References and Notes

(1) (a) Laboratoire de Chimie Minérale I, Université de Lille I. (b) Laboratoire de Chimie Moléculaire et des Solutions Ioniques d'Éléments de Transition, E.N.S.C.L.
(2) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975).
(3) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972).
(4) N. G. Connelly, *Inorg. Chim. Acta, Rev.*, **6**, 48 (1972); J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 134.
(6) F. M. Van Meter and H. M. Neumann, *J. Am. Chem. Soc.*, **98**, 1388 (1976).
(7) M. J. Blandamer, J. Burgess, and M. Dupree, *J. Chem. Soc., Dalton Trans.*, 63 (1977).
(8) (a) R. D. Archer, L. J. Suydam, and D. D. Dollberg, *J. Am. Chem. Soc.*, **93**, 6837 (1971); (b) R. D. Archer and D. D. Dollberg, *Inorg. Chem.*, **13**, 1551 (1974); (c) R. D. Gillard, C. T. Hughes, L. A. Kane Maguire, and P. A. Williams, *Transition Met. Chem.*, **1**, 226 (1976).
(9) F. Abraham, G. Nowogrocki, S. Sueur, and C. Bremard, *Acta Crystallogr., Sect. B*, **34**, 1466 (1978).
(10) C. Bremard, M. Muller, G. Nowogrocki, and S. Sueur, *J. Chem. Soc., Dalton Trans.*, 2307 (1977).
(11) S. Sueur, C. Bremard, and G. Nowogrocki, *J. Inorg. Nucl. Chem.*, **38**, 2037 (1976).
(12) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).
(13) P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 139 (1971).
(14) P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).
(15) P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).
(16) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 894 (1975).
(17) S. K. Wolfe and J. H. Swinehart, *Inorg. Chem.*, **14**, 1049 (1975).
(18) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", 2nd ed, Wiley, New York, N.Y., 1961, pp 173–177; (b) M. V. Olson and C. E. Behnke, *Inorg. Chem.*, **13**, 1329 (1974).
(19) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
(20) D. A. Buckingham, D. J. Francis, and A. M. Sargeson, *Inorg. Chem.*, **13**, 2630 (1974).
(21) T. A. Turney and G. A. Wright, *J. Chem. Soc.*, 2415 (1958).
(22) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6243 (1954).
(23) G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Am. Chem. Soc.*, **87**, 5785 (1965).
(24) The nitrosyl complexes Ru(dmvi)₂NOX (X = Cl, Br, OH, dmvi) are not soluble in water and do not possess deprotonation sites as Ru-(H₂vi)₂NOX: S. Sueur, C. Bremard, and G. Nowogrocki, *J. Inorg. Nucl. Chem.*, **38**, 2037 (1976).
(25) Me₂SO is not inert toward nitrosonium salts even when carefully purified but is inert toward the coordinated nitrosyl group.
(26) B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).
(27) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **12**, 2095 (1973).
(28) (a) J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 5928 (1968); (b) F. M. Lever and A. R. Powell, *J. Chem. Soc. A*, 1477 (1969).
(29) S. S. Isied and H. Taube, *Inorg. Chem.*, **15**, 3070 (1976).
(30) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **95**, 1825 (1973).
(31) (a) D. G. Bickley and N. Serpone, *Inorg. Chem.*, **15**, 948 (1976); (b) *ibid.*, **15**, 2577 (1976).
(32) T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 3318 (1970).
(33) A. Domenicano, A. Vaciano, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *J. Chem. Soc., Chem. Commun.*, 476 (1966).
(34) J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc. A*, 44 (1971); J. Burgess, *J. Chem. Soc., Dalton Trans.*, 1061 (1972).
(35) (a) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950); (b) P. Krumholz, *J. Chem. Soc.*, 60 (1956); (c) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **92**, 5319 (1970).
(36) R. H. Lane, F. A. Sedor, M. J. Gilroy, and L. E. Bennet, *Inorg. Chem.*, **16**, 102 (1977).
(37) J. G. Gordon and R. H. Holm, *J. Am. Chem. Soc.*, **92**, 5319 (1970).

Unusual Magnetic Properties in Two Copper(II) Chelates of Schiff Bases Derived from α-Amino Acids: A Dimeric Interaction in a Structural Linear Chain

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The magnetic properties of two unusual Schiff base copper(II) chelates, (N-salicylideneglycinato)aquocopper(II) hemihydrate and (N-salicylidene-α-aminoisobutyrato)aquocopper(II), have been measured as a function of temperature (1.6–160 K) and applied field strength (10–50 kOe). The data reveal that the exchange interaction in [Cu(N-sal=gly)H₂O]·0.5H₂O is predominantly between pairs of copper(II) ions in different structural chains rather than between an infinite linear array of copper(II) ions along the obvious crystallographic chain, in moderate magnetic fields. The dimer model yields an exchange energy, J, of -2.19 cm^{-1} with the intercluster exchange being only about -0.09 cm^{-1}. High-field isothermal magnetization data with the applied field stronger than the exchange energy, $H > 2J/g\beta$, indicate that the intercluster terms become significant as longer range interactions occur when the ground-state multiplicity changes. The data for the structurally similar [Cu(N-sal=aiba)H₂O] complex reveal interactions which are about an order of magnitude smaller ($J = -0.8$ cm^{-1}) than the glycinato analogue; in addition, the choice between the pair model and the linear-chain model is much less certain. The similarities and differences in the interactions present in both compounds are compared to their known crystallographic structures. The possibilities of long-range magnetic ordering in strong applied magnetic fields and of unusual adiabatic cooling are postulated for [Cu(N-sal=gly)H₂O]·0.5H₂O.

