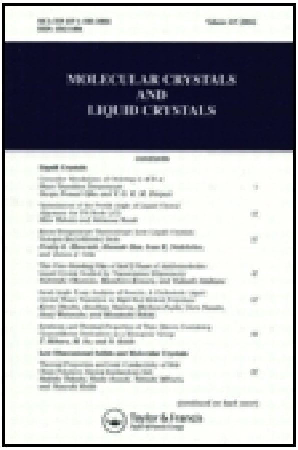

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Magnetic Properties of the Single Crystals of Layered Cu(II) and Co(II) Complexes with 3-Imidazoline Nitroxides

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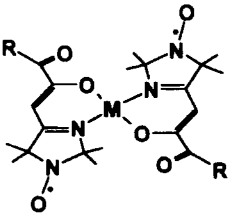
Single crystals of Cu(II) and Co(II) complexes with stable nitroxides 4-(2'-ethoxycarbonyl-2'-oxoethylidene)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (HL^1) and 4-(2'-methoxycarbonyl-2'-oxoethylidene)-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (HL^2) have been investigated by the static magnetic susceptibility method. It was found that bulk ferromagnetic ordering is inherent in layered CuL^1_2 and α-CuL^2_2 at ~ 5 K. Easy magnetization axes were determined for both compounds. At the same time, the complex β-CuL^2_2, possessing a molecular structure, does not show noticeable anisotropy in the region 2–300 K. For the layered complex CoL^1_2, the magnetic transition temperature, if any, is lower than 2 K. In the whole range 2–300 K, the single crystals of CoL^1_2 show a rather high anisotropy of magnetic susceptibility.

Keywords: magnetic susceptibility; single crystal; ferromagnetic ordering

INTRODUCTION

Active studies of molecular magnets stimulate investigations of the anisotropy of magnetic properties on single crystal samples. Recently, first publications on the anisotropy of magnetic susceptibility of molecular magnets based on Ni(II) and Mn(II) complexes have appeared.[1-3] Here we report on our studies of the anisotropy of magnetic properties of heterospin layered polymers of Cu(II) and Co(II) complexes with enaminoketone derivatives of 3-imidazoline nitroxide - CuL^1_2, α-CuL^2_2, β-CuL^2_2, and CoL^1_2.



ML^x_2

R=C(O)OC_2H_5 : CuL^1_2 , CoL^1_2

R=C(O)OCH_3 : CuL^2_2

EXPERIMENTAL

Synthesis, structure, and results of investigations of the magnetic properties of powdered CuL^1_2 and CoL^1_2 are described elsewhere.[4 - 6]

Synthesis of α-CuL^2_2 and β-CuL^2_2. To the warm solution of 0.245 g of HL^2 in 25 ml of methanol was added with stirring a solution of 0.1 g of $Cu(CH_3COO)_2 H_2O$ in 8 ml of water. After 20 minutes the precipitate was filtered off, washed with methanol, and boiled in 125 ml of methanol for 40 min. The resulting solution was filtered and left overnight at room temperature. The following day the green crystals of the complex were filtered off, washed with methanol, and dried in air. Yield 50 %. Found: C 48.7, H 6.1, N 10.4; Calc. for $CuC_{22}H_{32}N_4O_8$: C 48.6, 5.9, 10.3. After repeated prolonged (for 2.5 h) boiling in methanol (the concentration of the complex was 0.12 g in 100 ml of methanol) and subsequent storage of the solution at room temperature, single crystals of β-CuL^2_2 (light brown needles) precipitated. The single crystals of the β - modification also formed when the compound was crystallized from toluene. Recrystallization from CCl_4 yielded single crystals of α-CuL^2_2 (green parallelepipeds). When the complex was recrystallized from acetonitrile, perfect single crystals of α-CuL^2_2 and β-CuL^2_2 formed in approximately equal amounts; these compounds may be easily separated mechanically. A mixture of these modifications, now as smaller crystals, also results from recrystallization of the complex from benzene. It is important to emphasize that contact of CuL^2_2 with ethanol should be avoided in the synthesis of the complex and in all subsequent procedures. With ethanol present in the solution, the methoxy group in the side chain of the ligand is quickly replaced by the ethoxy group to form CuL^1_2. The melting point of α-CuL^2_2 is 240-241 °C. On heating to 205-210 °C the brown crystal of β-CuL^2_2 is transformed into the green crystal of α-CuL^2_2 and then melts at the same temperature as α-CuL^2_2 does. The narrow intense band ν(C=O) of the ester group is found at 1716 cm^{-1} in the spectrum of α-CuL^2_2 and at 1725 cm^{-1} in the spectrum of β-CuL^2_2.

