Magnetic Properties of Hexakis(pyridine *N*-oxide)nickel(II) Tetrafluoroborate

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The magnetic anisotropy of the title compound has been determined from 4.58 to 300 K and the average susceptibility has been measured down to 1.98 K at field strengths ranging from 10 to 50 kG. The results are interpreted on a point-charge model for D_{3d} symmetry using the parameters $A_2^0\langle r^2\rangle$ = 925 cm^{-1}, ρ_4 = 4 920 cm^{-1}, F_2 = 1 306 cm^{-1}, F_4 = 93 cm^{-1}, ζ = 550 cm^{-1}, and k = 1.0. It is suggested that the trigonal distortion of the nickel ion increases as the temperature is decreased to 100 K. The low-temperature anisotropy and magnetization are consistent with the compound being antiferromagnetic with T_N < 2 K.

THE compound [Ni(pyo)$_6$][BF$_4$]$_2$ (pyo = pyridine *N*-oxide) belongs to a large isomorphous series where the metal ion is in a site of S_6 symmetry.[1] For a metal surrounded by six identical ligands having non-linear M–X–Y bonds (in this case Ni–O–N) the highest site symmetries possible are S_6 and D_3. The former is generally favoured since it minimizes the non-bonding interactions between the ligands and is found in hexakis complexes of antipyrene [2,3] and imidazole [4] as well as pyridine *N*-oxide. D_3 Symmetry is sometimes found in tris chelate complexes [5,6] and also in the hexakisurea compounds of trivalent first-row transition metals.[7,8] In the latter case, hydrogen bonding between urea molecules plays an important part in the structure and probably helps to counteract the increased ligand–ligand repulsion.

In a previous paper [9] we discussed the point-charge crystal-field model for D_3 symmetry and showed that four parameters were needed rather than the three required by symmetry. The opposite is true in S_6 symmetry since a simple point-charge model is a function of only the six nearest neighbours and hence the effective symmetry is increased to D_{3d}. The latter symmetry requires three parameters whereas four are needed in S_6 since the crystal-field expansion in terms of spherical harmonics gives (1). The situation is further complicated

$$V_{S6} = aY_2^0 + bY_4^0 + c(Y_4^3 - Y_4^{-3}) + id(Y_4^3 + Y_4^{-3}) \quad (1)$$

by the imaginary term in the potential and the calculations involved are much longer. In the present case, the site symmetry was assumed to be D_{3d} since the crystal field would be expected to be dominated by the co-ordinated oxygen atoms. In addition, a point-charge calculation in terms of the parameters ρ_2, ρ_4, and θ [10] may give some insight into the importance of small angular distortions. This approach has been used before in discussing the magnetism of the rare-earth antipyrene iodides where a point-charge model is even more useful since the number of crystal-field parameters is reduced from nine to four.[11]

EXPERIMENTAL

Pyridine *N*-oxide was supplied by Pfaltz and Bauer and was shaken with an excess of 2,2′-dimethoxypropane (dmp) until it dissolved in the methanol–acetone mixture produced by hydrolysis of the dmp. Nickel(II) tetrafluoroborate hexahydrate (Alfa Inorganics) was similarly treated with dmp and added to the previous solution. The yellow-green precipitate which formed was filtered off and dissolved in MeCN–dmp (20 : 1). Slow evaporation of the solvent produced pale green rhombohedral crystals of [Ni(pyo)$_6$]-[BF$_4$]$_2$. Crystals of the isomorphous [Zn(pyo)$_6$][ClO$_4$]$_2$ were prepared in a similar manner and the axes of both crystals were located by *X*-ray crystallography. The magnetization and average susceptibility was measured on a modified Oxford Instruments magnetometer, while the magnetic anisotropy was measured by the Krishnan critical-torque method.[12] The apparatus and calibration procedures have been described previously.[9] The average susceptibility was corrected for a diamagnetic contribution of -408×10^{-6} cm^3 mol^{-1} using standard tables.[13] The anisotropy was corrected by assuming the diamagnetic anisotropy to be the same as in [Zn(pyo)$_6$][ClO$_4$]$_2$ where $10^6(\chi_\parallel - \chi_\perp)$ was found to be 111 cm^3 mol^{-1}. The anisotropy was not measured above 200 K since the crystal anisotropy was very small due to the approximate cancellation of the diamagnetic and paramagnetic contributions.