Introduction

Ordinarily one expects the structural and magnetic properties of a given substance to be intimately related[1-6] with the dimensionality of the magnetic or electrical interactions that are present reflecting the lattice dimensionality.[3] For example, a cluster of two interacting magnetic ions should obey a theoretical model whose statistics treat only the pair of interacting spins. Systems in which there are interactions between a small number of spins in a definable cluster within a macroscopic crystal are considered to be zero-dimensional (0-D) from a lattice viewpoint.[3] Each cluster is assumed to be isolated from neighboring clusters in the crystal structure,

and interactions of spins of the individual clusters with the spins on neighboring clusters are assumed to be absent. This basic idea may be generalized to include one-dimensional chains (1-D) and two-dimensional layers (2-D). Eventually such a process leads to the ultimate reality of a three-dimensional (3-D) crystal structure in which there are more or less equally interacting near neighbors.[3]

The above simplified description of the effects of lattice dimensionality on the isotropic Heisenberg exchange interaction rarely applies to real chemical systems.[3,6-8] Crystal packing requirements and weak *interunit* bonding or hydrogen bonding often occur and these features can give rise to ad-

ditional pathways for electrical[4] or exchange interactions[3] between electrons on different units. The consequences of these additional pathways for interactions lead to magnetic lattice dimensionality "crossovers" and eventually to long-range magnetic order[9] or superconductivity.[4] For example, dichlorobis(pyridine)copper(II), Cu(py)$_2$Cl$_2$, is a 1-D magnetic chain whose *intrachain* exchange, J, is much stronger than the *interchain* exchange, J'. Nonetheless, the small coupling between chains is sufficiently strong to cause long-range magnetic order at very low temperatures.[10] Most of the experimental results to date[3,7-10] have been concerned with systems which show an *increase* in "magnetic dimensionality" as the temperature is lowered. It is of importance to note that the reverse situation, a lattice dimensionality *decrease*, can also occur. The Peierls[11] or "spin-Peierls"[12] transition can take a 1-D ensemble, via an appropriate distortion, to a 0-D dimerized array.

It is of considerable interest to study systems which display one type of structural dimensionality but another form of "magnetic dimensionality". Historically, the most famous example is Cu(NO$_3$)$_2$·2.5H$_2$O. In a series of elegant experiments, Friedberg and his co-workers have shown that the zero-field susceptibility,[13] magnetic specific heat,[14] and high-field isothermal magnetization[15] could be rather well described by a simple model of two copper(II) ions coupled by weak Heisenberg isotropic exchange plus a small *interdimer* exchange. From three independent measurements prior to 1970 (some of which extended down to 0.5 K), it was concluded that Cu(NO$_3$)$_2$·2.5H$_2$O was a dimeric cluster with a singlet ground state lying about 3.5 cm^{-1} below an excited triplet state. However, later structural studies by Garaj[16] and Morosin[17] revealed that the molecular structure did not consist of discrete clusters of copper(II) ions but was a zigzag linear array of copper(II) ions bridged by oxygen atoms from a bidentate nitrate ion. A great deal of current interest in Cu(NO$_3$)$_2$·2.5H$_2$O has been generated because of its unusual cooling properties under adiabatic demagnetization conditions[18-22] and because of the unusual superexchange pathways.[23] The unusual magnetic and cooling properties have stimulated a considerable amount of theoretical work aimed at trying to understand the subtle exchange processes present in this compound.[24,25] Quite recently Van Tol et al.[26] have shown conclusively that Cu(NO$_3$)$_2$·2.5H$_2$O does show long-range magnetic order but only over a limited range of strong external fields near the point where the lowest component of the excited triplet state crosses the ground singlet.

Recent investigations in our laboratories have also revealed several examples of compounds with noncongruent structural and magnetic dimensionalities. The magnetic properties of Cu(NH$_3$)$_2$CO$_3$, a compound in which copper(II) ions are bridged by carbonate ligands to form chains,[27] may be described by a simple dimeric model even though there are only weak hydrogen bonds between chains.[28] Likewise, the structural data for the dichloro- and dibromo[2-(2-amino-ethyl)pyridine]copper(II) complexes reveal a "ladderlike" arrangement with strongly bound dimers forming the rungs of the ladder while weaker out-of-plane halide bridges form the sides.[29,30] The observed magnetic properties are best described by an alternating chain model[32] or a "spin-ladder"[24] since neither the pair nor the linear models are appropriate.

