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A Binuclear Ni(II) Complex with 2,2′:6′,2″-terpyridine Exhibiting Ferromagnetic Exchange Coupling

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The study of exchange-coupled polynuclear complexes is an active area of coordination chemistry. In particular, significant progress has been made in the understanding of the exchange interaction phenomena [1–5]. Ni(II) cluster compounds have been the focal points of several recent magnetic susceptibility studies. Complexes have been found with antiferromagnetic exchange interaction as well as ferromagnetic interactions [3–5].

When the 2,2′:6′,2″-terpyridine ligand (terpy) reacts in a ratio 1:1 with the Ni(II) ion it forms the monoterpyridine complexes with general formulae $Ni(terpy)X_2 \cdot nH_2O$ (X = halide, pseudohalide), which can be either discrete or polynuclear molecules [6–10].

The spectroscopic and magnetic properties of the thiocyanate compound have been studied by Judge and Baker [6]. They proposed a polymeric $[Ni(terpy)(NCS)_2]$ structure with thiocyanate bridges. The dimeric hypothesis was eliminated because the increase in the observed magnetic moment with decreasing temperature was lower than that expected for a dimer with the $S = 2$ ground state. Nevertheless, the effect of nickel(II) single-ion zero-field splitting was not considered. Because of our interest in the magnetic behavior of these kinds of compounds we have carried out a reexamination of the properties of this compound.

Experimental

Synthesis

$[Ni(terpy)(NCS)_2]$ was prepared by a different method from that of the literature [6]. Excess of a saturated KNCS aqueous solution was added to a warm aqueous solution containing 0.400 g (0.980 mmol) of the $[Ni(terpy)Cl(H_2O)_2]Cl \cdot H_2O$ complex previously prepared [8]. The resulting solution was evaporated to obtain a solid product. The obtained green precipitate was isolated after filtration, washed with distilled water, and dried *in vacuo* over P_2O_5 for 24 h. Crystallizations of the precipitate from different solvents did not give crystals of relatively good quality for the X-ray diffraction study. *Anal.* Calc. for $C_{15}H_{11}N_3NiN_2C_2S_2$: C, 50.0; N, 17.2; H, 2.7; Ni, 14.4. Found: C, 49.9; N, 17.2; H, 2.6; Ni, 14.2%.

Physical Measurements

The IR spectrum was recorded on a Perkin-Elmer 1430 spectrophotometer. Magnetic susceptibility measurements were performed on powdered samples in the temperature range 4.2–100 K using a SQUID SHE magnetometer, in a magnetic field of 0.1 T, a value at which the magnetization versus magnetic field curve was still linear at 4.2 K. Experimental susceptibilities were corrected for the diamagnetic contributions and for the temperature-independent paramagnetism (TIP), estimated to be 100×10^{-6} emu/mol. A Brucker EPR 200tt spectrometer equipped with a standard low-temperature device, operating at X-band calibrated by an NMR probe for the magnetic field and an HP 5342 A frequency counter for the microwave frequency ($\nu = 9.47$ G Hz) was used to record the EPR powder spectra of the complex at different temperatures.

Results and Discussion

The interest of the IR spectrum lies mainly in the bands due to the NCS groups. The IR spectrum exhibits two bands at 2130 and 2105 cm^{-1} due to the ν(CN) stretching vibrations. The band corresponding to the ν(CS) stretching vibration appears at 797 cm^{-1}. The δ(NCS) bending mode is observed at 472 cm^{-1}. The high frequences of the ν(CN) stretching vibrations suggest the presence of normal 'end-to-end' NCS bridges. In the IR spectrum of the related $[Cu(paphy)(NCS)(SCN)]_2$ complex (where the two copper(II) ions are linked in an unusual way through the N end of two *N*-thiocyanate bridging groups) the ν(CN) stretching vibrations are observed at 2090 and 2070 cm^{-1} [11].

The variation of reciprocal molar magnetic susceptibility versus temperature is shown in Fig. 1. The high temperature data ($T > 50$ K) are well described by a Curie–Weiss law, $\chi = C/(T - \theta)$ with $\theta = +7.5$ K and $C = 1.10$ emu K/mol ($g = 2.097$). The positive temperature intercept indicates that the main interactions are ferromagnetic. The data are also plotted, in Fig. 2, as $\chi_m T$ versus T, where $\chi_m T = \mu_{eff}^2/8$. The product $\chi_m T$ increases with decreasing temperature due to a ferromagnetic exchange coupling and reaches a maximum of 1.58 emu K/mol at 7.40 K.