Calculations were made using a general computer program described previously.[14,15] The equation for the matrix elements of spin–orbit coupling given in ref. 15 has a misprint: the phase factor should be $(-1)^{-J-L'-S}$. The magnetization calculations were programmed by Dr. P. D. W. Boyd and were based on the equations given by Vermaas and Groenveld.[16] The definition of parameters is the same as reported previously with $\alpha = 30°$,[9] and is essentially the

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same as that given by Gerloch *et al.*[10] The room-temperature magnetic moment of $[Ni(pyo)_6][BF_4]_2$ (3.24 B.M.) is in reasonable agreement with values obtained on other $[Ni(pyo)_6]X_2$ compounds ($X = ClO_4$, 3.32 [17] and 3.30;[18] X = Br 3.14 [19] and 3.28 [18]). All the magnetic moments were calculated from the equation $\mu = 2.828(\chi T)^{\frac{1}{2}}$.*

RESULTS AND DISCUSSION

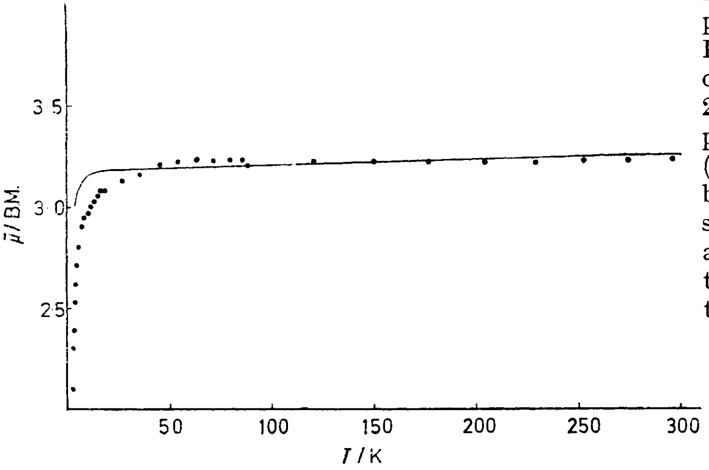

FIGURE 1 Average moment calculated using $A_2^0\langle r^2\rangle = 925$ cm^{-1}, $\rho_4 = 4\,920$ cm^{-1}, $F_2 = 1\,306$ cm^{-1}, $F_4 = 93$ cm^{-1}, $\zeta = 550$ cm^{-1}, and $k = 1.0$. (●), Experimental values

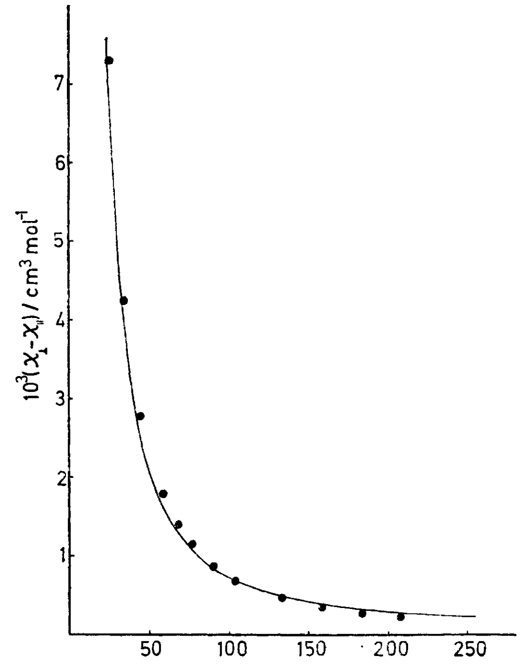

FIGURE 2 Calculated anisotropy for parameters in Figure 1. (●), Experimental values