Two additional compounds, (N-salicylideneglycinato)-aquocopper(II) hemihydrate[33] and (N-salicylidene-α-aminoisobutyrato)aquocopper(II),[34] have properties which yield information on this problem. Complexes of this general type (see Figure 1) have attracted considerable attention in recent years since they have been widely used as model systems for nonenzymatic transamination reactions in biological systems (for a comprehensive review of this aspect of the

Cu(N-sal=α-AA)·H$_2$O

AA = glycine, R = H

AA = α-aminoisobutyric acid, R = CH$_3$
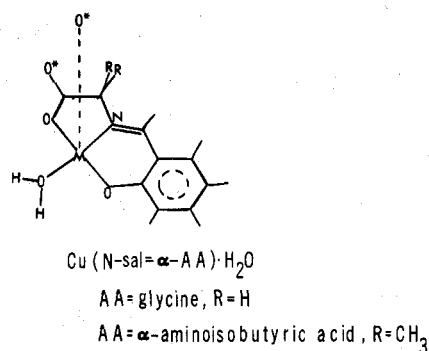
Figure 1. Generalized molecular structure of the copper Schiff base chelates derived from salicylaldehyde and α-amino acids. The oxygen atom marked by an asterisk is the "free" carboxyl oxygen which propagates the linear chain.

chemistry of these complexes see ref 35). The biochemical relevance of these compounds has stimulated crystallographic investigations of several members of the series, including the glycinato[36] and α-aminoisobutyrato[37] derivatives mentioned above. The outstanding crystallographic features of both of these complexes are those of a structural linear chain of copper ions bridged by carboxylate oxygen atoms, but, as shown in this article, the magnetic properties of these species are quite different from those expected from the structural data.
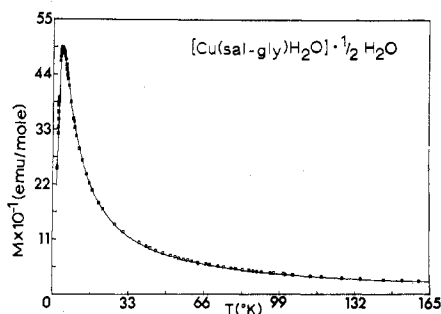
Experimental Section

Preparation of the Complexes. [Cu(N-sal=gly)H$_2$O]·0.5H$_2$O. Since there is some confusion in the literature concerning the preparation of this complex,[33,38,39] we give here the details of the procedure used in this study.

Glycine, 6.10 g (0.08 M), was dissolved in a small amount of water (~50 mL). The solution was filtered and added slowly to a solution of salicylaldehyde (0.08 M) in 95% ethanol at 70 °C; this mixture was stirred vigorously for 10 min and then treated with additional portions of water to keep the Schiff base in solution. A solution of copper acetate monohydrate (0.08 M) in the minimum amount of water was then added to the stirred solution of the Schiff base. Large quantities of a bright green needlelike product separated over a period of 20 min. Apparently this bright green material is [Cu(N-sal=gly)H$_2$O·4H$_2$O,[40] since the color and morphology of the crystals appear identical. The desired complex was obtained by slow crystallization (~3 weeks) of the above product from a mixture of aqueous ethanol (H$_2$O–ethanol, 2:1 v/v) at room temperature. Very small, dark green prisms were carefully harvested and allowed to air-dry. Anal. Calcd for [Cu(C$_9$H$_2$NO$_3$)H$_2$O]·0.5H$_2$O: C, 40.38; H, 3.76; N, 5.23. Found: C, 40.68; H, 4.0; N, 5.20.

Cu(N-sal=(α-aiba))H$_2$O. This complex was prepared and recrystallized by Nakahara's method.[34] Anal. Calcd for Cu(C$_{11}$H$_{11}$NO$_4$)·H$_2$O: C, 46.07; H, 4.57. Found: C, 45.87; H, 4.42. Microanalyses of both compounds were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Susceptibility and isooerstic (constant-field) magnetization measurements were made on finely powdered samples using a PAR Model 155 VSM; details of the temperature measurements and calibrations of the magnetometer are described in detail elsewhere.[41] These measurements were carried out at field strengths of 10 kOe.

High-field isothermal magnetization data were obtained from a PAR Model 150-A VSM from 10 to 50 kOe. Data collected at 4.2 K were obtained by flooding the sample zone with liquid helium and collecting the data point by point in both increasing and decreasing fields; the superconducting solenoid was placed in the persistent mode for approximately 1 min during collection of each data point. For temperatures below 4.2 K, the sample and sample zone were pumped down to a convenient temperature in zero applied field, the voltage across the Ga–As diode thermometer was noted and recorded, and the pressure in the cryostat was measured by an external pressure gauge (Bourdon tube-type) attached to the cryostat vacuum line. The magnetic field was then energized to a desired value, a data point was collected, and the pressure and the voltage across the diode were monitored. Upon reaching the highest attainable field strength, the

Figure 2. Experimental magnetization vs. absolute temperature (squares) at a constant applied field of 10 kOe. The theoretical curve is the best fit to eq 2 and 3 with parameters listed in Table I.
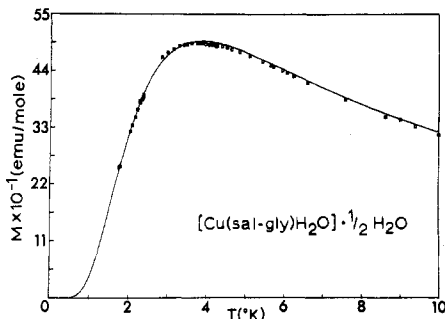

Figure 3. Expanded-scale view of the lowest temperature data from Figure 2.

data were then recollected with decreasing field strength, and the solenoid was deenergized. Once back at zero field, the temperature and pressure were again measured. If either the temperature (at $H = 0$) or the "rough" pressure had changed (1–2%) during the isotherm, then the entire data set was considered to be in error and those data were discarded. The characteristics of our cryostat were such that the lowest attainable temperature (~ 1.4 K) could not be maintained for extended time periods owing to overloading of the vacuum systems.

