Magnetization Studies of Hexakis(pyridine *N*-oxide)nickel(II) Tetrafluoroborate and Perchlorate down to 2 K

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The principal magnetizations of $[Ni(pyo)_6][BF_4]_2$ and average magnetization of $[Ni(pyo)_6][ClO_4]_2$ have been measured from 2 to 20 K at magnetic-field strengths up to 50 kG (pyo = pyridine *N*-oxide). The magnetization of $[Ni(pyo)_6][BF_4]_2$ parallel to the *c* axis can be reproduced by the spin-Hamiltonian parameters $g_{\parallel} = 2.28$ and $D = 5$ cm^{-1}. The perpendicular magnetization is reduced by antiferromagnetic exchange interactions with $T_N < 2$ K. The average magnetization of $[Ni(pyo)_6][ClO_4]_2$ is similar to that of the tetrafluoroborate salt indicating that the exchange interactions in the two compounds are also similar.

A d^8 ion in an octahedral site has a three-fold degenerate $^3A_{2g}$ ground state which is split into a singlet and a doublet by a crystal field of S_6 symmetry. Since the $^3A_{2g}$ (O_h) state is orbitally non-degenerate, the splitting occurs by second- and higher-order interaction with excited energy levels. The isotropic part of the mixing increases the orbital contribution to the *g* value and the magnetic susceptibility, while the anisotropic part gives rise to the zero-field splitting and the magnetic anisotropy. In most cases the zero-field splitting is of the order 0—5 cm^{-1} and an isotropic *g* value close to 2.25 is found. Any *g*-value anisotropy is generally too small to be observed in the presence of the zero-field splitting.[1]

In $[Ni(pyo)_6][BF_4]_2$ (pyo = pyridine *N*-oxide) the lowest excited level [2] is at *ca.* 8 000 cm^{-1} and hence the magnetism can be adequately described within the spin-Hamiltonian formalism at temperatures sufficiently low that ligand diamagnetism and second-order Zeeman terms are negligible. In the present case, the errors would be *ca.* 1% at 20 K and the system can be described by the spin Hamiltonian (1). The zero-field splitting is equal to

$$H = D[S_z^2 - \tfrac{1}{3}S(S+1)] + g_{\parallel}\beta H_z S_z + g_{\perp}\beta H_x S_x \quad (1)$$

D and is positive when the singlet level is lowest. Previous studies[3] of $[Ni(pyo)_6][BF_4]_2$ have indicated that, for temperatures above 30 K, $g_{\parallel} = g_{\perp} = 2.28$ and *D ca.* 4 cm^{-1}. The large zero-field splitting explains the absence of an e.p.r. spectrum at normal magnetic-field strengths. It was also suggested that $[Ni(pyo)_6][BF_4]_2$ was antiferromagnetic with $T_N < 2$ K, and the present paper describes magnetization studies of both the perchlorate and tetrafluoroborate salts in support of that postulate. Low-temperature magnetization studies conducted in this laboratory on the isomorphous salts $[M(pyo)_6][ClO_4]_2$ (M = Fe, Cu, or Co) indicate that these compounds are also antiferromagnetic with $T_N < 2$ K. A recent paper on the cobalt compound mentions that there is a specific heat anomaly at 0.42 K.[4]

EXPERIMENTAL

The compound $[Ni(pyo)_6][ClO_4]_2$ was prepared in the same way as the tetrafluoroborate salt,[3] and the magnetization and average susceptibility were measured using equipment described previously.[5] The crystallites of $[Ni(pyo)_6][ClO_4]_2$ tended to align at 4.2 K as the magnetic field was increased to 50 kG and the magnetization was determined by mixing the compound with petroleum jelly.* The absolute value of the magnetization was determined by comparing the values in petroleum jelly with those obtained on a pure sample at a magnetic field strength of 10 kG over the range $4.2 < T < 20$ K. Single-crystal magnetization values of $[Ni(pyo)_6][BF_4]_2$ were determined by mounting crystals (*ca.* 30 mg) on a glass rod which was suspended from the Sartorius microbalance by a quartz fibre 40 μm in diameter. The crystal axes were located by *X*-rays. It was difficult to correct for the diamagnetic contribution of the suspension system and to position the crystal exactly in the calibrated part of the magnetic field, and hence the principal magnetizations were 'locked in' to the indirect values obtained at low field strengths and temperatures from 6.5 to 20 K. The indirect values were determined from the magnetic anisotropy and average susceptibility. This procedure is quite important in the present case since the magnetic anisotropy is not particularly large. Magnetic moments were calculated using the formula $\mu = 2.828(\chi T)^{\frac{1}{2}}$.†

