65; Cu, 19.13. Found: C, 33.03; H, 3.39; N, 12.69; Cu, 19.43.

Compound 5b. A further sample of the ligand solution (4.6 cm^3, 0.0047 mol) used in the preparation of **5a** was added to cupric acetate monohydrate (2.0 g, 0.01 mol) in ethanol (150 cm^3). Sodium perchlorate (4.0 g, 0.032 mol) in ethanol (50 cm^3) was added, and after evaporation at room temperature to 75 cm^3, a blue amorphous solid was obtained. The solid was recrystallized from water (20 cm^3) to give, after filtering followed by washing with acetone and air drying, a crystalline blue material; yield 0.85 g. Anal. Calcd for $C_{17}H_{22}N_4O_{11}Cl_2Cu_2$: C, 31.11; H, 3.38; N, 8.54; Cu, 19.36. Found: C, 31.23; H, 3.51; N, 8.60; Cu, 19.53.

Compound 6a. The ligand (2.95 g, 0.099 mol) in methanol (50 cm^3) was added dropwise to a stirred mixture containing pyrazole (0.7 g, 0.01 mol) and cupric nitrate trihydrate (4.8 g, 0.02 mol) in methanol (65 cm^3). Potassium hydroxide (2.24 g, 0.04 mol) in methanol (40 cm^3) was added to give a thick purple precipitate. Additional potassium hydroxide solution was added to give the mixture an apparent pH of 11.5. After the addition of water (20 cm^3), the mixture was stirred and the product was collected. It was washed with water, methanol, and acetone. Recrystallization, to give small purple crystals, was achieved by Soxhlet extraction with chloroform; yield 1.5 g. Anal. Calcd for $C_{20}H_{18}N_4O_3Cu_2$: C, 49.08; H, 3.71; N, 11.45; Cu, 25.96. Found: C, 48.99; H, 3.73; N, 11.46; Cu, 26.37.

Compound 6b. Cupric acetate monohydrate (4.0 g, 0.02 mol) was dissolved in a mixture of water (50 cm^3) and methanol (300 cm^3). To this solution was added the ligand (2.95 g, 0.01 mol) in methanol (75 cm^3). The resulting mixture was allowed to stand for 3 days and then reduced to 100 cm^3 by evaporation on a water bath. The mixture was allowed to stand overnight and then filtered to give a residue that was washed with water and methanol. This product was dissolved in hot methanol (200 cm^3). After filtration, water (50 cm^3) was added to the filtrate. After evaporation of this solution to ca. 100 cm^3 on a water bath, the resulting mixture was cooled and filtered. The residue was washed with water and methanol; yield 2.7 g. Anal. Calcd for $C_{19}H_{18}N_2O_5Cu_2$: C, 47.40; H, 3.77; N, 5.82; Cu, 26.40. Found: C, 47.28; H, 3.69; N, 5.70; Cu, 26.89.

Compound 6c. The ligand (0.32 g, 0.001 mol) was dissolved in chloroform (20 cm^3) and filtered to remove trace quantities of potassium chloride. The filtrate was evaporated to dryness on a rotary evaporator, and the residue was dissolved in methanol (10 cm^3). To this solution was added pyrazole (0.1 g, 0.0015 mol) in methanol (5 cm^3). The mixture was added to a stirred solution of cupric perchlorate hexahydrate (0.74 g, 0.002 mol) in methanol (10 cm^3). Addition of potassium hydroxide (0.22 g, 0.004 mol) in methanol (5 cm^3) gave a green precipitate. The mixture was evaporated to dryness on a rotary evaporator to give a residue, which was dissolved in chloroform. The chloroform extract was washed with water (3 × 50 cm^3), dried over anhydrous magnesium sulfate, and filtered. Ethanol (10 cm^3) was added to the green filtrate. After 2 h, dark red crystals began to form, which were collected and recrystallized from chloroform (30 cm^3) to which pyrazole (0.1 g, 0.0015 mol) and ethanol (10 cm^3) were added. The solution was allowed to evaporate at room temperature to give red crystals, which were collected and washed with ethanol; yield 0.32 g. Anal. Calcd for $C_{22}H_{22}N_4O_3Cu_2$: C, 51.06; H, 4.28; N, 10.83; Cu, 24.56. Found: C, 51.12; H, 4.25; N, 10.74; Cu, 24.68.

Compound 7a. The ligand was prepared by the reaction of acetylacetone (10 g, 0.1 mol) and 1,3-diaminopropan-2-ol (4.5 g, 0.05 mol) at room temperature. The solution was diluted to 100 cm^3 with ethanol/methanol to give a stock solution, which was used for the preparation of the copper(II) complexes **7a–c**. The ligand solution (5 cm^3, 0.005 mol) was added to a stirred solution of cupric nitrate trihydrate (2.4 g, 0.01 mol) in ethanol (50 cm^3). A mixture of pyrazole (0.35 g, 0.0051 mol) and potassium hydroxide (1.0 g, 0.018 mol) in ethanol (20 cm^3) was added to give a purple precipitate, which was collected by filtration and washed with ethanol. The product was dissolved in chloroform (130 cm^3), and after filtration, the filtrate was allowed to evaporate at room temperature to 25 cm^3. The solid material so obtained was collected, washed with ethanol, and air-dried; yield 1.1 g. Anal. Calcd for $C_{16}H_{22}N_4O_3Cu_2$: C, 43.14; H, 4.98; N, 12.58; Cu, 28.53. Found: C, 43.12; H, 5.06; N, 12.66; Cu, 28.43.