Electron paramagnetic resonance spectra were obtained on a Varian E-3 spectrometer operating at X band (~ 9.5 GHz). Powder spectra were observed at room temperature and at 77 K. The magnetic field was calibrated by NMR resonance techniques (^{1}H) using a Magnion G-502 precision gaussmeter and a Hewlett-Packard 5340-A frequency counter.

Results

The magnetization data for Cu(N-sal=gly)H$_2$O·0.5H$_2$O are shown in Figures 2–4. Constant-field data were collected at an applied field strength of 10 kOe over the temperature range 1.6–160 K (see Figures 2 and 3). The data are seen to go through a maximum near 3.5 K and rapidly approach zero as T approaches zero. Surprisingly, this is just the behavior one expects for a simple spin pair coupled by a Heisenberg exchange interaction between centers. However, we must also emphasize that since the exchange energy is quite small, the effects of the applied magnetic field are noticeable only at low temperatures or in strong magnetic fields. Since the Zeeman energy at $H = 10$ kOe and the singlet–triplet splitting are of the same order of magnitude (~ 1 and 4 cm^{-1}, respectively), it should then be possible to force the lowest component of the triplet excited state (i.e., $M_s = -1$) to cross the singlet ground state when the Zeeman energy is larger than the zero-field singlet–triplet splitting, $H > 2J/g\beta$ (see Figure 4 for the sketch of the zero-field and Zeeman energies). We have measured the magnetization of the glycinato derivative along isotherms in applied fields below the zero-field singlet–triplet splitting and have scanned through the region where the level crossing occurs; these data are shown in Figure 5. Inspection of the isothermal data does show an anomaly in the magnetization near 40 kOe at $T = 1.72$ K. McGregor et al.[41] and Berger et al.[15] have discussed this phenomenon in detail and have
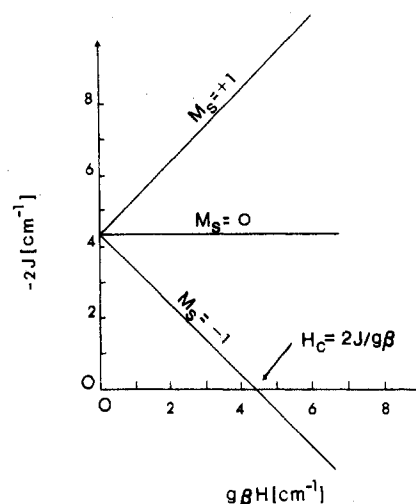
Figure 4. Sketch of the zero-field exchange energy vs. Zeeman energy for a weakly coupled pair of spins. The exchange energy, $2J$, is negative and the $S = 0$ state is collinear with the horizontal axis.
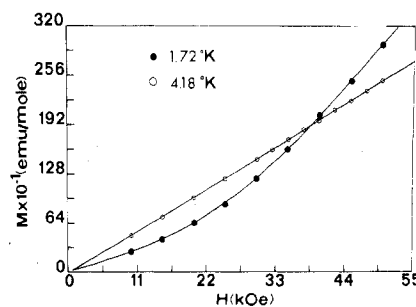
Figure 5. High-field isothermal magnetization data for the glycinato complex [Cu(sal-gly)H$_2$O]·0.5H$_2$O. The solid lines represent the best fit to eq 2 and 3 with the parameters listed in Table I.
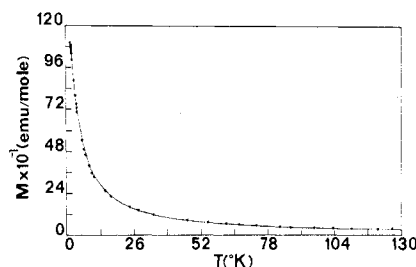
Figure 6. Observed constant field (10 kOe) magnetization vs. temperature for the α-aminoisobutyrato complex Cu(sal-α-aiba)H$_2$O. The theoretical curve is the best fit to the dimer model in eq 2 and 3 (see text for discussion of the parameters).

presented excellent graphical representations which show these effects.

The magnetization data (10 kOe) over the temperature interval 1.6–130 K for the aminoisobutyrato complex are shown in Figure 6. Even though the available structural data show that the two compounds are very similar, the magnetization data are quite different. Indeed, close inspection of the lowest temperature data for Cu(N-sal=α-aiba)H$_2$O fails to show any trace of a maximum. Thus, an interaction, if present, must be very small.

The values of the **g** tensor were measured directly from paramagnetic resonance spectra of powdered samples and the average value of the **g** tensor was also estimated from fitting the high-temperature data ($T = 20$ K) to the Curie–Weiss law. EPR spectra of the glycinato complex reflect the full **g** tensor anisotropy with $g_1 = 2.08$, $g_2 = 2.14$, $g_3 = 2.25$, and $g_{av} = 2.14$. In contrast to the sharp well-resolved lines of [Cu(N-sal= gly)H$_2$O]·0.5H$_2$O the EPR spectrum of Cu(N-sal=(α-

Table I. Magnetic Parameters for Cu(N-sal=(α-AA))H₂O

amino acid	EPR $\langle g \rangle$	Curie–Weiss law		best-fit parameters				model
		$\langle g \rangle$	Θ, K	J, cm⁻¹	g	γ	J', cm⁻¹	
glycine	2.16	2.11	−3.2	−2.195 ± 0.002	2.09 ± 0.003	−0.63 ± 0.035	−0.089	pair, eq 3 and 4, M vs. T
				−2.11 ± 0.05	2.11 ± 0.02	−2.24 ± 0.40	−0.32	pair, T = 4.2 isotherm
				−2.11 ± 0.15	2.10 ± 0.04	−2.42 ± 0.60	−0.35	pair, T = 1.72 isotherm
α-aminoisobutyric acid	2.17	2.09	−1.5	−0.81 ± 0.2	2.09 ± 0.03	−2.03 ± 0.03	−0.29	pair, M vs. T
				−0.74 ± 0.3	2.05 ± 0.41			linear chain [44],[45]

