Magnetic Properties of the Dioxime Complex 2,3-Diamino-1,4-diazabuta-1,3-diene-1,4-diol-bis(2,3-diamino-4-hydroxy-1,4-diazabuta-1,3-dien-1-olato)cobalt(II)

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Crystals of the title complex in the low-spin state ($S = 1/2$) exhibit one-dimensional ferromagnetic interactions along the *b*-axis.

The development of magnetic interactions in metal–ion complexes with a stack arrangement is of interest in exploring the design of organic ferromagnetic compounds. Metal–ion complexes with glyoximes are well known to possess a variety of stack structures;[1] however their magnetic properties have not been examined in detail. In this study, we report that the title compound, $[CoL_2(HL)]$, with a slipped-stack arrangement is an $S = 1/2$ 1-D ferromagnet along the stacking axis.

$$\underset{\text{HL}}{\text{HON=C(NH}_2\text{)–C(NH}_2\text{)=NOH}}$$

$[CoL_2(HL)]$ was obtained in 35–40% yield as dark purple crystals from a warm aqueous solution (100 cm^3) containing $[Co^{II}(OAc)_2]\cdot4H_2O$ (10 mmol) and the dioxime HL (20 mmol) under nitrogen,[2] and its composition was confirmed by IR spectroscopy and elemental analyses to be $[Co^{II}(C_2H_5N_4O_2)_2(C_2H_6N_4O_2)]$. The complex is monoclinic, space group $C2/c$ and its structure consists of chains of planar $Co^{II}L_2$ units stacked along the *b*-axis, through long Co–N bonds to terminal N atoms of the adjacent molecular units; the stacked chains form sheets in the *bc* plane.[2]

The ESR behaviour of $[CoL_2(HL)]$ crystals was examined over the temperature range 123–298 K. The spectra were characterized by the combination of a broad absorption band centred at an average *g* value (g_{av}) of 2.35 with a very weak but distinct hyperfine splitting (hfs) pattern centred at a g_z value of 2.012, which results from the interaction of the unpaired electron with the ^{59}Co nucleus ($I = 7/2$), with $A_{Co} = 12$ mT. The absence of any hfs signal from ^{14}N ($I = 1$) nuclei on the apical sites means that the interaction between the Co and the N atoms is as weak as in the case of $Co^{II}(Hdmg)_2$ (H_2dmg = butane-2,3-dione dioxime) in frozen water and alcoholic solvents and much weaker than that observed in strongly coordinating media like pyridine.[3] The g_{av} value of 2.35

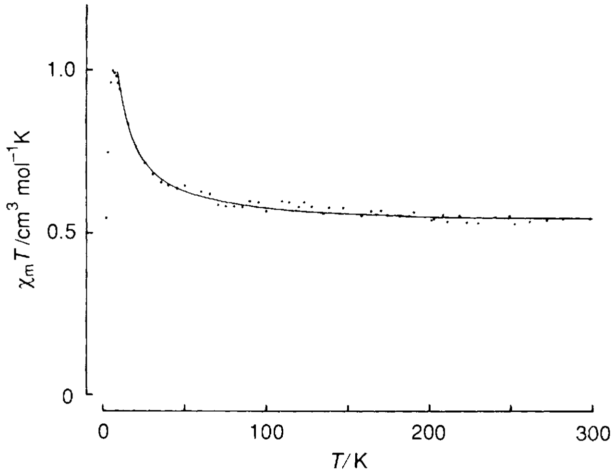

Fig. 1 Molar susceptibility × temperature *vs.* temperature for $[CoL_2(HL)]$. The solid line is theoretical.

remains constant over the above temperature range, while the hfs signal centred at $g_z = 2.012$ weakens significantly with a decrease in temperature. Provided that the system is isotropic, the S value can be estimated through the relationship $\mu_{eff}/\mu_B = g[S(S + 1)]^{1/2}$, where μ_{eff} is the effective magnetic moment. If a μ_{eff} value of 2.05 μ_B, as described below, and $g = g_{av} = 2.35$, the S value is calculated to be 0.505, which is consistent with the $S = 1/2$ ground state, *i.e.*, the low-spin state.

The magnetic properties of $[CoL_2(HL)]$ crystals were examined by means of a Squid magnetometer at 2–100 K and a VSM instrument at 77–298 K. $\mu_{eff} = 2.05\ \mu_B$ at 298 K, consistent with the values of Co^{II} complexes with a square-planar coordination geometry. The magnetic data are plotted as $\chi_m T$ (χ_m = molar magnetic susceptibility, T = temperature) *vs.* T in Fig. 1. A marked rise in $\chi_m T$ at temperatures lower than 50 K indicates the transition to a phase with dominant ferromagnetic interactions. It is shown on the basis of crystallographic information on $[CoL_2(HL)]$ that this result could be reasonably interpreted in terms of a dominant ferromagnetic spin-ordering within the stack chain along the b-axis and a secondary antiferromagnetic interaction between the chains in the bc plane. Thus, we assume tentatively the isotropic $S = 1/2$ Heizenberg model based on a high-temperature Padé expansion (eqn. 1),[4] modified by the addition of a mean-field correction (eqn. 2) to account for the interchain interactions,[5] where $K = J/2kT$; J is the ferromagnetic coupling constant, Z is the number of nearest-neighbour chains ($Z = 2$ in this study), J' is the exchange integral for the magnetic interaction between the nearest-neighbour chains, and the other symbols have their usual meanings. The parameter values were determined to be consistent with the observed results in Fig. 1 as follows: $J = 9.04\ cm^{-1}$ and $J' = -0.005\ cm^{-1}$ at temperatures 10–298 K with a value of $g = g_{av} = 2.35$. The good agreement indicates the existence of ferromagnetic intrachain interactions along the b-axis accompanied by a very weak interchain antiferromagnetic interaction in the bc plane. The principal mechanism of super-exchange could operate through the interaction of the Co d_{z^2} (the highest partially occupied magnetic orbital) with the two apical N atoms which form the π systems of the adjacent complex molecules along the stack chain, similar to the $(pda)Cu(ox)_2$ system (pda = propylenediammonium; ox = oxalate).[6]

$$\chi_m{}'T = (N\mu_B{}^2g^2/4k)[(1.0 + 5.79\,9916\,K + 16.902\,653K^2 + 29.376\,885K^3 + 29.832\,959K^4 + 14.036\,918K^5)/(1.0 + 2.797\,991\,6K + 7.008\,678\,0K^2 + 8.653\,864\,4K^3 + 4.574\,311\,4K^4)]^{2/3} \quad (1)$$

$$\chi_m(corr) = \chi_m{}'/[1 - (2ZJ'/Ng^2\mu_B{}^2)\,\chi_m{}'] \quad (2)$$

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