Compound 7b. The ligand solution (5 cm^3, 0.005 mol) was added to cupric acetate monohydrate (2.0 g, 0.01 mol) in ethanol (150 cm^3). The mixture was reduced in volume to 50 cm^3 on a hot plate. After cooling, the blue crystalline product was collected by filtration, washed with ethanol, and air-dried; yield 1.6 g. This product was recrystallized from chloroform (60 cm^3)/ethanol (15 cm^3) to give 1.2 g of dark blue crystals. Anal. Calcd for $C_{15}H_{22}N_2O_5Cu_2$: C, 41.19; H, 5.07; N, 6.40; Cu, 29.05. Found: C, 41.15; H, 5.08; N, 6.38; Cu, 29.35.

Compound 7c. The ligand solution (5 cm^3, 0.005 mol) and 3,5-dimethylpyrazole (0.7 g, 0.0073 mol) in methanol (5 cm^3) was added to cupric perchlorate hexahydrate (3.7 g, 0.01 mol) in methanol (10 cm^3). Addition of potassium hydroxide (0.84 g, 0.015 mol) in methanol (15 cm^3) to the deep green solution produced a thick, dark blue precipitate. The mixture was filtered, and the residue, after being washed with methanol, was recrystallized from chloroform (30 cm^3) and ethanol (10 cm^3) to give blue needlelike crystals; yield 1.0 g. Anal. Calcd for $C_{18}H_{26}N_4O_3Cu_2$: C, 45.66; H, 5.53; N, 11.83; Cu, 26.84. Found: C, 45.58; H, 5.49; N, 11.91; Cu, 26.97.

Compound 7d. The ligand was prepared by reacting a filtered solution of 1,5-diaminopentan-3-ol[24] (3.8 g, 0.02 mol) in methanol (30 cm^3) and potassium hydroxide (2.3 g, 0.041 mol) in methanol (20 cm^3) with acetylacetone (4.0 g, 0.04 mol). The mixture was allowed to stand overnight and then evaporated to dryness on a rotary evaporator. The residue was dissolved in chloroform (30 cm^3), which was washed with water (3 × 10 cm^3) and then dried over anhydrous magnesium sulfate. The chloroform solution was filtered and evaporated to dryness to give 4 g of the ligand. The methoxy-bridged analogue of **7d** was prepared as follows: the ligand (2.42 g, 0.008 mol) in methanol (25 cm^3) was added to cupric perchlorate hexahydrate (6.0 g, 0.016 mol) in methanol (15 cm^3). Potassium hydroxide (1.0 g, 0.018 mol) in methanol (10 cm^3) was added to the mixture to give a purple precipitate, which was collected by filtration and washed with methanol and chloroform. The filtrate was allowed to evaporate at room temperature to give a crystalline product, which was collected and washed with methanol; yield 1.25 g. When some of this product (0.75 g) was recrystallized from dichloromethane (20 cm^3) and methanol (10 cm^3), 0.45 g of pure compound resulted. Anal. Calcd for $C_{16}H_{26}N_2O_4Cu_2$: C, 43.93; H, 5.99; N, 6.40; Cu, 29.05. Found: C, 43.90; H, 5.92; N, 6.48; Cu, 29.43. When a solution of this methoxy-bridged analogue (0.5 g, 0.011 mol) and pyrazole (0.15 g, 0.0022 mol) in chloroform (40 cm^3)/methanol (15 cm^3) was evaporated at room temperature, compound **7d** was obtained as a crystalline material. It was filtered, washed with methanol, and air-dried; yield 0.2 g. Anal. Calcd for $C_{18}H_{26}N_4O_3Cu_2$: C, 45.66; H, 5.54; N, 11.83; Cu, 26.84. Found: C, 45.53; H, 5.43; N, 11.78; Cu, 27.33.

Crystal Data for 6a·H$_2$O. Grey/black parallelepiped-shaped crystals of **6a**·H$_2$O were obtained from crystallization of **6a** from warm dichloromethane and evaporation over ethanol. The crystal system, orthorhombic, and preliminary unit cell were obtained from precession photographs. A crystal, 0.05 × 0.03 × 0.26mm^3, was mounted about the *b* axis. Refined cell dimensions were obtained from axial reflections by ω ($h00$, $00l$) and μ ($0k0$) scans on a Stoe Weissenberg diffractometer using Mo Kα radiation and a graphite monochromator. The relevant crystal data are given in Table I.