Table II. Selected Structural Data

amino acid	space group	Z^a	Cu–Cu, Å intra-chain	Cu–Cu, Å inter-chain	Z'^b
glycine	$C2/c$	8	5.33	5.003	4
α-aminoisobutyric acid	$P2_1/c$	8	4.85	5.00	~4

^{a} Number of molecules per cell. ^{b} Number of nearest neighbors.
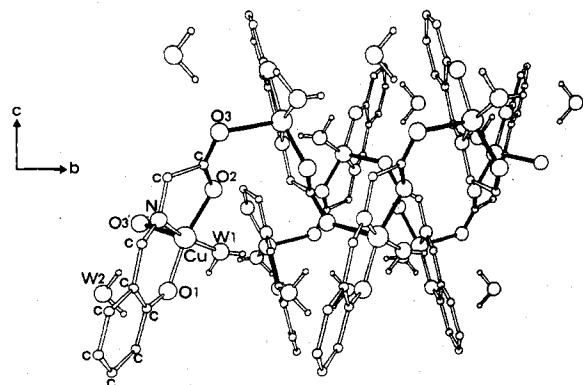
Figure 7. Projection of the unit cell of the glycinato complex ([Cu(N-sal=gly)H₂O]·0.5H₂O) onto the bc plane. The bonds which propagate the chains running parallel to the b axis are blackened. The labeling scheme is that of ref 36, and W1 and W2 represent the coordinated and "free" water molecule, respectively.

aiba))H₂O revealed only a single broad (~700 G) line centered near g = 2.17; no temperature dependence of the EPR lines of either compound was observed down to 77 K. The estimated values of $\langle g \rangle$ from the susceptibility data for the glycine (g = 2.11) and aminoisobutyrato (g = 2.09) complex were in agreement with these measured directly from the resonance data (see Table I).

Discussion

Structural Data. The gross structural features of both complexes are very similar (see Table II).[36,37] As noted above, the prominent structural feature of both complexes is the presence of a zigzag linear chain which is formed by the coordination of a "free" carboxyl oxygen atom from an adjacent molecule to the apical site of the roughly square-pyramidal array of donor atoms about a particular copper ion. This leads to an unusual three-atom bridge, Cu–O–C–O–Cu, and a spiraling chain of copper(II) ions running approximately parallel to the crystal b axis. In Figures 7 and 8, projections onto the bc plane of the unit cells of both complexes are shown. The bonds which propagate the chain running the b axis are blackened or dashed for clarity. This arrangement leads to the result that the copper–copper separation (5.33 Å) within a chain in the glycinato complex is substantially longer than the copper–copper separation between chains (5.00 Å). In the aminoisobutyrato complex, the reverse situation obtains, with the *intrachain* copper–copper distance (4.85 Å) being shorter than the *interchain* distance of 5.00 Å. It is of further interest to note that in Cu(N-sal=α-aiba)H₂O, nearest-neighbor copper ions within a given chain are crystallographically and magnetically independent of each other while copper ions in
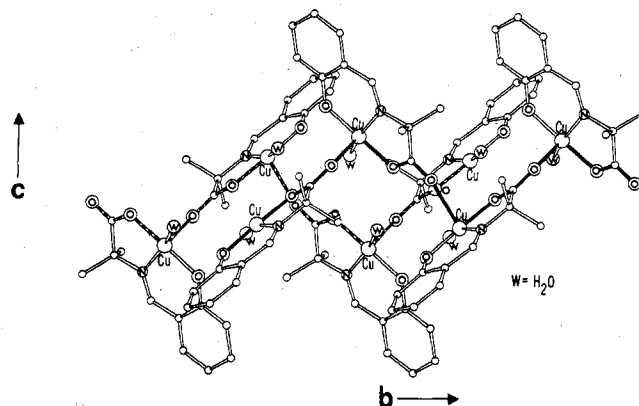

Figure 8. A projection of the unit cell of Cu(N-sal=(α-aiba))H₂O onto the bc plane. Only atoms bonded to copper are labeled. The two chains which spiral along the b axis are blackened and dashed for clarity.
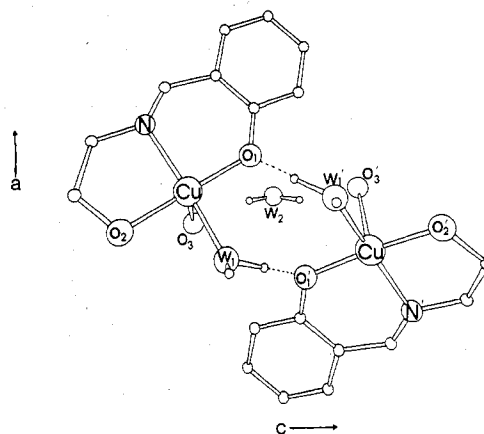

Figure 9. A projection along the b axis of [Cu(N-sal=gly)H₂O]·0.5H₂O showing the close contacts established between copper ions in *different* chains. The free water molecule, W2, lies on a crystallographic twofold axis.

different chains are related by inversion centers. Thus, an antisymmetric exchange term of the form $D(S_1 \times S_2)$ will be allowed along the chain but forbidden between chains.[43] In the glycinato complex, such a term is allowed along the chain and between the nearest-neighboring chains but forbidden between next-nearest-neighboring chains.

