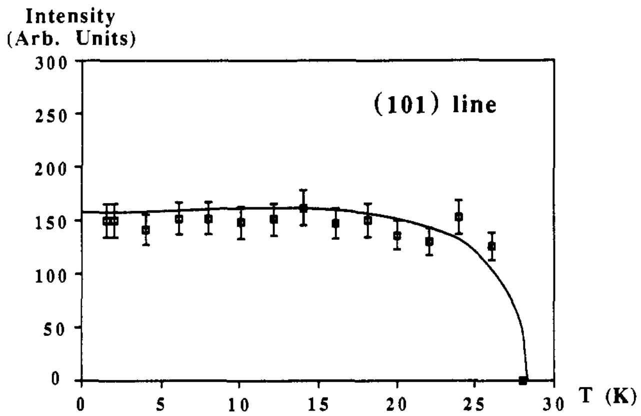

Figure 8. Temperature dependence of (101) line intensity.

diffraction pattern corresponding to that hypothesis is given in Figure 7. The variation of the intensity of the (101) magnetic line vs. temperature is given in Figure 8 and leads to an ordering temperature of $T_N = 28 \pm 1$ K.

Conclusions

We may conclude from this investigation that the linear chain hydrated fluoride $Tl_2MnF_5{\cdot}H_2O$ behaves as a 1D magnetic material like the other already investigated $A_2MF_5{\cdot}H_2O$ compounds. Within the infinite $(MnF_5)_n^{2n-}$ chains, MnF_6 octahedra are characterized by elongated Mn–F bridging distances enhanced by a Jahn–Teller effect associated with high-spin Mn(III). In the Tl phase the bridging angle β is close to the optimum 180° value, β(Mn–F–Mn) = 179.2°, and the corresponding intrachain exchange constant J/k (approximately −22 K) is in good agreement with the previously proposed dependence of J/k on $\cos^2 \beta$. Therefore, within a large temperature range ($70 \lesssim T \lesssim 300$ K), the prevailing coupling mechanism is an antiparallel intrachain coupling via σ superexchange, whereas below $T_N = 28$ K the magnetic chains participate in 3D interactions.

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Registry No. $Tl_2MnF_5{\cdot}H_2O$, 138604-22-5.

Supplementary Material Available: Tables of experimental data for the crystal structure determination and anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Studies of a Syn-Anti Carboxylate-Bridged Helix-like Chain Copper(II) Complex

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The preparation, magnetic properties, and crystal and molecular structure of $[CuL(H_2O)]_n$ are described (L stands for the doubly deprotonated form of 1,3-dimethyl-5-((2-carboxyphenyl)azo)barbituric acid). The crystals are orthorhombic, of space group $P2_12_12_1$, with cell constants $a = 8.171$ (1) Å, $b = 10.302$ (3) Å, $c = 17.006$ (5) Å, and $Z = 4$. The structure was solved and refined to $R = 0.052$. The copper(II) ions are in a distorted square-pyramidal environment. They are sequentially bridged by carboxylate groups in the syn-anti conformation, resulting in the formation of infinite zigzag (or helix-like?) chains running parallel to the a axis. From magnetic susceptibility measurements, the complex is found to exhibit ferromagnetic intrachain interactions with an exchange coupling of $J/k = 4.8$. Magnetic and structural parameters of this and other related complexes are compared, and some magneto–structural trends are discussed.

Introduction

Historically, antiferromagnetic exchange coupling in a dinuclear complex was first observed in $Cu_2(CH_3COO)_4{\cdot}2H_2O$, in which two copper(II) ions are bridged symmetrically by four acetate groups.[1,2] Subsequently a variety of related complexes[3-5] were considered, all displaying substantial antiferromagnetic interactions. This behavior has been theoretically rationalized at various levels of sophistication,[6,7] but it is obvious empirically that these strong antiferromagnetic interactions have to be related to the syn-syn configuration adopted by the triatomic O–C–O bridges.

Indeed, much smaller (antiferro- or ferromagnetic) interactions were found for complexes in which syn-anti bridges are operative.[8-13] It may be noted that structurally characterized examples of this syn-anti configuration are to date far less numerous than those with the syn-syn configuration. This is unfortunate since, due to their geometry, syn-anti bridges would allow a great variety of structural and magnetic characteristics to be observed.