Data Collection. Intensity data were collected for the levels $h0l$ to $h7l$ in the range $0 < 2\theta < 50°$ with use of the ω-scan technique. Corrections for Lorentz,[30] polarization, and absorption[31] effects were made to give 2550 unique reflections. Maximum and minimum transmission factors were 0.91 and 0.56.

Solution and Refinement of the Structure. The positions of the Cu atoms were determined by direct methods.[31] Subsequent difference Fourier syntheses revealed the positions of the remaining non-hydrogen

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(30) Data reduction program AUPTP.

(31) Sheldrick, G. M. "SHELX: Programme for Structural Solution"; University of Cambridge: Cambridge, 1976.

Table I. Crystal Data for **6a**[a]

formula: $C_{20}H_{20}Cu_2N_4O_4$	syst: orthorhombic
mol wt: 507.48	space group: *Pbcn*
$Z = 8$	$a = 14.983$ (2) Å
$d_{calcd} = 1.744$ g cm^{-1}	$b = 8.276$ (5) Å
μ(Mo Kα) = 22.07 cm^{-1}	$c = 31.163$ (4) Å
$F(000) = 2008$	$V = 3864.2$ Å^3
	$\lambda = 0.7107$ Å

[a] The structure was determined for the monohydrate.

Table II. Fractional Coordinates (×10^4) for **6a**·H_2O

atom	*x*	*y*	*z*
Cu(1)	2898 (1)	7486 (4)	8244 (1)
Cu(2)	2625 (1)	5451 (3)	9167 (1)
N(1)	3935 (10)	6870 (21)	8590 (5)
N(2)	1755 (9)	8071 (20)	8005 (5)
N(3)	1379 (9)	5176 (21)	9296 (5)
N(4)	3800 (9)	6068 (20)	8992 (5)
O(1)	2185 (8)	6485 (21)	8667 (4)
O(2)	3576 (7)	8432 (17)	7787 (4)
O(3)	3039 (8)	4169 (17)	9627 (4)
O(1w)	0	1347 (24)	7500
C(1)	1299 (16)	6512 (33)	8608 (8)
C(2)	5253 (14)	6472 (27)	8911 (6)
C(3)	4791 (12)	7079 (25)	8543 (6)
C(4)	3228 (12)	9184 (28)	7449 (6)
C(5)	3818 (12)	9840 (25)	7150 (6)
C(6)	3533 (12)	10597 (29)	6774 (7)
C(7)	2634 (13)	10760 (30)	6701 (6)
C(8)	2039 (14)	10141 (28)	6976 (7)
C(9)	2304 (12)	9347 (26)	7365 (5)
C(10)	1622 (12)	8787 (26)	7633 (6)
C(11)	986 (12)	7557 (33)	8270 (6)
C(12)	787 (14)	6042 (29)	8997 (7)
C(13)	1029 (13)	4366 (28)	9604 (6)
C(14)	1570 (13)	3533 (28)	9921 (6)
C(15)	1101 (14)	2747 (28)	10260 (6)
C(16)	1551 (14)	1954 (30)	10587 (7)
C(17)	2443 (16)	1893 (29)	10580 (6)
C(18)	2951 (14)	2627 (29)	10266 (6)
C(19)	2526 (15)	3505 (26)	9918 (6)
C(20)	4604 (10)	5880 (23)	9148 (6)

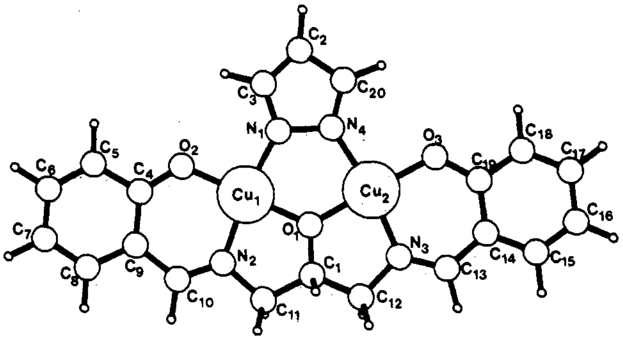

Figure 1. Atom numbering for the monohydrate of compound **6a**. The mole of water of crystallization is not shown.