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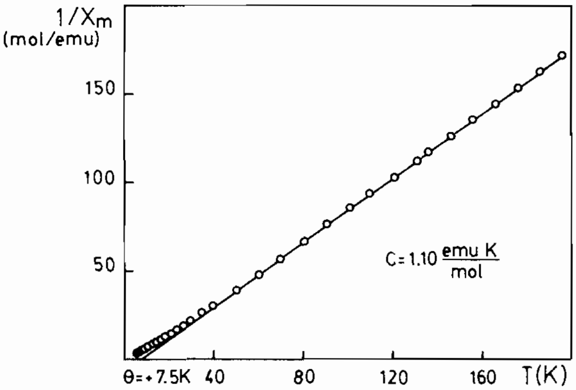

Fig. 1. Reciprocal susceptibility vs. temperature variation.

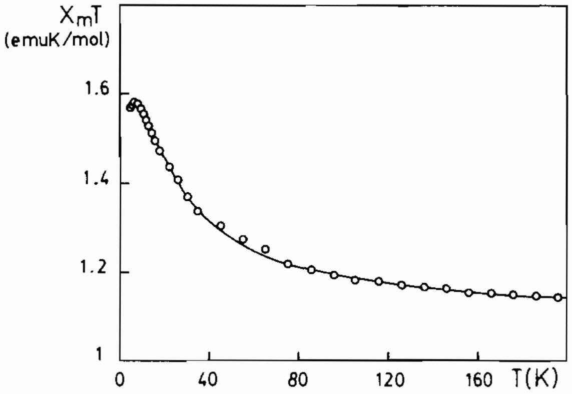

Fig. 2. Thermal evolution of the product χ_mT. The full line represents the calculated curve using a Ginsberg expression for a nickel(II) dimer.

The experimental data have been fitted using the analytic expression given by Ginsberg *et al.* [1] for a magnetically isotropic Ni(II) dimer. The theoretical equations account for an intradimer exchange integral J and nickel(II) single-ion zero-field splitting D, as well as an interdimer magnetic exchange J' that is treated in the molecular field approximation. The solid curve in Fig. 2 shows the excellent agreement between observed and calculated values of χ_mT obtained with the following parameters:

$J/K = +7.1$ K; $D/K = -6.2$K; $Z'J' = 0.02$ K

The g value was fixed at 2.097, as determined by the Curie–Weiss plot. The D and $Z'J'$ parameters are not well determined because the effects of these parameters are most important in the low-temperature region where the experimental uncertainties are greatest. Nevertheless, the estimation of J is only weakly correlated with D and $Z'J'$, thus the calculated J value appears accurately determined. According to the above results, the increase in χ_mT with decreasing temperature is a consequence of the intradimer ferromagnetic exchange coupling. The effect of the single ion zero-field splitting is quantitatively similar to an antiferromagnetic interdimer interaction and causes the low-temperature decrease observed in χ_mT. Similar magnetic behavior was observed by Ginsberg *et al.* ($J/K = +6.5$ K; $D/K = -4.8$ K) [1] for the related compound $[Ni_2(en)_4(NCS)_2]I_2$ [12].

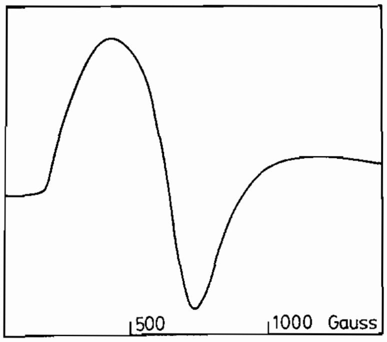

Fig. 3. X-band EPR spectrum of a powdered sample of $[Ni(terpy)(NCS)_2]_2$ at 4.2 K.

The X-band EPR spectra were recorded over a temperature range of 4.2–150 K. At 4.2 K a relatively strong signal was observed at about 620 G (see Fig. 3). No signal has been observed at 3200 G. Following energy level calculations made with the J and D values obtained from magnetic measurements, this signal is ascribed to the allowed transition between the ground state $S = 2, M_S = 0$ and the first excitated state $S = 2, M_S = 1$. This signal has been also observed for the compound $[Ni(terpy)(N_3)_2]_2 \cdot 2H_2O$ [9]. The intensity of the absorption line decreases with increasing temperature according to the magnetic behavior. The signal disappears above 100 K because the spin-lattice relaxation time of Ni(II) becomes too short.

The above results allow us to propose a ferromagnetically coupled dimeric structure for the compound $[Ni(terpy)(NCS)_2]_2$, where the two metallic centers are linked through the end-to-end thiocyanate bridges.

Acknowledgements

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