RESULTS AND DISCUSSION

In $[Ni(pyo)_6][BF_4]_2$ the zero-field splitting is positive and as the temperature decreases the doublet level is depopulated and the parallel magnetic susceptibility decreases to a value dependent on the second-order Zeeman effect. This is small since the nearest excited state is at *ca.* 8 000 cm^{-1} and hence the magnetic moment at low fields effectively approaches zero. If the magnetic field parallel to the *c* axis is then increased, the $|-1\rangle$ component of the doublet becomes thermally populated and the susceptibility increases (see Figure 1). Thus at temperatures below *ca.* D/k the susceptibility increased with increasing field as is shown in Figure 2. At higher temperatures the behaviour was normal and the susceptibility decreased with increasing field. The experimental values at 10 and 40 kG are also shown in Figure 2 and it is seen that they are consistent with $D = 5$ cm^{-1}. For $g_{\parallel} = 2.28$ and $D = 5$ cm^{-1} the $|-1\rangle$ and $|0\rangle$ states become degenerate at 47 kG and experimentally it was

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* Throughout this paper: 1 G = 10^{-4} T; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

† To convert into S.I. units, χ is multiplied by $4\pi \times 10^{-6}$ and the magnetic moment is then given by the expression $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

[1] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970.

[2] J. Reedijk, *Rec. Trav. chim.*, 1969, **88**, 499.

[3] D. J. Mackey and S. V. Evans, *J.C.S. Dalton*, 1976, 2004.

[4] R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Amer. Chem. Soc.*, 1976, **98**, 685.

[5] D. J. Mackey, S. V. Evans, and R. L. Martin, *J.C.S. Dalton*, 1976, 1515.

found that the force on the sample of $[Ni(pyo)_6][BF_4]_2$ for $H||C$ began to oscillate as the field increased and it was not possible to obtain accurate values for the parallel magnetic susceptibility for $30 < H < 50$ kG and $2 < T < 20$ K. The scatter in the experimental values can be seen in Figures 2 and 3. The reason for this behaviour is not known and no such effect was observed in measurements of the average or perpendicular magnetic susceptibility. In principle, the zero-field splitting can be determined from the variations in magnetization with magnetic-field strength. The zero-field splitting in $[Fe(OH_2)_6][SiF_6]$ has been measured by this method [6,7] and no mention was made of any instabilities occurring for magnetic-field strengths in the crossover region. The method cannot be used in the present case since there is too much scatter in the experimental values to eliminate thermal-population effects by extrapolation to $T = 0$ K and because slightly higher magnetic-field strengths would be needed.

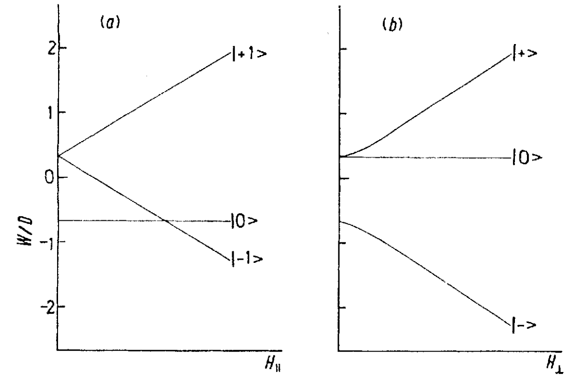

FIGURE 1 Splitting of an $S = 1$ state by a uniaxial crystal field in the presence of an external magnetic field parallel (*a*) and perpendicular (*b*) to the unique molecular axis