Table III. Bond Distances (Å) for **6a**·H_2O

Cu(1)- - -Cu(2)	3.359 (4)		
Cu(1)–O(1)	1.888 (13)	C(2)–C(3)	1.431 (26)
Cu(2)–O(1)	1.896 (14)	C(2)–C(20)	1.316 (24)
Cu(1)–O(2)	1.917 (12)	C(1)–C(11)	1.441 (29)
Cu(2)–O(3)	1.888 (13)	C(1)–C(12)	1.487 (29)
Cu(1)–N(1)	1.960 (15)	C(4)–C(5)	1.395 (25)
Cu(1)–N(2)	1.929 (14)	C(4)–C(9)	1.415 (23)
Cu(2)–N(3)	1.924 (14)	C(5)–C(6)	1.395 (26)
Cu(2)–N(4)	1.913 (14)	C(6)–C(7)	1.372 (25)
N(1)–N(4)	1.430 (20)	C(7)–C(8)	1.340 (26)
N(1)–C(3)	1.304 (20)	C(8)–C(9)	1.434 (26)
N(2)–C(10)	1.318 (22)	C(9)–C(10)	1.400 (24)
N(2)–C(11)	1.479 (22)	C(13)–C(14)	1.453 (26)
N(3)–C(12)	1.474 (23)	C(14)–C(15)	1.425 (26)
N(3)–C(13)	1.282 (22)	C(14)–C(19)	1.433 (27)
N(4)–C(20)	1.309 (19)	C(15)–C(16)	1.387 (26)
O(1)–C(1)	1.341 (24)	C(16)–C(17)	1.339 (29)
O(2)–C(4)	1.329 (22)	C(17)–C(18)	1.379 (27)
O(3)–C(19)	1.379 (27)	C(18)–C(19)	1.452 (26)

Table IV. Bond Angles (deg) for **6a**·H_2O

Cu(1)–O(1)–C(2)	125.1 (7)	N(4)–N(1)–C(3)	107.4 (15)
N(2)–Cu(1)–O(2)	94.7 (6)	N(4)–C(20)–C(2)	115.2 (19)
N(2)–Cu(1)–O(1)	83.0 (6)	N(1)–C(3)–C(2)	109.8 (18)
N(1)–Cu(1)–O(1)	87.1 (6)	N(2)–C(11)–C(1)	109.0 (16)
O(2)–Cu(1)–O(1)	176.3 (6)	C(3)–C(2)–C(20)	102.9 (18)
N(1)–Cu(1)–O(2)	95.5 (6)	N(3)–C(13)–C(14)	121.9 (18)
N(1)–Cu(1)–N(2)	169.0 (6)	C(13)–C(14)–C(15)	116.4 (18)
N(4)–Cu(2)–O(3)	93.7 (6)	C(13)–C(14)–C(19)	124.2 (20)
N(3)–Cu(2)–O(1)	83.6 (6)	C(14)–C(15)–C(16)	121.4 (19)
N(3)–Cu(2)–O(3)	95.3 (6)	C(16)–C(17)–C(18)	123.1 (23)
N(4)–Cu(2)–N(3)	170.0 (7)	C(18)–C(19)–O(3)	118.1 (20)
O(3)–Cu(2)–O(1)	172.6 (7)	C(14)–C(19)–C(18)	116.2 (21)
N(4)–Cu(2)–O(1)	88.0 (6)	N(2)–C(10)–C(9)	124.4 (17)
Cu(1)–O(1)–C(1)	117.1 (14)	C(10)–C(9)–C(4)	124.9 (19)
Cu(2)–O(1)–C(1)	117.7 (13)	C(10)–C(9)–C(8)	117.0 (17)
Cu(1)–N(1)–N(4)	119.4 (10)	C(9)–C(4)–O(2)	125.1 (18)
Cu(2)–N(4)–N(1)	120.2 (10)	C(9)–C(4)–C(5)	117.3 (19)
Cu(1)–O(2)–C(4)	124.9 (11)	C(8)–C(9)–C(4)	118.1 (18)
Cu(2)–O(3)–C(19)	124.7 (13)	C(9)–C(8)–C(8)	122.1 (20)
Cu(1)–N(1)–C(3)	133.1 (14)	C(8)–C(7)–C(6)	120.6 (23)
Cu(2)–N(4)–C(20)	135.1 (13)	C(6)–C(5)–C(4)	122.8 (18)
Cu(1)–N(2)–C(11)	113.9 (12)	C(5)–C(4)–O(2)	117.6 (16)
Cu(1)–N(2)–C(10)	125.9 (12)	C(7)–C(6)–C(5)	118.9 (20)
Cu(2)–N(3)–C(13)	128.0 (14)	C(19)–C(14)–C(15)	119.4 (19)
Cu(2)–N(3)–C(12)	113.2 (12)	C(17)–C(16)–C(15)	119.4 (22)
O(1)–C(1)–C(11)	115.7 (20)	C(19)–C(18)–C(17)	120.5 (22)
O(1)–C(1)–C(12)	113.2 (20)	O(3)–C(19)–C(14)	125.7 (20)
C(11)–N(2)–C(10)	120.2 (15)	N(3)–C(12)–C(1)	109.4 (18)
C(12)–N(3)–C(13)	118.8 (15)	C(20)–N(4)–N(1)	104.6 (14)
C(11)–C(1)–C(12)	125.8 (21)		

atoms. All hydrogen atom positions were calculated with C–H distances fixed at 0.965 Å. The structure was refined by a full-matrix least-squares method (copper and oxygen atoms except O(1w) anisotropically, the remaining atoms isotropically). The weighting scheme was refined and converged to $w = 1.8813/[\sigma^2(F_o) + 0.001468 F^2{}_o]$, $R = 7.62\%$, and $R_w = 7.19\%$ for 1033 reflections [$I > 2.5\sigma(I)$]. All scattering factors were taken from ref 32. A diagram of the compound, including the atom-numbering system, is shown in Figure 1. Final atomic parameters (excluding calculated hydrogen atoms) are given in Table II. Tables III and IV contain the data on molecular geometry. Tables containing structure factors, anisotropic thermal parameters, calculated hydrogen atom parameters, and least-squares planes and atomic deviations from these planes have been deposited as supplementary material.