The crystal structures of α-CuL^2_2 and β-CuL^2_2 differ significantly. The crystals of β-CuL^2_2 are triclinic, with the unit cell parameters: a = 5.761(3), b = 10.026(4), c = 11.241(5) Å, α = 100.12(3), β = 99.35(4), γ = 99.67(4)°,V = 617.7(4) $Å^3$, space group $P\bar{1}$, Z = 1, d_{CALC} = 1.463 g/cm^3. The crystals of α-CuL^2_2 are monoclinic, a = 11.929(3), b = 10.830(3), c = 11.190(4) Å, β = 111.31(2)°, V = 1346.8(7) $Å^3$, space group $P2_1/c$, Z = 2, d_{CALC} = 1.342 g/cm^3. The experimental reflections of the single crystals were collected on a CAD-4 four-circle automatic diffractometer at room temperature using a standard procedure (λMo Kα, graphite monochromator, $\theta/2\theta$ scanning with a variable rate, $2\theta_{MAX}$ = 54.1° and 2712 I_{hkl} observed from 2984 reflections measured for β-CuL^2_2, $2\theta_{MAX}$ = 49.94° and 1992 I_{hkl} observed from 2093 reflections measured for α-CuL^2_2). The structures were solved by the heavy atom method, and positions of all nonhydrogen atoms were refined anisotropically (R = 0.0570 for β-CuL^2_2, R = 0.0600 for α-CuL^2_2). H atoms were partially located in a series of electron density difference syntheses and then refined isotropically together with nonhydrogen atoms. All structure solution and refinement calculations were performed using SHELX 97 software.

The magnetic susceptibility of the (~1 mg) single crystals of the complexes was measured on a Quantum Design MPMS-5s SQUID magnetometer in the temperature range 2-300 K at the strength of applied magnetic field up to $45 \cdot 10^3$ Oe. For each single crystal of CoL^1_2, CuL^1_2, and α-CuL^2_2, the measurements were accomplished in three mutually perpendicular directions; the Y and Z directions coincided with the unit cell axes. For β-CuL$^2_2$, all measurements were performed along the unit cell axes. In the calculations of the molar magnetic susceptibility χ, the diamagnetic corrections for the complexes were applied additively. The temperature dependence of the effective magnetic moment was calculated by the formula $\mu_{eff} = [(3k/N\mu_B^2)\chi T]^{1/2}$.

RESULTS AND DISCUSSION

The crystal structure of β-CuL$^2_2$ is molecular (Fig. 1). The centrosymmetric square environment of the Cu atom in the β-CuL$^2_2$ molecule involves the O and N donor atoms of the deprotonated enaminoketone groups of the bidentate-coordinated L^2 with Cu-O and Cu-N distances of 1.895(2) and 2.029(2) Å, respectively, and the chelate angle O-Cu-N of 90.67(8)°.

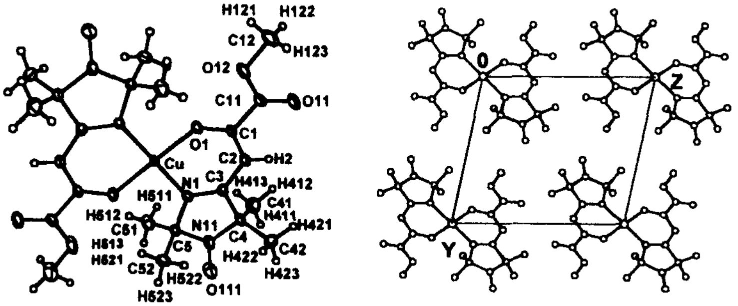


FIGURE 1 Molecular structure and projection of the structure of β-CuL$^2_2$ on the (100) plane.

The β-CuL$^2_2$ molecule is virtually planar. The deviations of atoms from the rms plane (the atoms of the methyl and methoxy groups are disregarded) do not exceed 0.08 Å. The shortest distances between the paramagnetic centers of the neighboring molecules (the metal atoms and nitroxyl O atoms) are 4.040 and 6.099 Å for $-{\bullet}O\cdots O{\bullet}-$ and $Cu\cdots O{\bullet}-$, respectively, and the intramolecular $Cu\cdots {\bullet}\text{-}O$ distances are 5.460 Å.