A good strategy to force RCO_2^- groups to adopt the syn-anti configuration would be their incorporation into a polydentate

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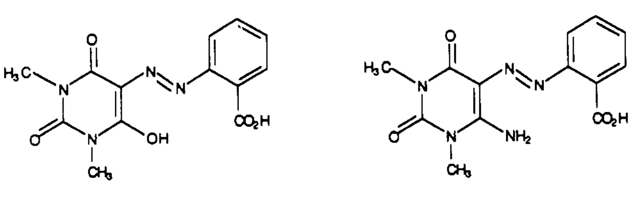

L H2   L' H2

Figure 1. Schematic representation of the ligands: LH_2 = 1,3-dimethyl-5-((2-carboxyphenyl)azo)barbituric acid; $L'H_2$ = 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil.

ligand, as illustrated in our previous paper.[12] Indeed, the use of the ligand $L'H_2$ (Figure 1), allowed us to isolate a quasi-tetrahedral tetranuclear copper(II) complex with four bridging RCO_2^- groups in the syn-anti configuration.

The present paper is devoted to a new example which illustrates a new structural possibility offered by bridging syn-anti RCO_2^- groups. Indeed, from the ligand LH_2 (Figure 1) which is closely related to the aforementioned $L'H_2$ ligand, we succeeded in preparing a ferromagnetic chain or helix-like complex, $[CuL(H_2O)]_n$.

Experimental Section

Synthesis and Characterization. The ligand LH_2 (1,3-dimethyl-5-((2-carboxyphenyl)azo)barbituric acid) was prepared by coupling diazotized anthranilic acid with 1,3-dimethylbarbituric acid.[14] The compound was recrystallized from dioxane/water (3:1). Yield: 90%. Anal. Calcd for $C_{13}H_{12}N_4O_5$: C, 51.32; H, 3.95; N, 18.42. Found: C, 51.32; H, 3.96; N, 18.45.

The complex $[CuL(H_2O)]_n$ was prepared by adding solid copper nitrate trihydrate (0.80 g, 3.3 mmol) to a stirred suspension of LH_2 (1.0 g, 3.3 mmol) in 100 mL of methanol/water mixture (10:1) at room temperature. After 10 min, a black homogeneous solution was obtained. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of the aqueous solution. They were filtered off, washed with methanol, and air-dried. Yield: 81%. Anal. Calcd for $C_{13}H_{12}CuN_4O_6$: C, 40.68; H, 3.13; N, 14.60; Cu, 16.56. Found: C, 40.25; H, 3.25; N, 14.90; Cu, 16.5.

Physical Measurements. Magnetic susceptibility data were collected on powdered samples of the title compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants[15] and for TIP.

EPR spectra were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz.

X-ray Data Collection. Single-crystal data collection was performed at ambient temperature on a Nicolet P3F diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The unit cell parameters for the dark blue needlelike crystal were obtained from least-squares refinement of 25 well-centered reflections ($20° < 2\theta < 30°$). The data were corrected for Lorentz and polarization factors and for dispersions. The three check reflections collected after every 60 reflections showed no significant intensity decrease during the course of data collection.

Structure Determination and Refinement. The structure was solved using the SHELXS system and subsequent ΔF syntheses.[16] The anisotropic refinement of all non-hydrogen atoms of the molecule converged to R = 0.058 and R_w = 0.050. The strongest hydrogen atom maximum of each methyl group was selected at this stage from the ΔF map. The other hydrogen atoms were placed at their calculated positions (C–H = 0.95 Å). In the final refinement, all non-hydrogen atoms of the complex molecule were refined anisotropically, but the hydrogen atoms were not refined.

The function minimized was $\sum w(\Delta F)^2$ ($w = 1/\sigma(F^2)$), resulting in a final R value of 0.052 (R_w = 0.039) for all 2293 non-zero reflections. The scattering factors were those included in the program system, and anomalous dispersion corrections were applied.[17] All calculations were carried out with a VAX 8650 computer, and refinements and all subsequent calculations, with the XTAL program system.[18]