Magnetic Measurements and Data Fitting. The magnetic susceptibilities of the solid complexes were determined over the temperature range 4.2–300 K with an Oxford Instruments Faraday balance. Main fields of 10 or 40 kG were used depending on the magnitude of the susceptibility. The gradient field was 1000 G cm^{-1}. Measurements were made manually between 20 and 300 K. Temperatures below 30 K were measured on a carbon resistor, while above this a copper/constantan thermocouple was employed. The observed data were fitted by least-squares methods to the Bleaney–Bowers equation by allowing for the presence of monomer impurity.[4a,24] The fitting program allowed any of the parameters *g*, *J* and percent monomers to be varied. A fixed value of 60 × 10^{-6} cm^3 mol^{-1} per Cu was employed for the TIP contribution. The quality of fit was estimated by means of a discrepancy index $[\Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}{}^2]^{1/2}$. Each point used in the least-squares refinement was given equal weight; the weights were set to unity in the discrepancy index. All the compounds were analytically pure and contained no water.

Spectral Measurements. These have been described in an earlier publication.[24]

Results and Discussion

The crystal structure of one of the compounds (**6a**) and other physical properties described in this paper indicate that ligand

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(32) "International Tables for X-Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

(33) (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. (b) Angelici, R. J. "Synthesis and Technique in Inorganic Chemistry"; W. B. Saunders: London, 1977; p 213.

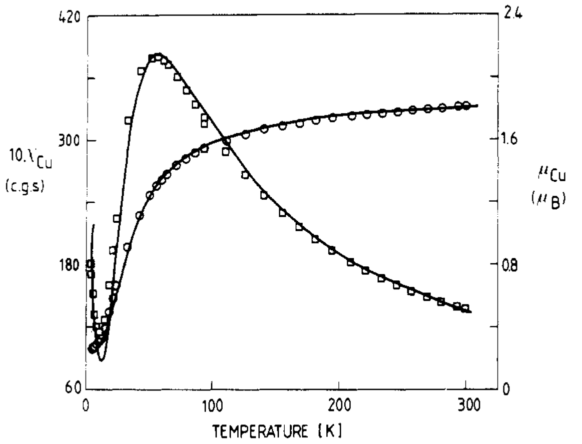

Figure 2. Temperature-dependent magnetic susceptibility (□) and moment (○) (per Cu) of compound **5a**. Solid lines are calculated by using parameters given in Table VII.

Table V. Molar Conductance of the Compounds[a,b]

compd	Λ,[c] Ω^{-1} cm^2 mol^{-1} MeOH	DMF	H_2O
4a	167	149	198
4b	188	147	223
5a	172	146	191
5b	175	147	220

[a] Concentration range (0.9–1.2) × 10^{-3} M. [b] The following ranges are expected for 1:2 electrolytes: for MeOH 160–220, for DMF 130–170, and for H_2O 235–273 Ω^{-1} cm^2 mol^{-1} for 10^{-3} M concentration.[33] [c] Molar conductance.

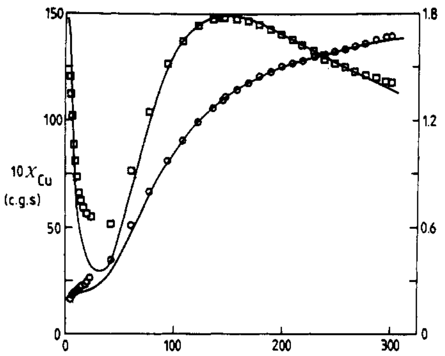

Figure 3. Temperature-dependent magnetic susceptibility (□) and moment (○) (per Cu) of compound **6b**. Solid lines are calculated by using parameters given in Table VII.

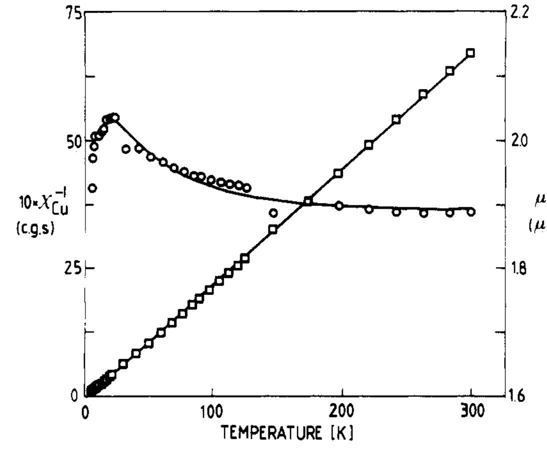

Figure 4. Temperature-dependent reciprocal susceptibility (□) and moment (○) (per Cu) of compound **7b**. Solid lines are calculated by using parameters given in Table VII.

backbones 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol form pentadentate ligands when condensed with various aldehydes. As shown previously[24] for a series of related compounds having single-atom (X = OH^-, Cl^-, OR^-) exogenous bridges, the hydroxyl group of the secondary alcohol function is readily deprotonated in the presence of 2 equiv of copper(II) to give compounds in which the pentadentate ligand binds two copper ions. In the present series of compounds, **4**–**7**, the exogenous bridge is occupied by a pyrazolate or acetate ion. It is of interest to note that pyrazole readily replaces a single-atom bridge in some cases. Compounds **4a** and **7d**, for example, may be prepared by adding pyrazole to the corresponding single-atom-bridged species.