As far as we are aware, no single-crystal spectra of $[Ni(pyo)_6]X_2$ compounds have been reported although there have been a number of measurements on mulls and by diffuse reflectance.[17,20] The spectra are discussed by Reedijk [21] and we have used the values of Dq and B given by him ($Dq = 820$ cm^{-1}, $B = 840$ cm^{-1}). Assuming $F_2 \approx 14F_4$ this gives $F_2 = 1\,306$ cm^{-1}, $F_4 = 93$ cm^{-1}, and $\rho_4 = 6Dq = 4\,920$ cm^{-1} and these values were used in subsequent calculations. As mentioned previously [9] the calculated susceptibilities are quite insensitive to the values of F_2 and F_4 provided that $B = F_2 - 5F_4$ remains constant. For $7\,000 \leqslant \rho_2 \leqslant 30\,000$ cm^{-1} the anisotropy and average susceptibility were independent of ρ_2 provided that $A_2^0\langle r^2\rangle = \frac{3}{2}\,\rho_2(3\cos^2\theta - 1)$ remained constant. This is due to the fact that distortions from octahedral symmetry tend to be dominated by the Y_2^0 term in the crystal-field potential.[9,22] For reasonable values of ρ_2 and ζ the observed sign of the anisotropy ($\chi_\perp > \chi_\parallel$) could only be reproduced for $\theta < \theta_{oct.} = 54.736$, corresponding to a trigonal elongation, and plots of calculated $\Delta\chi$ against θ ($50 \leqslant \theta \leqslant \theta_{oct.}$) were almost linear over the temperature range $20 \leqslant T \leqslant 300$ K. The anisotropy was quite dependent on ζ, but it was not possible to reproduce the correct temperature dependence for $400 \leqslant \zeta \leqslant 600$ cm^{-1} although higher values were favoured. As expected for an orbital-singlet ground state, the variation of $\chi_\parallel$ and $\chi_\perp$ with k was small and the anisotropy could still not be fitted over the whole temperature range for $0.8 \leqslant k \leqslant 1.0$. The orbital-reduction factor, k, was therefore left as 1.0. (For lower values of k, comparable fits to the experimental data could be obtained by increasing the values of (ζ/ρ_4) and $|A_2^0\langle r^2\rangle|$.) Between 30 and 100 K it was possible to obtain a reasonable fit to the anisotropy but the calculated values were too high at both higher and lower temperatures. A compromise set of parameters producing a reasonable fit to $\bar{\mu}$ and $\Delta\chi$ for $30 \leqslant T \leqslant 300$ K is $\zeta = 550$ cm^{-1} and $A_2^0\langle r^2\rangle = 925$ cm^{-1}. The calculated and observed values are shown in Figures 1 and 2. The value of ζ is in reasonable agreement with that predicted from the simple formula $\bar{\mu} = 2.828[1 + 12(\zeta/10\rho_4)]$. The zero-field splitting (D) was calculated to be 3.5—4.0 cm^{-1} (defined as positive for the lowest singlet level) depending on the values of $A_2^0\langle r^2\rangle$ and ζ used. In $[Ni(pyo)_6][BF_4]_2$ it is conceivable that the trigonal crystal field could be a function of temperature since the effective angle that each metal–ligand bond makes with the C_3 axis (θ) could change, as has already been suggested in studies on the rare-earth antipyrene

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* 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 G = 10^{-4} T, 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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iodides.[11] This would be less likely to occur in a tris-chelate complex where the molecular geometry is more constrained by the steric requirements of the chelate rings and no such effect was observed in our studies of $[Ni(NH_2CH_2CH_2NH_2)_3][NO_3]_2$.[9] In the present case, it is suggested that the trigonal distortion of the nickel ion increases as the temperature is decreased to 100 K. For $\rho = 15\,000$ cm^{-1}, θ would have to decrease by *ca.* 0.15° between 200 and 100 K and such a small change would have a negligible effect on the average moment. It is considered unlikely that there is a phase change since the crystal can be cycled between 300 and 4.6 K without shattering, and since there was no change in the setting position of the crystal with temperature (the crystal was mounted parallel to one of the hexagonal axes in the *ab* plane).

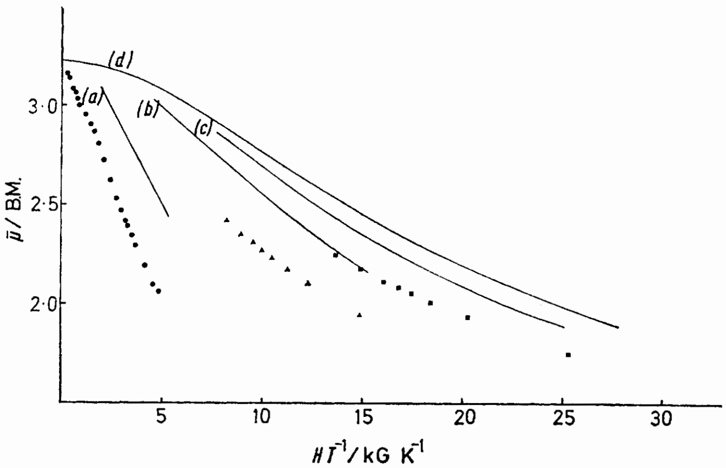

FIGURE 3 Calculated magnetic moments at field strengths of 10 (*a*), 30 (*b*), and 50 kG (*c*) for $g = 2.275$ and $D = 4$ cm^{-1}. Curve (*d*) is the Brillouin function. The experimental values at 10 (●), 30 (▲), and 50 kG (■) are shown for comparison