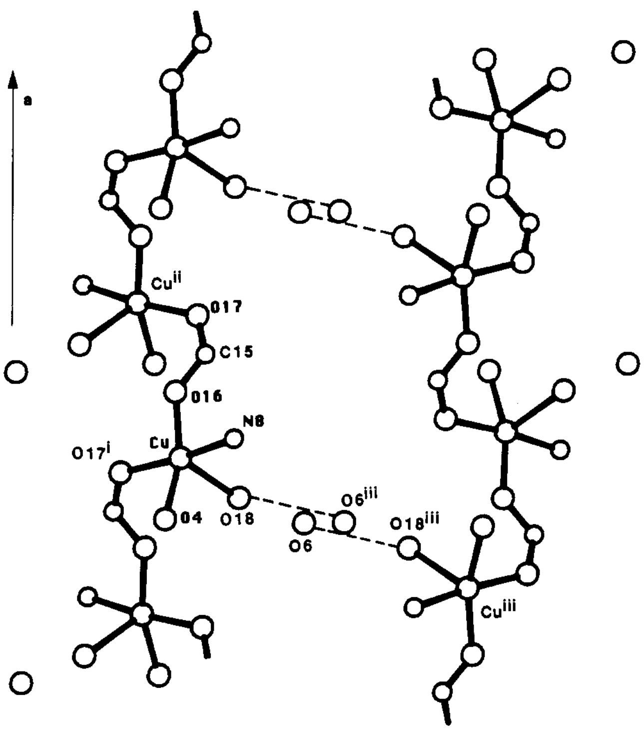

Figure 2. Simplified view of the chains propagating along the a axis with the interchain hydrogen bonds. Key: (i) $x - {}^1/_2, -y - {}^1/_2, -z$; (ii) $x + {}^1/_2, -y - {}^1/_2, -z$; (iii) $-x, y - {}^1/_2, -z + {}^1/_2$.

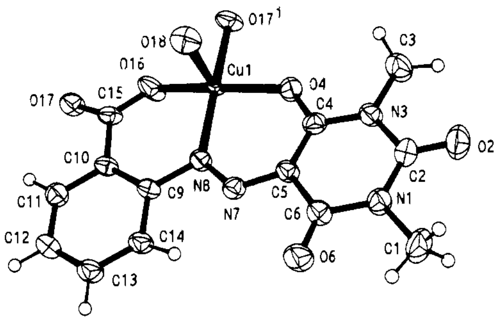

Figure 3. Ortep view of the mononuclear fragment. i = $x - {}^1/_2, -y - {}^1/_2, -z$.

Table I. Crystallographic Data for $[CuL(H_2O)]_n$

chem formula $C_{13}H_{12}CuN_4O_6$	T = 20 ± 1 °C
fw = 383,8	λ = 0.710 69 Å
space group $P2_12_12_1$	ρ_{obsd} = 1.69 g·cm^{-3}
a = 8.174 (1) Å	ρ_{calcd} = 1.78 g·cm^{-3}
b = 10.302 (3) Å	μ = 16.3 cm^{-1}
c = 17.006 (5) Å	transm coeff = 1.00–0.96
V = 1432 Å^3	
Z = 4	R = 0.052
$F(000)$ = 780	R_w = 0.039

Results and Discussion

Description of the Structure. The most salient feature of the structure results from the fact that copper(II) ions are bridged sequentially by syn-anti carboxylate groups to form infinite chains. These chains extend along the crystallographic a axis (Figure 2).

A view of the mononuclear fragment with the numbering scheme indicated is given in Figure 3. The crystallographic data and the final non-hydrogen atomic coordinates are given in Tables I and II, respectively, while the intramolecular bond distances and angles are listed in Table III.

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Table II. Fractional Atomic Coordinates and Isotropic Thermal Parameters with Esd's in Parentheses for $[CuL(H_2O)]_n$