Crystal Structure of 6a·H_2O. The pentadentate binucleating function of the ligand in **6a** is shown clearly in Figure 1. Important bond lengths and angles are given in Tables III and IV. The copper atoms are bridged by the oxygen atom O(1) from the secondary alkoxo substituent of the ligand and N(1) and N(4) from the pyrazolate moiety. Both Cu(1) and Cu(2) exhibit the coordination arrangements {O(2)N(2)Cu(1)N(1)O(1)} and {O(3)N(4)Cu(2)N(3)O(1)}. The crystal of the compound studied was a monohydrate. However, the water molecule is not coordinated. Unlike a similar compound containing an exogenous OH^- bridge that we have previously reported,[24] the present compounds shows no evidence for interdimer interactions. The four Cu(1)–N(2), Cu(2)–N(3), Cu(1)–N(1), and Cu(2)–N(4) bond lengths are 1.929, 1.924, 1.960, and 1.913 Å, while the Cu(1)–O(1), Cu(2)–O(1), Cu(1)–O(2), and Cu(2)–O(3) bond lengths are 1.888, 1.896, 1.917, and 1.888 Å, respectively. The intramolecular Cu(1)- - -Cu(2) distance is 3.359 Å. The Cu(1)–O(1)–Cu(2) angle is 125.1°, and this represents a significant opening up of this angle to accommodate the large ligand bite of the pyrazolate bridge. Recently reported structures containing the endogenous alkoxo bridge in ligands based on the 1,3-diaminopentan-2-ol backbone with exogenous azido and acetate bridges have corresponding Cu–O–Cu angles of 130.6 and 136°, respectively.[10]

Physical Properties in Solution. The ionic multiple-atom-bridged complexes **4a**–**d** exhibit almost ideal 1:2 electrolyte behavior in solution (Table V), and there is no evidence for significant structural changes on dissolution. The electronic absorption

Table VI. Electronic Absorption Spectral Data[a]

compd	λ_{max},[a] nm (ϵ, M^{-1} cm^{-1}) solid	$CHCl_3$	MeCN	DMF	MeOH	H_2O	Me_2SO
4a	585		600 (325)	617 (298)	610 (237)	615 (147)	
4b	650		665 (164)	667 (164)	637 (163)	620 (119)	
5a	605		618 (274)	625 (241)	630 (266)	625 (218)	
5b	630		647 (233)	653 (256)	650 (240)	645 (189)	
6a	560	570 (680)	570 (587)	570 (642)			580 (615)
6b	590	622 (494)	630 (396)	642 (375)			650 (361)
6c	610	588 (443)					
7a	575	560 (546)					
7b	603	608 (590)					
7c	595	592 (370)					
7d	590, 510			580 (400)			

[a] Spectra were not measured for those parts in this table where entries are missing.

Table VII. Magnetic Parameters for the Pyrazolate- (**4a**, **5a**, **6a**, **6c**, **7a**, **7c**, **7d**) and Acetate-Bridged (**4b**, **5b**, **7b**) Complexes[a]

compd	μ_{Cu}(295 K), μ_B	J,[b] cm^{-1}	g	% monomer
4a	0.94	−270	2.00	2.5
4b	1.37	−140	2.20	9.5
5a	1.81	−32	2.14	3.6
5b	1.92	54	2.08	0.2
6a	1.38	−120	2.00	0
6b	1.61	−83	2.13	2.4
6c	diamag	>−500		
7a	1.49	−100	2.03	0.3
7b	1.92	19	2.10	0
7c	1.56	−95	2.00	0.2
7d	0.64	−358	2.00	1.3

[a] Tables of ξ_{Cu} vs. T are available from Dr. K. S. Murray. [b] $2J$ = singlet–triplet splitting; TIP ($N\alpha$) = 60×10^{-6} cm^3 mol^{-1} per Cu.

spectra (Table VI) consist of broad featureless bands with absorption maxima generally at wavelengths lower than those of the single-atom-bridged analogues. With the possible exception of **4b**, the spectra indicate that the coordination geometry of the copper centers is square planar.[34,35]