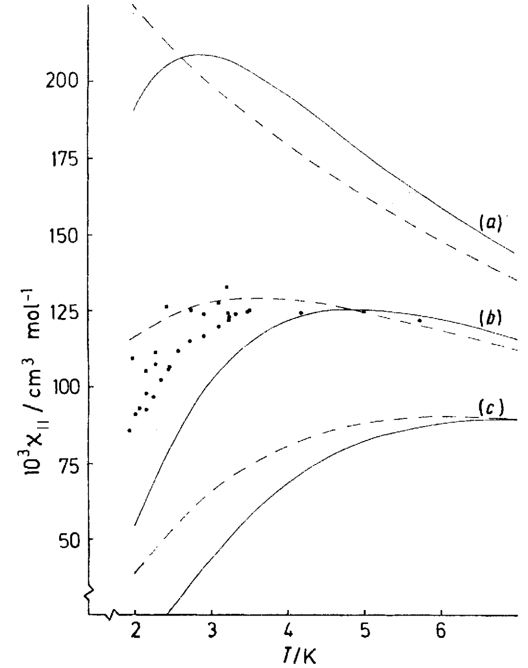

FIGURE 2 Magnetic susceptibility parallel to the *c* axis of $[Ni(pyo)_6][BF_4]_2$ at 10 (●) and 40 kG (■). The calculated curves are for $g_{\parallel} = 2.28$ and $D = 3$ (*a*), 5 (*b*), and 7 cm^{-1} (*c*) at magnetic-field strengths of 10 (——) and 40 kG (— — —)

Although there are small discrepancies between the calculated and experimental values of $\mu_{\parallel}$, the agreement is reasonable and suggests there is little magnetic exchange parallel to the *c* axis. This is to be expected if the parallel exchange constant is small compared with D since the $|\pm1\rangle$ doublet would be depopulated before magnetic ordering could occur. The situation in the *ab* plane is more complicated since the $|+1\rangle$, $|0\rangle$, and $|-1\rangle$ states are mixed by the magnetic field and can be described by the nomenclature $|+\rangle$, $|0\rangle$, and $|-\rangle$ (see Figure 1). In this case the magnetic moment does not approach zero as the temperature is decreased. The calculated and experimental magnetic moments are compared in Figure 4 and the low value of the experimental moment can only be explained by the presence of antiferromagnetic exchange interactions. The discontinuity of the curves at $\mu_{\perp}$ *ca.* 2.95 B.M. corresponds

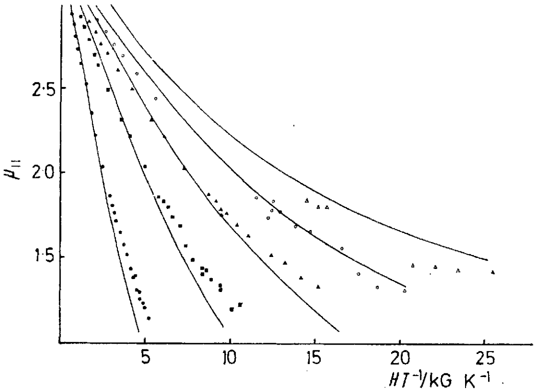

FIGURE 3 Calculated parallel magnetic moments for $g_{\perp} = 2.28$ and $D = 5$ cm^{-1}. The experimental points for $[Ni(pyo)_6][BF_4]_2$ at magnetic field strengths of 10 (●), 20 (■), 30 (▲), 40 (○), and 50 kG (△) are shown for comparison

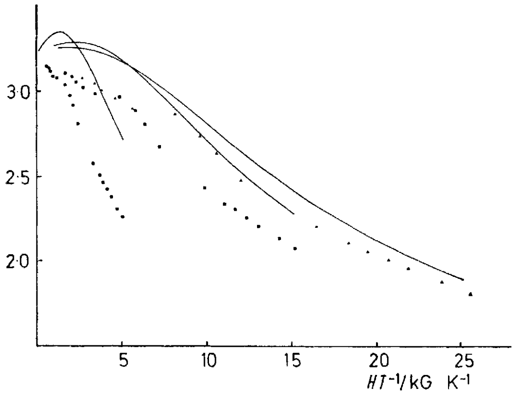

FIGURE 4 Calculated perpendicular magnetic moments for $g_{\perp} = 2.28$ and $D = 5$ cm^{-1}. The experimental values for $[Ni(pyo)_6][BF_4]_2$ at magnetic field strengths of 10 (●), 30 (■), and 50 kG (▲) are shown for comparison