atom	*x/a*	*y/b*	*z/c*	*U*,[a] Å^2
Cu(1)	0.21450 (6)	–0.12348 (5)	0.03121 (3)	0.0207 (2)
O(2)	–0.4081 (4)	0.2428 (3)	0.0389 (2)	0.056 (2)
O(4)	0.0185 (4)	–0.0305 (3)	0.0065 (2)	0.039 (2)
O(6)	–0.0005 (4)	0.2651 (3)	0.2196 (2)	0.048 (2)
O(16)	0.4284 (4)	–0.1954 (3)	0.0252 (2)	0.051 (2)
O(17)	0.6706 (3)	–0.2617 (3)	0.0609 (2)	0.040 (2)
O(18)	0.0834 (4)	–0.2639 (3)	0.1208 (2)	0.051 (2)
N(1)	–0.1978 (5)	0.2602 (3)	0.1262 (2)	0.038 (2)
N(3)	–0.1941 (4)	0.1041 (3)	0.0245 (2)	0.033 (2)
N(7)	0.1775 (4)	0.0846 (3)	0.1443 (2)	0.031 (2)
N(8)	0.2744 (4)	–0.0016 (3)	0.1141 (2)	0.030 (2)
C(1)	–0.2813 (7)	0.3709 (5)	0.1639 (3)	0.058 (3)
C(2)	–0.2756 (6)	0.2061 (4)	0.0623 (3)	0.039 (2)
C(3)	–0.2704 (6)	0.0526 (5)	–0.0477 (3)	0.053 (3)
C(4)	–0.0449 (5)	0.0579 (4)	0.0476 (2)	0.033 (2)
C(5)	0.0275 (5)	0.1117 (4)	0.1160 (2)	0.029 (2)
C(6)	–0.0516 (5)	0.2151 (4)	0.1589 (2)	0.034 (2)
C(9)	0.4282 (5)	–0.0064 (4)	0.1561 (2)	0.029 (2)
C(10)	0.5501 (5)	–0.0988 (4)	0.1386 (2)	0.029 (2)
C(11)	0.6924 (5)	–0.1019 (4)	0.1854 (2)	0.037 (2)
C(12)	0.7166 (6)	–0.0140 (4)	0.2462 (2)	0.038 (2)
C(13)	0.5992 (6)	0.0783 (4)	0.2611 (3)	0.040 (3)
C(14)	0.4563 (5)	0.0836 (4)	0.2170 (2)	0.035 (2)
C(15)	0.5468 (5)	–0.1923 (4)	0.0720 (3)	0.032 (5)

[a] *U* has been defined as $U = {}^1/_3\sum_i\sum_j U_{ij}(a_i{}^*a_j{}^*)(a_i{\cdot}a_j)$.

Table III. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for $[CuL(H_2O)]_n$

Cu(1)–O(4)	1.913 (3)	N(3)–C(3)	1.476 (6)
Cu(1)–O(16)	1.902 (3)	N(3)–C(4)	1.367 (5)
Cu(1)–O(17)^i	1.995 (3)	N(7)–N(8)	1.296 (5)
Cu(1)–N(8)	1.949 (3)	N(7)–C(5)	1.346 (5)
Cu(1)–O(18)	2.359 (3)	N(8)–C(9)	1.447 (5)
O(2)–C(2)	1.214 (6)	C(4)–C(5)	1.418 (6)
O(4)–C(4)	1.260 (5)	C(5)–C(6)	1.443 (6)
O(6)–C(6)	1.227 (5)	C(9)–C(10)	1.410 (6)
O(16)–C(15)	1.253 (5)	C(9)–C(14)	1.409 (6)
O(17)–C(15)	1.253 (5)	C(10)–C(11)	1.409 (6)
N(1)–C(1)	1.475 (6)	C(10)–C(15)	1.488 (6)
N(1)–C(2)	1.378 (6)	C(11)–C(12)	1.389 (6)
N(1)–C(6)	1.397 (6)	C(12)–C(13)	1.374 (6)
N(3)–C(2)	1.401 (5)	C(13)–C(14)	1.389 (6)
O(4)–Cu(1)–O(16)	162.4 (1)	O(2)–C(2)–N(3)	120.5 (4)
O(4)–Cu(1)–O(17)^i	88.5 (1)	N(1)–C(2)–N(3)	116.5 (4)
O(4)–Cu(1)–O(18)	93.9 (1)	O(4)–C(4)–N(3)	117.3 (4)
O(4)–Cu(1)–N(8)	92.7 (1)	O(4)–C(4)–C(5)	124.5 (4)
O(16)–Cu(1)–O(17)^i	83.8 (1)	N(3)–C(4)–C(5)	118.2 (4)
O(16)–Cu(1)–O(18)	102.3 (1)	N(7)–C(5)–C(4)	126.3 (4)
O(16)–Cu(1)–N(8)	93.4 (1)	N(7)–C(5)–C(6)	112.4 (3)
O(17)^i–Cu(1)–N(8)	173.9 (1)	C(4)–C(5)–C(6)	121.1 (4)
O(17)^i–Cu(1)–O(18)	93.5 (1)	O(6)–C(6)–N(1)	119.1 (4)
O(18)^i–Cu(1)–N(8)	92.4 (1)	O(6)–C(6)–C(5)	125.6 (4)
Cu(1)–O(4)–C(4)	125.8 (3)	N(1)–C(6)–C(5)	115.3 (3)
Cu(1)–O(16)–C(15)	131.8 (3)	N(8)–C(9)–C(10)	122.2 (3)
Cu(1)–O(17)^i–C(15)^i	127.0 (3)	N(8)–C(9)–C(14)	118.9 (4)
C(1)–N(1)–C(2)	116.2 (4)	C(10)–C(9)–C(14)	118.9 (4)
C(1)–N(1)–C(6)	118.7 (4)	C(9)–C(10)–C(11)	118.7 (4)
C(2)–N(1)–C(6)	125.1 (4)	C(9)–C(10)–C(15)	125.8 (4)
C(2)–N(3)–C(3)	116.7 (3)	C(11)–C(10)–C(15)	115.5 (3)
C(2)–N(3)–C(4)	123.6 (3)	C(10)–C(11)–C(12)	121.5 (4)
C(3)–N(1)–C(4)	119.5 (3)	C(11)–C(12)–C(13)	119.3 (4)
N(8)–N(7)–C(5)	123.8 (3)	C(12)–C(13)–C(14)	121.0 (4)
Cu(1)–N(8)–N(7)	125.1 (3)	C(9)–C(14)–C(13)	120.6 (4)
Cu(1)–N(8)–C(9)	123.6 (3)	O(16)–C(15)–O(17)	120.9 (4)
N(7)–N(8)–C(9)	111.0 (3)	O(16)–C(15)–C(10)	120.9 (4)
O(2)–C(2)–N(1)	123.0 (4)	O(17)–C(15)–C(10)	118.0 (4)