Magnetic Properties. Plots of χ_{Cu} and μ_{Cu} vs. T for representative samples are shown in Figures 2–4. As is commonly observed, many of the antiferromagnetically coupled complexes show a rapid increase in χ_{Cu} at low temperature due to a mononuclear impurity. The decrease in χ_{Cu} displayed by the ferromagnetically coupled complex **7b** (Figure 4) is probably due to intramolecular antiferromagnetic coupling. The data were fitted to the Bleaney–Bowers equations for coupled $S = {}^1/_2$ ions by using a least-squares fitting routine. The susceptibility equation allowed for the presence of a percentage of monomeric impurity that was assumed to have the same g value as the dimer.[4a,24]

We have previously described, in some detail, problems that can arise in attempting to simultaneously fit the whole of the χ_{Cu} vs. T plot in cases (such as those shown in Figures 2 and 3), where there is a minimum followed by a steep rise in χ_{Cu} at low temperatures.[24] The small observed forces in the region of the minimum give rise to relatively large errors in χ_{Cu} in this region. Therefore, in one or two cases in which a choice had to be made between acceptable fits, emphasis was given to the high-temperature fit as the effect of the Cu- - -Cu coupling dominates the high-temperature region and gives rise to the characteristic temperature dependence of χ_{Cu}. The resulting g and J values are given in Table VII, and the best-fit plots are shown in Figures 2–4.

Some interesting general trends emerge from the data in Table VII:

(i) Variation in the exogenous bridging group shows that pyrazolate gives stronger antiferromagnetic coupling than acetate, i.e., a more negative J. This probably is a result of the conjugated pyrazolate ring providing a more favorable superexchange pathway.

(ii) Within the endogenous alkoxo bridge (a) a longer $-CH_2-$ chain gives a more negative J, a factor that is presumably due to increased ligand flexibility, and (b) a saturated $-CH_2NH-$ linkage gives a less negative J than the unsaturated imine, $-CH{=}N$, linkage.

(iii) The terminal salicylaldimine group gives a more negative J than terminal 2-pyridinimine or acetylacetonimine ligands.

In comparing the present data to those obtained for single-atom-bridged analogues[24] (i.e., X = OH^-, Cl^-, OR^-), it is also possible to conclude that the order of decreasing negative J when all is kept constant except X is

$$OR^- \approx \text{pyrazolate} > \text{acetate} \approx OH^- > Cl^-$$

Since the observed J value is made up of antiferromagnetic and ferromagnetic contributions, which in turn are influenced by a variety of structural and electronic factors, the detailed reasons for these variations in J can be quite complex. In order to try to probe into these reasons in more detail, we turn now to the structure/magnetism relationship in specific examples where the crystal structures of the compounds are known.

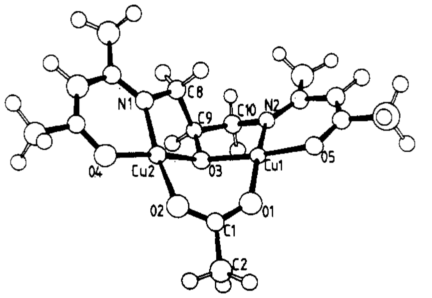

Figure 5. Molecular structure of compound **7b**. See Table VIII and ref 29 for further details.

Table VIII. Comparison[a] of Magnetic and Structural Features of Two Isomers of the Acetate-Bridged Complexes **7b**[29] and **7b′**[37]

	7b	**7b′**
J, cm^{-1}	19	−82
r(Cu- - -Cu), Å	3.24	3.50
Cu(1)–O(3)–Cu(2), deg	114.3	133.3
solid angle around O(3), deg	335.5	~360
coplanarity of {CuO_3N} "planes"	noncoplanar	~coplanar[b]

[a] In ref 29 and 37, the compounds are labeled [$Cu_2apaca(CH_3CO_2)$]. [b] Dihedral angle between {CuO_3N} planes 5.4°.

The pyrazolate-bridged complex **6a** displays antiferromagnetic coupling of medium strength. The pertinent structural features include an intramolecular Cu- - -Cu distance of 3.359 (4) Å, a Cu–O–Cu angle of 125.1 (7)°, and planar geometry around each Cu atom. Despite the short methylene chain and consequent geometric strain within the pentadentate ligand, the two {CuN_2O_2} chromophores are essentially coplanar. The angles around the bridging alkoxo oxygen add up to 359.9°, indicative of pseudotrigonal geometry. We return below in more detail to this particular feature. It is becoming evident, from the present study, and by comparison with other trigonal-planar alkoxo- or phenoxo-bridging examples, that distortions from trigonal-planar toward pyramidal bonding around the endogenous oxygen atom leads to a less negative J value.[36] In the specific case of **7b**, it leads to net ferromagnetism.