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[6] F. Varret, Y. Allain, and A. Miedan-Gros, *Solid State Comm.*, 1974, **14**, 17.

[7] F. Varret, *J. Phys. Chem. Solids*, 1976, **37**, 257.

to a definite change in gradient of the plots of $\mu_\perp$ against T at *ca.* 9 K. No such change was observed for $\mu_\parallel$.

The mechanism of the exchange interaction is not obvious since the *X*-ray crystal-structure determination of $[Ni(pyo)_6][BF_4]_2$ indicates that the $[BF_4]^-$ groups are not involved in hydrogen bonding between neighbouring $[Ni(pyo)_6]^{2+}$ cations. The structure consists of sheets of cations perpendicular to the *c* axis with each $[Ni(pyo)_6]^{2+}$ group surrounded by six others at 12.49 Å. Each cation also has six nearest neighbours in adjacent planes at 9.58 Å and the overall packing of the $[Ni(pyo)_6]^{2+}$ cation is intermediate between simple cubic and close-packed cubic. The Ni–Ni distances in $[Ni(pyo)_6][ClO_4]_2$ are virtually the same as in the tetrafluoroborate salt and one would therefore expect similar exchange interactions. The low-temperature magnetizations of the two compounds are very similar as can be seen in Figure 5. The value of $\bar{\mu}$ (at a field strength of 10 kG) is slightly lower in the perchlorate salt even at temperatures where exchange effects should be negligible and it would seem that the zero-field splitting is slightly greater than in the tetrafluoroborate salt. At room temperature $\bar{\mu}$ should depend only on ζ, Dq, and the orbital reduction factor, k, and the values are the same within experimental error.

In a previous paper, it was suggested that the zero-field splitting increased as the temperature decreased and a value of 3.5—4 cm^{-1} was obtained from the magnetic anisotropy between 30 and 300 K.[3] The value of 5 cm^{-1} obtained below 10 K is in agreement with this suggestion and it is likely that a temperature-dependent zero-field splitting is common in metal complexes containing only unidentate ligands. Similar effects have been observed in other compounds including the rare-earth antipyrene iodides[8] and $[Ni(OH_2)_6][SiF_6]$.[9] In these cases, the central metal is also in a site of S_6 symmetry.

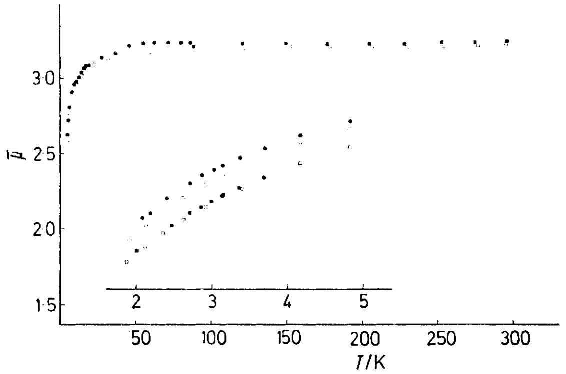

FIGURE 5 Average magnetic moments of $[Ni(pyo)_6][BF_4]_2$ (● and ■) and $[Ni(pyo)_6][ClO_4]_2$ (○ and □) from 2 to 300 K at magnetic-field strengths of 10 (circles) and 40 kG (squares)

[6/900 *Received*, 11*th May*, 1976]

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[8] M. Gerloch and D. J. Mackey, *J.C.S. Dalton*, 1972, 1555.

[9] R. P. Penrose and K. W. H. Stevens, *Proc. Phys. Soc.*, 1950, **A63**, 29.