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Ferromagnetic Interactions in a Cobalt(II) Complex of 1-(2-Pyridylazo)-2-Phenanthrol

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SHORT COMMUNICATION Ferromagnetic Interactions in a Cobalt(II) Complex of 1-(2-Pyridylazo)-2-Phenanthrol

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The cobalt (II) chelates of 1-(2-pyridylazo)-2-phenanthrol (PAPL) have been previously studied and the average magnetic susceptibility studied down to 80K¹ Two distinct complexes were isolated: (i) a green complex, $Co(PAPL)_2 \cdot 2C_2H_5OH$, which separates out from an alcoholic medium and (ii) a pink complex, $Co(PAPL)_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$, which is formed when (i) is dissolved in chloroform. The conversion between (i) and (ii) is reversible. Magnetic measurements on the green complex revealed antiferromagnetic interactions whereas the pink complex was thought to possess a spin equilibrium between high (S = 3/2) and low (S = 1/2) forms of cobalt (II).¹ Magnetic measurements on the pink complex have now been extended to 4K using the previously described SQUID susceptometer.²

The magnetic properties of solid $Co(PAPL)_2$. $4C_2H_5OH \cdot 1/3CHCl_3$ fall into three distinct regions, depending on temperature and applied field strength. These are illustrated in Figures 1 and 2 (magnetic moments were calculated using $\mu = 2.828 (\chi T)^{1/2}$). Above about 100K the average magnetic moment is independent of magnetic field strength and rises steadily from about 2.3 B.M. 10 nearly 3.6 B.M. at 300K. In this temperature region the present data agree with the earlier work.¹ Between 100 and 30K the magnetic moment is nearly constant (~2.4 B.M.) and also independent of applied magnetic field strength. Below 30K the magnetic moment rises and passes through a maximum near 6K. It is also quite field dependent, increasing substantially as the applied magnetic field decreases. For example in the lowest applied field we used (8.26 mT) the magnetic moment rises to 6.5 B.M. at 5.8K before dropping to 6.0 B.M. at 4K. The position of the maximum also changes slightly, rising from 5.8K in 8.26 mT to nearly 7K in 34.67 mT.

To check whether the interaction was present in the solution state several measurements were made with a sample of $Co(PAPL)_2 \cdot 4C_2 H_5 OH \cdot 1/3 CHCl_3$ dissolved in acetone (the material was most soluble in acetone). Because of the uncertainty in the solution molecular weight and the actual concentration the raw solution magnetization data (in 8.26 mT and corrected for diamagnetic effects) were normalized to 2.4 B.M. at 30K. As shown in Figure 1 the moments fall gently with decrease in temperature as would probably be expected from an isolated cobalt(II) ion. We deduce from this tha ferromagnetic impurities are probably not important an so intermolecular interaction between cobalt(II) ions is probably responsible for the unusual solid state behavior

The data above 30K indicate that the compound probably possesses a genuine spin equilibrium between 300-100K with predominantly low spin molecules between 70 and 30K. Below 30K magnetic interaction is evident. The rise in magnetic moment and its field dependence is reminiscent of the magnetic properties of manganese phthalocyanine (MnPc).³ Further we might expect the interaction to be Ising-like because of the anisotropic nature of the single-ion properties of the cobalt(II) ion.⁴ This often leads to a canted antiferromagnetic structure and would agree qualitatively with the present magnetic field dependence and the eventual drop in magnetic moment below 5.8K. The quite large magnetic field effects which are observed here are also often associated with low dimensional co-operative phenomena⁵ but in the absence of any structural data it is at this stage futile to speculate any further.



FIGURE 1 The magnetic moment of powder (\triangle) and solution (•) samples of Co(PAPL)₂·4C₂H₅OH·1/3CHCl₂ in 8.26 mT (see text).



FIGURE 2 The magnetic moment of a powder sample of $Co(PAPL)_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$ as a function of temperature and applied magnetic field strength.

All attempts to grow a crystal of the material have so far failed.

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