In the structure of α-CuL^2_2, the centrosymmetric square environment of the copper atom (Cu-O 1.913(2), Cu-N 2.061(2) Å, O-Cu-N angle 90.49(9)°) is similar to that in β-CuL^2_2 and is completed to the square bipyramid by the nitroxyl O atoms of the adjacent molecules of the complexes where the Cu-O • - distances are 2.513(3) Å and the Cu-O-N angle is 158.0(2)° (Fig. 2). The geometrical characteristics of ligands L^2 do not practically change (Table I) and the ligands remain flat.

TABLE I Bond distances (Å) and angles (deg) in L^2 of β-CuL^2_2 and α-CuL^2_2

distance	β-CuL^2_2	α-CuL^2_2	distance	β-CuL^2_2	α-CuL^2_2
O1-C1	1.289(3)	1.284(3)	C3-C4	1.510(3)	1.522(4)
N1-C3	1.316(3)	1.312(4)	C4-N11	1.458(3)	1.453(4)
N1-C5	1.486(2)	1.475(4)	C4-C41	1.524(3)	1.533(5)
C1-C2	1.361(3)	1.359(4)	C4-C42	1.525(3)	1.522(5)
C1-C11	1.523(3)	1.502(5)	N11-O111	1.270(2)	1.266(3)
C11-O11	1.198(3)	1.191(4)	N11-C5	1.478(3)	1.488(4)
C11-O12	1.324(3)	1.298(4)	C5-C51	1.518(3)	1.507(5)
O12-C12	1.450(3)	1.465(5)	C5-C52	1.520(3)	1.508(5)
C2-C3	1.423(3)	1.402(4)			
angle	β-CuL^2_2	α-CuL^2_2	angle	β-CuL^2_2	α-CuL^2_2
C1-O1-Cu	129.4(1)	129.5(2)	N11-C4-C3	98.8(2)	99.0(3)
C3-N1-C5	110.1(2)	111.4(2)	N11-C4-C41	110.9(2)	110.2(3)
C3-N1-Cu	124.2(1)	122.8(2)	C3-C4-C41	113.2(2)	112.6(3)
C5-N1-Cu	125.6(1)	125.8(2)	N11-C4-C42	110.2(2)	109.6(3)
O1-C1-C2	127.1(2)	126.0(3)	C3-C4-C42	112.0(2)	113.0(3)
O1-C1-C11	116.2(2)	116.6(3)	C41-C4-C42	111.1(2)	111.8(4)
C2-C1-C11	116.7(2)	117.4(3)	O111-N11-C4	123.7(2)	123.3(3)
O11-C11-O12	124.5(2)	122.1(4)	O111-N11-C5	121.9(2)	122.4(3)
O11-C11-C1	124.0(2)	125.1(4)	C4-N11-C5	114.2(2)	114.1(3)
O12-C11-C1	111.5(2)	112.8(3)	N11-C5-N1	101.9(2)	101.4(2)
C11-O12-C12	115.7(2)	118.7(3)	N11-C5-C51	108.1(2)	108.1(3)
C1-C2-C3	122.4(2)	124.1(3)	N1-C5-C51	111.9(2)	112.7(3)
N1-C3-C2	126.1(2)	126.8(3)	N11-C5-C52	108.4(2)	107.4(3)
N1-C3-C4	114.9(2)	113.9(3)	N1-C5-C52	112.4(2)	112.5(3)
C2-C3-C4	119.0(2)	119.3(3)	C51-C5-C52	113.4(2)	113.7(4)

Direct coordination of the paramagnetic centers of the ligands of the neighboring molecules by the Cu atom leads to formation of polymer layers, which are parallel to the (100) plane (Fig. 2). The Cu···•-O distances inside the bischelate fragments $\{CuL^2_2\}$ are 5.487 Å. CuL^1_2 has a similar structure.

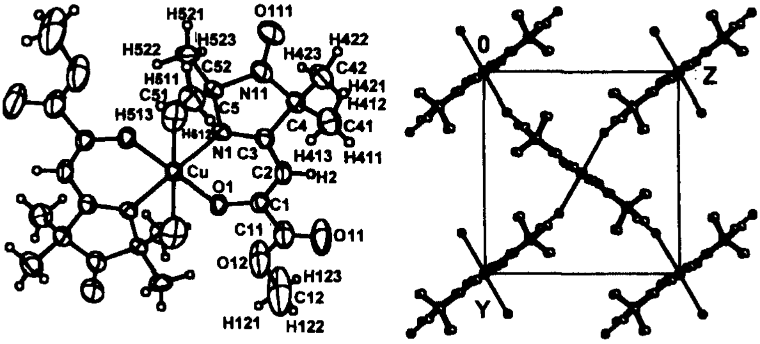


FIGURE 2 Structure of the bischelate fragment and projection of the structure of α-CuL^2_2 on the (100) plane.