The surrounding of each copper ion is (4+1). Four short bonds of ca. 2.0 Å are formed with one nitrogen and three oxygen atoms from the ligand L, while a water molecule is coordinated at a longer distance (2.359 (3) Å). Of the four nearest neighbors, three (O(4), O(16), and N(8)) are afforded by the ligand which surrounds the copper ion. The fourth donor is the oxygen atom O(17)^i belonging to the carboxylate group of an adjacent and symmetry-related (i: $x - {}^1/_2, -y - {}^1/_2, -z$) fragment. The corresponding bond (1.995 (3) Å) is somewhat longer than the two other Cu–O bonds (1.902 (3) and 1.903 (3) Å).

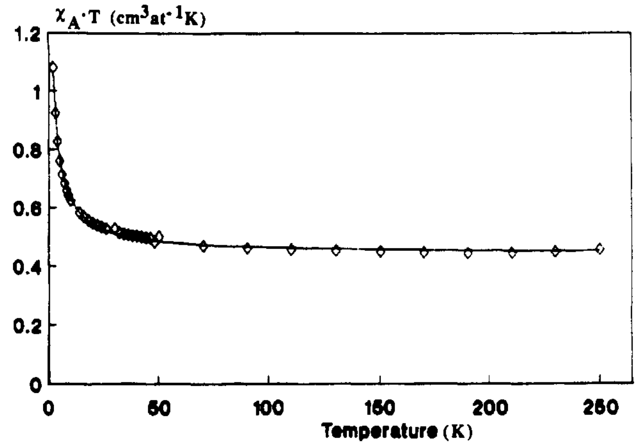

Figure 4. Experimental (◇) and calculated (—) temperature dependence of $\chi_A T$.

The (4+1) coordination mode is compatible with two idealized geometries: square pyramidal and trigonal bipyramidal. According to the procedure described by Muetterties,[19] the shape of the polyhedron can be considered as SP, since the TBP deformation amounts to 13%. In a SP description, the basal plane is defined by O(4), N(8), O(16), and O(17)^i whereas the apical position is occupied by O(18) from a water molecule, in accordance with the relatively large Cu–O(18) distance. Deviations from planarity up to ca. 0.09 Å are observed for the equatorial donor atoms. As usual, the copper atom is displaced by 0.184 (2) Å from the mean plane toward the axial donor.

The tridentate behavior of the ligand results in the formation of two six-membered rings which have in common the Cu–N(8) bond. Both rings are not far from being planar, since the maximum deviation is ca. 0.13 Å. The dihedral angle between the two related mean planes is 8.77(9)°. A greater planarity characterizes the barbituric and phenyl rings for which the maximum deviations are ca. 0.03 and 0.01 Å, respectively.