Since the molecules within a chain spiral along the b axis, relatively close interchain contacts are established between the coordinated water molecule of one copper atom to the phenolic or carboxyl oxygen atoms of a neighboring chain. These interactions are of prime importance in the glycinato complex since the relative positions of the coordinated water molecule (W1) and the "free" water molecule (W2) allow extensive hydrogen bonding between chains.[46,47] A view (along the b axis) of two copper ions in different chains in the glycinato complex is shown in Figure 9. The distances from the phenolic oxygen atoms (O1 and O1') to the hydrogen atoms of the neighboring coordinated water molecules (W1 and W1') are 2.61 Å (dashed line). In addition, the "free" water molecule (W2) which is situated on a twofold axis forms weak hydrogen

bonds to the apical carboxyl oxygens (O3 and O3′) of 2.95 Å and to the hydrogen atoms of the coordinated water molecule of 2.30 Å. In the aminoisobutyrato complex, similar close contacts of 2.67 Å exist between an in-plane carboxyl oxygen and the oxygen atom of the coordinated water molecule of a neighboring chain. However, the relative orientation of the chelate rings and the absence of a water molecule between chains lead to no additional close contacts in the aminoisobutyrato complex.

Magnetic Data. The Hamiltonian for an isotropic Heisenberg exchange interaction of a spin-pair system in a nonzero applied magnetic field is given by

$$H = -2J\hat{S}_1 \cdot \hat{S}_2 + g\beta HS + D[S_z^2 - S(S + 1)/3] + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (1)$$

where $\hat{S}_1 = \hat{S}_2$ are the spin operators, $S = S_1 + S_2$ is the total spin, and H is the applied magnetic field. The parameters D and E are zero-field splitting tensors of the $S = 1$ state. Thus, in zero applied field, the isotropic exchange interaction $(-2JS_1 \cdot S_2)$ couples the spins S_1 and S_2 into a new set of states of singlet and triplet spin multiplicity, and these states can be further split by the Zeeman interaction in an applied magnetic field (neglecting the smaller D and E terms). In this particular example, an exact expression for the magnetization can be easily derived, and the magnetization per mole of $S = \frac{1}{2}$ ions is given by eq 2.[15] Interactions which may give rise to deviations from the pair model (interpair exchange, etc.) must

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1} \quad (2)$$

be accounted for by a molecular field correction term (3),

$$H_{eff} = H + \gamma M \quad (3)$$

where M is the magnetization resulting from the effective field and the isotropic exchange interaction, and γ is the molecular field parameter. Equations 2 and 3 may be solved by repeated iteration until a self-consistent solution is found.[15,41,42]

We have fitted the observed magnetization vs. temperature data ($H = 10$ kOe) for [Cu(N-sal=gly)H$_2$O]·0.5H$_2$O to eq 2 and 3 and find remarkable agreement with the pair model over the entire temperature range (1.6–160 K). Attempts to describe a susceptibility, $\chi = M_{obsd}/H$, in terms of the isotropic linear-chain model of Bonner and Fisher[44] failed. Thus, in moderate magnetic fields ($H \approx 10$ kOe), the pair model provides an excellent fit to the observed data with $g = 2.089 \pm 0.003$, $2J = -4.38 \pm 0.02$ cm^{-1}, and $\gamma = -0.63 \pm 0.033$; the mean fractional deviation (MFD), defined as $\sum [|M_{obsd} - M_{calcd}|/M_{obsd}]/N$, where N is the number of observations, of a data point from the theoretical curve was 0.787×10^{-2} for this fit. Within the molecular field approximation, γ is related to the interpair exchange by

$$Z'J' = \gamma Ng^2\beta^2/2 \quad (4)$$

where Z' is the number of nearest neighbors and J' is the interpair exchange energy. Since the number of nearest neighbors, Z', is 4 for a C-centered cell, a very small interpair exchange, $J' = -0.089$ cm^{-1}, may be calculated.

Since Bonner et al.[23,24] had noted that the effects of the additional exchange interactions became more significant when Cu(NO$_3$)$_2$·2.5H$_2$O was placed in strong magnetic fields, we have measured the isothermal magnetization of [Cu(N-sal=gly)H$_2$O]·0.5H$_2$O at temperatures above and below T_{max}. In agreement with the observations of those authors, we found that increasing deviations from the simple pair model in eq 2 and 3 were apparent in applied magnetic fields approaching $H_{cross} = |2J|/g\beta$. Thus, the best fit to the $T = 4.2$ K isotherm yields $g = 2.11 \pm 0.02$, $2J = 4.22 \pm 0.10$ cm^{-1}, and $\gamma = -2.24 \pm 0.40$ with the sum of the squares of the deviation, SD =

$\sum |M_{obsd} - M_{calcd}|^2/M_{obsd}^2$, being 0.312×10^{-4}. The major reason for including a much larger molecular field term was to fit the data above about 35 kOe more precisely. In further agreement with the above observation, the isotherm at 1.72 K required a still larger molecular field term, but within the precision of the fit nearly identical values for the singlet–triplet splitting were obtained; the parameters for this fit are $g = 2.10 \pm 0.04$, $2J = -4.22 \pm 0.30$ cm^{-1}, $\gamma = -2.42 \pm 0.60$, and SD $= 0.192 \times 10^{-3}$. Since strong magnetic fields will alter the population of the excited triplet state and eventually change the multiplicity of the ground state (at H_{cross}), the additional pathways for exchange, which are some 2 orders of magnitude smaller in moderate applied fields, become increasingly more important in strong fields at very low temperatures. In view of the chainlike arrangement of copper ions in this complex, it is tempting to attribute the enhanced interaction to superexchange along the one-dimensional path.