The measurements of μ_{eff}(T) along different directions for the β-CuL^2_2 single crystal did not show any pronounced anisotropy within the experimental error (Fig. 3). The magnetic behavior of β-CuL^2_2 is perfectly fitted by the model of weakly interacting molecular exchange clusters (solid line in Fig. 3). Theoretical treatment was performed using an approach suggested elsewhere.[7] The parameters of the optimal theoretical curve are $g = 2.00 \pm 0.03$, $J = 11.8 \pm 0.7$ cm^{-1}, $nJ' = -0.56 \pm 0.02$ cm^{-1}, where g is the effective g-factor of the Cu(II) ion, J is the energy of the intramolecular exchange interaction J′ is the averaged energy of the intermolecular exchange interaction, and n is the number of the closest neighbors of the exchange cluster. Figure 3 shows the dependences μ_{eff}(T) of the α-CuL^2_2 single crystal above 15 K. At high temperatures, the curves μ_{eff} (T) measured along different directions almost coincide for α-CuL^2_2 and CuL^1_2 as well as for β-CuL^2_2.

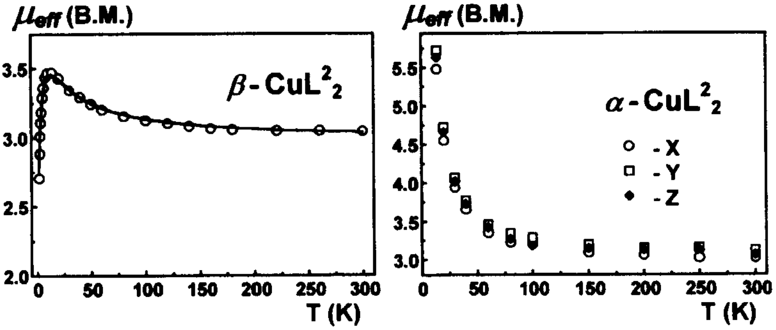


FIGURE 3 Dependences μ_{eff}(T) for the β-CuL^2_2 and α-CuL^2_2 single crystals. The experimental curves are shown by dots, the theoretica curve is a solid line.

At low temperatures the magnetic properties of layered polymeric α-CuL^2_2 and CuL^1_2 differ heavily from those of β-CuL^2_2, since exchange interactions in the bischelate fragment {CuL_2} are affected by ferromagnetic interactions in the exchange clusters >N••-O-Cu^{II}-O-••N<. As a result, below 10 K both solids exhibit a phase transition to the ferromagnetic state with T_c 5 K and 4.2 K for α-CuL^2_2 and CuL^1_2, respectively, and a strong anisotropy of magnetic susceptibility below the ordering temperature (Figures 4 and 5).