Regarding the carboxylate group, the two C–O distances are identical (1.253 (5) Å), while the related Cu–O distances differ (1.902 (3) and 1.995 (3) Å). The COO plane makes an angle of 8.5 (4)° with the plane of the phenyl ring to which it is linked. This causes a lowering of the conjugation, which is reflected in the length of the C(15)–C(10) bond (1.488 (6) Å).

As previously noted, each carboxylate group is in the syn-anti conformation and bridges two copper atoms via two equatorial positions. The bridging pathway Cu–O–C–O–Cu^{ii}, for instance (Figure 2), is asymmetric not only in its conformation but also with respect to the Cu–O bond lengths (vide supra). Furthermore, the copper atoms, Cu and Cu^{ii}, are pushed out of the COO plane by 0.240 (5) and 0.120 (5) Å, respectively.

The dihedral angle of the mean equatorial planes around Cu and Cu^{ii} is 46.4 (1)°, while the Cu···Cu^{ii} separation is 4.962 (1) Å. It may be noted that, within each equatorial plane, the two oxygen atoms involved in bridging to neighbor copper ions, namely O(16) and O(17)^i for Cu, are forced by the ligand rigidity to be in cis positions relative to each other.

Finally, keeping in mind the nonplanarity of the bridging network and the constancy of the Cu···Cu separation along the chain, the (Cu–O–C–O–Cu)$_n$ skeleton can be best visualized as a helix-like chain running parallel to the crystallographic *a* axis. However, if we think about the copper atoms only, they do form a sawlike planar figure.

Considering the short contacts shows that neighboring chains are interconnected by hydrogen bonds. Each of these bonds is established from an axially coordinated water molecule to one of the carbonyl groups of a neighboring barbituric ring. The related

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[19] Muetterties, E. L.; Guggenberg, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748 and supplementary material.

donor–acceptor distance ($O(18)–O(6)^{iii}$, Figure 2) is 2.814 (5) Å, and the shortest interchain Cu⋯Cu separation is 8.778 (2) Å.

Magnetic Properties. Static Magnetic Susceptibility. The temperature dependence of χT for a powdered sample of the complex is shown in Figure 4. When the temperature is lowered, the product χT increases steadily from a value of 0.456 emu·atom^{-1}·K at 250 K to a value of 1.080 emu·atom^{-1}·K at 2 K. This suggests a ferromagnetic behavior, as does the temperature dependence of χ^{-1}, which is well represented by a Curie–Weiss law with $\Theta = +3.43$ K and $C = 0.44_4$ K·cm^3·atom^{-1} ($g = 2.17_7$).

In keeping with the chain structure, the quantitative analysis of the data may be performed by a formula reported by Baker et al.[20] and based on the Padé approximants

$$X = [N\langle g\rangle^2\beta^2/4kT][(1 + A + BX^2 + CX^3 + DX^4 + EX^5)/(1 + A' + B'X^2 + C'X^3 + D'X^4)]^{2/3}$$

$$\begin{array}{ll} A = 5.797\,991\,6 & A' = 2.797\,991\,6 \\ B = 16.902\,653 & B' = 7.008\,678\,0 \\ C = 29.376\,885 & C' = 8.653\,864\,4 \\ D = 29.832\,959 & D' = 4.574\,311\,4 \\ E = 14.036\,918 & \end{array}$$

The best fit parameters for the data are $J/2k = 2.40$, $g = 2.13$, and $R = 2.50 \times 10^{-4}$. Attempts to improve the fit by taking into account interchain interaction via a mean-field approximation[21] failed. This may be due to the intrinsic low precision with which the J values are determined for ferromagnetic interactions and to the expected weakness of the interchain interactions. Indeed, structural data show that the Cu⋯Cu interchain separation is large and that the pathway which may likely mediate these interactions is extended. It comprises a water molecule, a hydrogen bond, and a CO group which is far removed from the related copper atom. Furthermore, this path involves an axial position where the spin densities are very weak. Nevertheless, measurements taken below 2 K are needed to evaluate the magnitude of the interchain effects.