The observed magnetization vs. temperature data for Cu(N-sal=(α-aiba))H$_2$O were fitted to eq 2 and 3, and only a marginal fit to this model was obtained with $g = 2.09 \pm 0.03$, $2J = -0.81 \pm 0.20$ cm^{-1}, $\gamma = -2.03 \pm 1.0$, and SD $= 0.239 \times 10^{-2}$. The absence of a singularity in the observed data, i.e., a maximum in M, made fitting difficult since fairly substantial changes in the parameters caused little change in the quality of the fit. It is surprising that the observed interaction is apparently so much smaller in this compound than in the glycinato analogue since the contacts between chains are comparable. However, in this compound, the *interchain* copper–copper distance (5.00 Å) is longer than the *intrachain* distance (4.85 Å). If the exchange pathway along the chemical chain is predominant, then one might expect a linear model to be more appropriate. To investigate this possibility, the data for Cu(N-sal=α-aiba)H$_2$O were compared to the linear Heisenberg chain model using the high-temperature series expansion of Baker et al.[45] Upon truncating the observed data to those above 4.2 K and defining a susceptibility as $\chi = M_{obsd}/H$, a rather poor fit to the observed data yielded $g = 2.05 \pm 0.04$, $2J = -0.74 \pm 0.30$ cm^{-1}, and SD $= 0.33 \times 10^{-2}$. Thus, within the limits of the fitted parameters, a clear choice of the appropriate model cannot be made. Most likely neither the pair nor the linear model are truly appropriate since the structural data suggest that the two exchange pathways are comparable.

It is of interest to compare the possible pathways for the superexchange interactions in these compounds. Apparently the large *intrachain* distances and a three-atom bridging arrangement make exchange along the chains quite weak. In the glycinato complex, this intrachain mechanism leads to very weak interactions, and the observed exchange involves superexchange through the extensive hydrogen bonds between ions in different chains. The presence of a "free" water molecule (W2) situated between chains and the relative orientation of the chelate rings in the glycinato complex makes this *interchain* pathway considerably more favorable. Thus, in moderate magnetic fields the magnetic properties of the glycinato compound are readily described by a dimeric model. In contrast, the structural features of Cu(N-sal=(α-aiba))·H$_2$O suggest that the two exchange pathways are comparable since the intrachain copper–copper distances are longer and the interchain hydrogen bonds are somewhat weaker than in the glycinato complex.

Conclusion

The observed magnetic properties of [Cu(N-sal=gly)-H$_2$O]·0.5H$_2$O can be readily described by a simple pair-model coupling two copper(II) ions even though an additional higher dimensional pathway is present. The singlet–triplet splitting of about 4.4 cm^{-1} allows a field-induced ground state change in strong applied fields such that $H_{app} > 2J/g\beta$. Increasing

deviations from the pair model are observed in strong fields and at very low temperatures, and these deviations can be ascribed to longer range interactions among the newly induced ground states of the antiferromagnetically coupled pairs. Thus, experiments such as cooling by adiabatic demagnetization[18-25] should be possible for this complex. In addition, it should be possible to observe long-range three-dimensional ordering at very low temperatures over a small range of effective fields near the singlet–triplet crossing. Recent work on Cu(N-O_3)$_2$·2.5H_2O,[26,48] whose gross structural features are very similar, has shown that long-range antiferromagnetic ordering does occur at 0.175 K in fields of about 36 kOe. In Cu(N-O_3)$_2$·2.5H_2O two additional exchange pathways exist (other than the pairwise interaction), and the choice between an alternating chain and spin-ladder model cannot be made easily. The structural differences of [Cu(N-sal=gly)H_2O]·0.5H_2O vs. the nitrate salt are unique in this respect since only one additional exchange pathway exists, namely, the "obvious" chemical chain.

The situation in [Cu(N-sal=(α-aiba))H_2O] is more difficult to describe. A combination of subtle structural variations outlined above apparently has dramatically modified the strength of the magnetic interactions. Thus, while similar paths between chains exist, the intrachain pathways become important because the shortest copper–copper distance is along this path. Our work cannot make a clear choice between the dimer and linear-chain models. Very low-temperature (<1 K) measurements are required to verify the appropriate magnetic model.

Registry No. Cu(N-sal=gly)H_2O, 36748-34-2; Cu(N-sal=(α-aiba))H_2O, 16788-10-6.