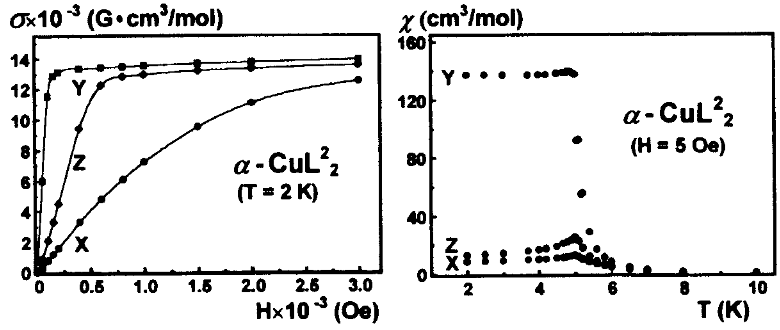


FIGURE 4 Dependences σ(H) and χ(T) for the α-CuL^2_2 single crystal

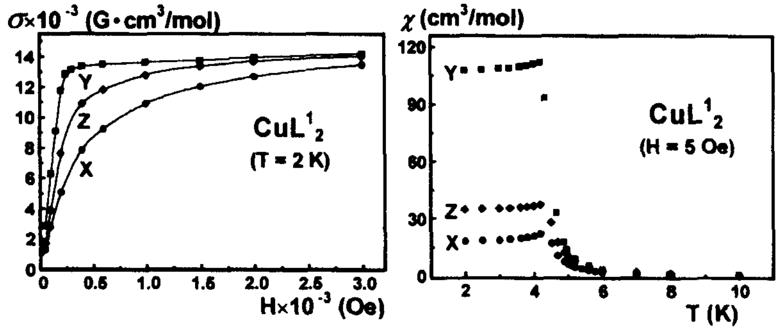


FIGURE 5 Dependences σ(H) and χ(T) for the CuL^1_2 single crystal

In both cases, the easy magnetization axis lies along the Y axis, which is the only symmetry axis of the crystals. The maximal value of σ at T = 2 K and H = 40 • 10^3 Oe is more than 15 • 10^3 G • cm^3/mol, which is close to saturation magnetization $Ng\mu_B S$ = 16.7 • 10^3 G • cm^3/mol for S = 3/2 and g = 2. One can assume that the anisotropy of magnetic properties of CuL^2_2 and CuL^1_2 is caused by magnetic interactions as in the case of classical ferromagnets.[8]

Figure 6 shows the results of measurements for CoL^1_2 single crystal. The layered polymeric structure of CoL^1_2 is close[5] to the CuL^1_2 one. In contrast to CuL^1_2, the exchange clusters >N • -O-Co^{II}-O- • N< have strong antiferromagnetic interactions.[4]

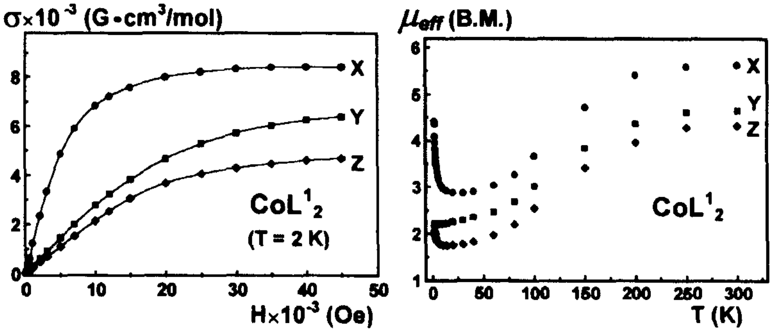


FIGURE 6 Dependences σ(H) and μ_{eff}(T) for the CoL^1_2 single crystal.

Below 50 K, a weaker (O-•N···Co^{II}···N•-O) exchange interaction of ferromagnetic type becomes pronounced, promoting formation of the magnetic moments of the polymer layers. As a result, at low temperatures μ_{eff}(T) increases for CoL^1_2, but the crystal is not magnetically ordered below 2 K. The anisotropy of magnetic properties of CoL^1_2 was observed over the whole temperature range under investigation. At room temperatures the anisotropy of μ_{eff}, in our opinion, is mainly caused by the anisotropy of the g-factor of the Co(II) ion. At low temperatures, the dependences μ_{eff}(T) differ along different directions. For the X and Z directions, μ_{eff} (T) increases sharply as the temperature decreases but tends to remain constant along the Y direction. This behavior may be attributed, among other things, to the anisotropic character of the exchange interaction. Along the Y axis this interaction is significantly weaker than that along the X and Z axes. The anisotropic behavior of CoL^1_2 also shows itself on the magnetization isotherms (Fig. 6). As can be seen in Fig. 6, a sharper curve σ(H) is observed along the X axis, which is perpendicular to the polymer layers. Along this direction, at T = 2 K and H = $45 \cdot 10^3$ Oe the magnetization is $8.4 \cdot 10^3$ G•cm^3/mol.

CONCLUSION

Thus, the magnetic properties of single crystal samples of Cu(II) and Co(II) complexes with stable organic radicals have been investigated. In the layered polymer complexes α-CuL^2_2 and CuL^1_2, we have found a phase transition to the ferromagnetic state at T_C of 5 K (α-CuL^2_2) and 4.2 K (CuL^1_2) and a strong anisotropy of magnetic susceptibility below the magnetic ordering temperature. For CoL^1_2, no transition to the magnetically ordered state has been found, and the anisotropy of magnetic properties, which is observed over the whole temperature range under study, may be caused by the anisotropic exchange interaction and by the anisotropy of the g-factor of the Co(II) ion.

Acknowledgment

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