EPR Spectroscopy. At room temperature the X-band spectrum of a powdered sample looks like that expected for a copper(II) ion in a $d_{x^2-y^2}$ ground state. The two main features are attributable to parallel ($g = 2.23_5$) and perpendicular ($g = 2.05_7$) components of an axially symmetrical spectrum. However "bumps" of very low intensity are discernible between these two features. Lowering the temperature causes the intensities of the "bumps" to increase. Clearly, a single-crystal study is needed to explain these data.

As noted previously for the few well-characterized copper(II) complexes with bridging syn-anti COO groups, the magnitudes of the exchange-coupling constants are small and the exchange is usually ferromagnetic.[8,10,21,23] Therefore, the behavior of the title complex is not unexpected. However, a point of interest is that two related complexes have been shown to be antiferromagnets.[9,13]

The first complex, $[Cu_2(OAc)_2A]_n$ (A is a macrocyclic ligand), is not a genuine example of a chain compound and is better viewed as a *pseudo*-dinuclear complex.[13] Furthermore, the carboxylate groups bridge pairs of copper ions from a basal position to an axial position. This results in a weak antiferromagnetic coupling ($-J \sim 1$ cm^{-1}). The second complex, $[Cu(NH_3)_2(OAc)Br]_n$,[9] is more relevant to the present discussion, since it bears a great resemblance to the title complex. In both complexes, square-pyramidal copper(II) ions are sequentially bridged by syn-anti carboxylate groups to form infinite chains. Furthermore, in both cases, each bridge links two equatorial positions. In spite of these structural similitudes, opposite magnetic behaviors do characterize these complexes. Indeed, $[Cu(NH_3)_2(OAc)Br]_n$ is antiferromagnetic with $J/k = -4.3$, while $[CuL(H_2O)]_n$ is ferromagnetic with $J/k = 4.8$.

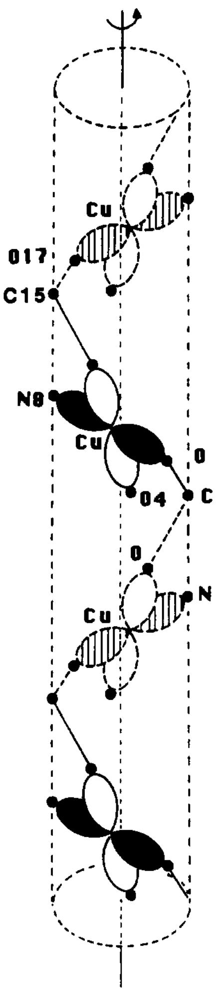

Figure 5. Schematic representation of the phase opposition along the helix-like chain.

A closer examination of the structural data strongly suggests that the origin of this sign reversal may be found in two facts: (i) in contrast to $[Cu(NH_3)_2(OAc)Br]_n$, for which the whole (⋯Cu⋯O⋯C⋯O⋯Cu)$_n$ skeleton is planar,[23] the helix-like structure of $[CuL(H_2O)]_n$ pushes the copper ions out of the related carboxylate plane; (ii) considering each copper ion, the two bridging oxygen atoms are trans to each other in $[Cu(NH_3)_2(OAc)Br]_n$ and cis in $[CuL(H_2O)]_n$.

The nonplanarity of the chain skeleton is expected to decrease the overlap density of the magnetic orbitals in the bridging region and to lower the antiferromagnetic contribution to such an extent that the ferromagnetic contribution becomes predominant. It is more difficult to decipher precisely the consequences of point ii. However, for both complexes, the magnetic orbitals are of the $d_{x^2-y^2}$ type with possibly some admixture of d_{z^2} character and their lobes point to the equatorial donors. In $[Cu(NH_3)_2(OAc)Br]_n$, the lobes directed to the bridging oxygen donors have the same phases, while, in $[CuL(H_2O)]_n$, due to the cis configuration, they have opposite phases (Figure 5). This implies that the space surrounding each bridge is divided into two parts by a nodal surface, with the net result of a very low overlap density of the magnetic orbitals. It may be noted that ferromagnetism has been observed for complexes where there is actually no phase opposition.[8] Finally, further work, experimental and theoretical, is needed to support our suggestion. Obviously, the main cause of ferromagnetism in the present complex is the nonplanarity of the chain skeleton.