References and Notes

(1) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975).
(2) W. E. Hatfield in "Theory and Applications of Molecular Paramagnetism", L. Mulay and E. Boudreaux, Ed., Wiley, New York, N.Y., 1976, Chapter 7.
(3) L. J. deJongh and A. R. Miedema, *Adv. Phys.*, **23**, 1 (1974).
(4) I. F. Shchegolve, *Phys. Status Solidi A*, **12**, 9 (1972).
(5) R. P. Shibaeva and L. O. Atovmyan, *Zh. Strukt. Khim.*, **13**, 546 (1972); *J. Struct. Chem. (Engl. Transl.)*, **13**, 546 (1972).
(6) W. E. Estes, J. W. Hall, and W. E. Hatfield, to be submitted for publication.
(7) W. E. Estes and W. E. Hatfield, to be submitted for publication.
(8) R. L. Carlin, *Acc. Chem. Res.*, **9**, 67 (1976).
(9) L. J. deJongh, *Physica B + C (Amsterdam)*, **82**, 247 (1976).
(10) W. Duffy, P. J. Venneman, D. Strandburg, and P. M. Richards, *Phys. Rev. B*, **9**, 2220 (1974).
(11) J. Ferraris, D. O. Cowan, V. Walatlea, and J. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973), and references therein.
(12) J. Bray, H. Hart, L. Interrante, I. Jacobs, J. Kasper, G. Watkins, S. Wee, and J. Bonner, *Phys. Rev. Lett.*, **35**, 744 (1975), and references therein.
(13) L. Berger, S. A. Friedberg, J. T. Schriempf, *Phys. Rev.*, **132**, 1057 (1963).
(14) S. Friedberg and C. Raquet, *J. Appl. Phys.*, **39**, 1132 (1968).
(15) L. Berger, S. A. Friedberg, and J. T. Schriempf, *J. Appl. Phys.*, **40**, 1149 (1969).
(16) J. Garaj, *Acta Chem. Scand.*, **22**, 1710 (1968).
(17) B. Morosin, *Acta Crystallogr., Sect. B*, **26**, 1203 (1970).
(18) M. Tachiki, T. Yamada, and S. Maekawa, *Proc. Int. Conf. Low Temp. Phys., 12th*, 687 (1971).
(19) T. Haseda, Y. Tokunga, R. Yamada, Y. Kukamitsu, S. Sakatsume, and K. Amaya, *Proc. Int. Conf. Low Temp. Phys., 12th*, 685 (1971).
(20) K. Cunayer, Y. Tokunaga, R. Yamada, Y. Ajro, and T. Hasodu, *Phys. Lett. A*, **28**, 732 (1969).
(21) Y. Tokunaga, S. Ikoda, J. Watamabe, and T. Hasada, *J. Phys. Soc. Jpn.*, **32**, 429 (1972).
(22) K. Cunaya, N. Yamashita, M. Matsukra, and T. Haseda, *J. Phys. Soc. Jpn.*, **37**, 1173 (1974).
(23) J. C. Bonner, S. A. Friedberg, H. Kobayashi, and B. E. Meyers, *Proc. Int. Conf. Low Temp. Phys., 12th*, 691 (1971).
(24) J. C. Bonner and S. A. Friedberg, *AIP Conf. Proc.*, **No. 18**, 1311 (1974).
(25) M. Tachiki and T. Yamada, *J. Phys. Soc. Jpn.*, **28**, 1413 (1970).
(26) M. W. Van Tol, K. M. Diederix, and N. J. Poulis, *Physica B + C (Amsterdam)*, **64**, 363 (1973).
(27) M. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B.*, **28**, 1607 (1972).
(28) D. Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **11**, 185 (1972).
(29) V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 1826 (1972).
(30) V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 1340 (1973).
(31) D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, **76**, 2707 (1972).
(32) W. Duffy and K. Barr, *Phys. Rev.*, **165**, 647 (1968).
(33) A. Nakahara, *Bull. Chem. Soc. Jpn.*, **32**, 1195 (1959).
(34) Y. Nakao, K. Sakurai, and A. Nakahara, *Bull. Chem. Soc. Jpn.*, **40**, 1536 (1967).
(35) D. L. Leussing in "Metal Ions in Biological Systems", Vol. 5, H. Siegel, Ed., Marcel Dekker, New York, N.Y., 1976, Chapter 1.
(36) T. Ueki, T. Ashida, Y. Sarada, and M. Kakudo, *Acta Crystallogr.*, **22**, 870 (1967), and references therein.
(37) H. Fujimoki, I. Oonishi, F. Muto, A. Nakahara, and Y. Komiyama, *Bull. Chem. Soc. Jpn.*, **44**, 28 (1971), and references therein.
(38) M. Kishita, A. Nakahara, and M. Kubo, *Aust. J. Chem.*, **17**, 810 (1964).
(39) (a) G. N. Weinstein, M. J. O'Connor, and R. H. Holm, *Inorg. Chem.*, **9**, 2104 (1970); (b) G. O. Carlisle and W. E. Hatfield, unpublished observations.
(40) T. Ueki, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Crystallogr., Sect. B*, **25**, 328 (1969).
(41) K. T. McGregor, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 421 (1976).
(42) E. D. Estes, W. E. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 2564 (1975).
(43) P. Erdos, *J. Phys. Chem. Solids*, **27**, 1705 (1966), and references therein.
(44) J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, **135**, 640 (1964).
(45) G. A. Baker, G. S. Rushbrooke, and H. E. Bilbert, *Phys. Rev. A*, **135**, 1273 (1964).
(46) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968, p 16 ff.
(47) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(48) K. M. Diederix, J. P. Groen, L. S. J. M. Henkens, T. O. Klaessen, and N. J. Poulis, *Physica B + C (Amsterdam)*, **93**, 99 (1978), and the references therein.