Complex **7b** provides a unique opportunity for comparison of its structural and magnetic properties[37] with those of a structural isomer (labeled **7b′**), which shows antiferromagnetic coupling (J = −82 cm^{-1}). The crystal structure of **7b′** has been compared to that of **7b** in a preliminary communication,[29] and important parameters are collected in Table VIII and Figure 5. It should be noted that **7b′** contains a molecule of water per binuclear unit, which is apparently not coordinated to a Cu atom (although the authors[37] do not specifically say this); complex **7b** is anhydrous. The binuclear units in **7b′** also pair up to form tetramers, a feature rather common to this area of chemistry.[24,36] Despite these differences, we feel that the following comments are valid with respect to the intramolecular Cu–Cu exchange interaction. The most obvious difference between the ferromagnetically coupled **7b** and antiferromagnetically coupled **7b′** is the noncoplanarity of the two Cu chromophores in **7b** and the coplanarity in **7b′**. This "folding" feature in **7b** is akin to the "roof-shaped" geometry noted by Kahn[4g] in various symmetrically bridged dihydroxo dimers. The consequent accidental orthogonality of the Cu $d_{x^2-y^2}$ magnetic orbitals postulated by Kahn to be responsible for reducing the $J_{antiferro}$ contribution relative to J_{ferro} seems to broadly hold true in the present asymmetrical species. However, what is evident

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from the structures of **7b** and **7b′**, but not in general from those of dihydroxo dimers, is the pyramidal disposition of bonding and nonbonding electron pairs around the alkoxo oxygen O(3) in **7b** and the trigonal arrangement in **7b′**. As indicated earlier, the geometry around the bridging oxygen gives a guide to the nature of the exchange coupling. We have recently published[38] one other example of a binuclear complex containing a pyramidally disposed phenoxo-bridging oxygen as well as an exogenous OH^- bridge. This compound also displayed net ferromagnetism. However, it also contained very tight Cu–O–Cu angles and short Cu–Cu distances within two coplanar cis-disposed square-pyramidal chromophores, which would also contribute to the reduced antiferromagnetism in that particular case. Since the dominant pathway for superexchange in complexes such as **7b** involves σ-type overlap between Cu ($d_{x^2-y^2}$) magnetic orbitals and oxygen p orbitals, it is difficult to see why the nature of the bridging oxygen orbitals (i.e., sp^2 or sp^3) should influence the coupling in the way that has been inferred. We feel that π-type overlap between out-of-plane Cu orbitals and the nonbonding pair on oxygen (p_z) may be more significant than is generally considered, leading to enhanced antiferromagnetism in the case of trigonal-planar oxygen and reduced antiferromagnetism in the case of pyramidal oxygen. This π-bonding suggestion was first put in an empirical way by Bertrand[39] and has been included in the later quantitative model of Gatteschi.[40] Very recently[41,42] it has been shown to be an important contribution to *J*-value variations in Cr(III) dimers, although this is perhaps to be expected in view of the symmetry of the magnetic orbitals or Cr(III), viz. $d_{xx(yz)}$.

Kida et al.[43] have very recently extended their studies on complexes of type **7b′**. Their results can be interpreted in terms of the ideas expressed here. Thus, an analogue of **7b′** with an acetyl group substituted at the γ-C of each terminal acac moiety shows r(Cu---Cu) = 3.13 Å, a dihedral angle between Cu chromophores of 54.6°, $\mu_{Cu} = 1.77\ \mu_B$, and $\theta = 24$ K. We ascribe the observed net ferromagnetism to an origin similar to that described for **7b**. The angles around O(3) will undoubtedly be ca. 330°. They have also solved the structure of **6b**: r(Cu---Cu) = 3.49 Å, Cu(1)–O(8)–Cu(2) = 134.5°, dihedral angle between Cu chromophores 18.7°. The geometry is generally similar to that of **7b′**, and the *J* values are similar (ca. $-83\ cm^{-1}$). Again, after one allows for the change in terminal bonding group and slightly larger dihedral angle, the results can be interpreted as described in the present paper. Kida et al. propose that the weaker observed antiferromagnetism in acetate-bridged complexes of the present type compared to that of a single-alkoxo-bridged parent species (without the acetate bridge) results from a competition between the two different magnetic-orbital-overlap pathways, viz. Cu–O_2–CR–Cu and Cu–OR–Cu, which may have *opposite* phase relative to each other (see ref 4g for background theory). While this effect may contribute in part, it cannot be the sole determinant since the related dibridged species **6c** and **7d** display very strong antiferromagnetism.

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Registry No. 4 (X = OH), 97703-64-5; **4a**, 97703-49-6; **4b**, 97703-51-0; **5a**, 97703-53-2; **5b**, 97703-55-4; **6a**, 97703-56-5; **6b**, 97703-57-6; **6c**, 97703-58-7; 7 (*n* = 2, X = MeO), 97703-62-3; **7a**, 97719-80-7; **7b**, 97703-59-8; **7c**, 97703-60-1; **7d**, 97703-61-2; pyridine-2-carbaldehyde, 1121-60-4; 1,3-diaminopropan-2-ol, 616-29-5; acetylacetone, 123-54-6; 1,5-diaminopentan-3-ol, 38595-00-5.

Supplementary Material Available: Listings of observed and calculated structure factors, calculated hydrogen atom parameters, anisotropic thermal parameters, and least-squares planes (9 pages). Ordering information is given on any current masthead page.

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