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Supplementary Material Available: Tables S1-S4, listing crystal data and details of data collection, fractional atomic coordinates and isotropic thermal parameters, anisotropic thermal displacement parameters, and least-squares plane equations for $[CuL(H_2O)]_n$ (5 pages); a listing of calculated and observed structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Oxamidato Complexes. 2. Copper(II) and Nickel(II) Complexes with Oxamide-*N*,*N'*-diacetic Acid: Solution Study, Synthesis, Crystal Structures, and Magnetic Properties

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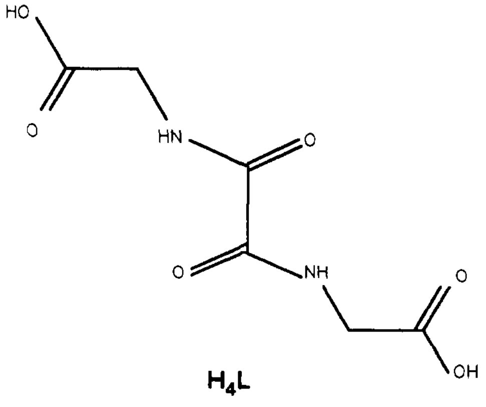
The complex formation between Cu(II) and Ni(II) and oxamide-*N*,*N'*-diacetic acid (H_4glyox, H_4L) has been studied by potentiometry in aqueous solution at 25 °C in 0.1 mol dm^{-3} $NaNO_3$. The two first acidity constants of H_4L were $pK_{a1} = 2.86$ (1) and $pK_{a2} = 3.64$ (1). The logarithms of the equilibrium constants for its Cu(II) and Ni(II) complexes according to the equations $M^{2+} + H_2L^{2-} \leftrightarrow M(H_2L)$ and $2M^{2+} + H_2L^{2-} \leftrightarrow M_2L + 2H^+$ were 2.62 (1) and −2.18 (1) for Cu(II) and 1.93 (1) and −11.09 (1) for Ni(II), respectively. Two new compounds of formulas $\{[Cu(H_2glyox)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**) and $[Ni_2(glyox)(H_2O)_6]\cdot 4H_2O$ (**2**) have been synthesized, and their crystal structures have been determined by X-ray crystallographic methods. The compounds crystallize in the monoclinic system, space groups $P2_1/m$ and $P2_1/c$, respectively, with cell dimensions $a = 6.0070$ (4) Å, $b = 22.329$ (1) Å, $c = 5.8015$ (3) Å, $\beta = 105.784$ (5)°, and $Z = 2$ for **1** and $a = 6.9885$ (7) Å, $b = 9.0530$ (6) Å, $c = 14.250$ (1) Å, $\beta = 99.655$ (7)°, and $Z = 2$ for **2**. The structure of **1** was solved by direct methods and that of **2** by the heavy-atom method. Least-squares refinements converged at $R = 0.026$ in both cases. The structure of **1** consists of infinite chains in which the oxamidato ligand, deprotonated only at the carboxylate groups, is bis-monodentate. The copper atom is situated at a mirror plane in a distorted square-pyramidal environment. The copper-copper intrachain separation is 13.321 Å. The structure of **2** consists of neutral binuclear units in which the oxamidato ligand is fully deprotonated and acts in a bis-tridentate fashion. Nickel coordination is distorted octahedral. The nickel-nickel intramolecular separation is 5.368 Å. The magnetic properties of **1** and **2** have been investigated in the 4.2-300 K temperature range. A Curie law is observed for **1**, whereas a relatively strong antiferromagnetic coupling is observed for **2**, evidenced by a rounded maximum in the susceptibility curve at ~41 K ($J = -25$ cm^{-1} and $g = 2.25$, where J is the exchange parameter in the isotropic Hamiltonian $\hat{H} = -J\hat{S}_A\cdot\hat{S}_B$). These magnetic behaviors are easily understood in the frame of a localized-orbital model of exchange interactions. We discuss the striking influence of acid-base properties upon the coordination ability of the ligand and the very different physical properties which can result therefrom.

Introduction

N-Substituted and N,N'-disubstituted oxamides such as I have played a key role in the design of polymetallic systems. The versatility of these ligands, which is based on (i) the wide variety of substituted derivatives which can be realized, yielding different numbers of chelate rings with different donor atoms, (ii) their easy cis-trans conformational change affording symmetric and asymmetric oxamidato bridges, and (iii) the bidentate character of the mononuclear metal-oxamidato complex,[2-4] allows the formation of di,[2c,4a,b,5-8] tri-,[9] and tetranuclear[10] complexes as well as bi-



H_4L

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