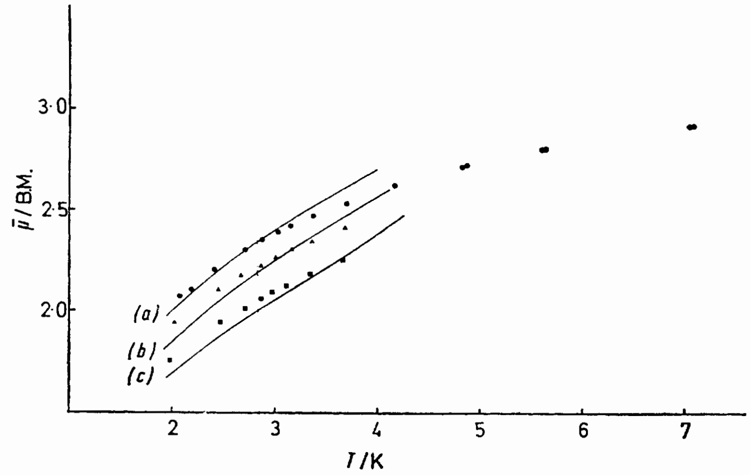

FIGURE 4 Calculated magnetic moments at field strengths of 10 (*a*), 30 (*b*), and 50 kG (*c*) for $g = 2.275$ and $D = 7$ cm^{-1}. The experimental values at 10 (●), 30 (▲), and 50 kG (■) are shown for comparison

The low-temperature magnetization (1.98—3.70 K) cannot be fitted to the parameters derived from the results at temperatures above 30 K. For $g = 2.275$ and a zero-field splitting $D = 4$ cm^{-1} the calculated moments are much higher than the experimental values at all field strengths used, as can be seen in Figure 3. The zero-field splitting causes large deviations from the Brillouin function. A better fit for $\bar{\mu}$ can be obtained for $D = 7$ cm^{-1} (Figure 4), but the agreement is not particularly good and cannot be improved significantly by varying D or g or by using anisotropic g values. In addition, a larger value of D at lower temperatures would imply that the experimental anisotropy would be greater than that calculated from the parameters obtained above 30 K. The reverse is true (Figure 5) and it is postulated that the compound is antiferromagnetic with $T_N < 2$ K. This would also explain why the average moment decreases more rapidly than expected as the temperature is decreased from 30 K (Figure 1). Using the relation $\bar{\mu} = 2.828[\chi(T + 1.8)]^{\frac{1}{2}}$ the average moment was found to be 3.25 ± 0.03 B.M. for the range $5.6 \leqslant T \leqslant 300$ K. At lower temperatures the moment calculated from this

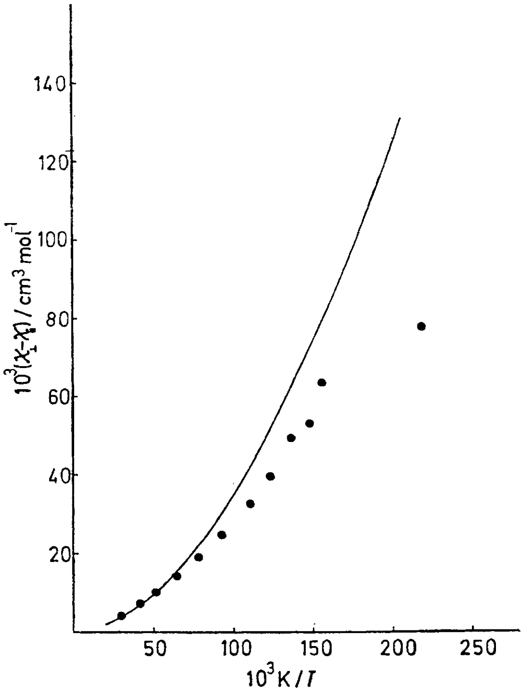

Figure 5 Calculated anisotropy for $A_2^0\langle r^2\rangle = 925$ cm^{-1}, $\rho_4 = 4\,920$ cm^{-1}, $F_2 = 1\,306$ cm^{-1}, $F_4 = 93$ cm^{-1}, $\zeta = 550$ cm^{-1}, and $k = 1.0$. (●), Experimental values

expression decreased significantly as the effect of the zero-field splitting became more important.

Conclusions.—There is an ambiguity of space group ($R3$ or $R\bar{3}$) in the crystal-structure determination of $[\mathrm{Ni(pyo)_6}][\mathrm{BF_4}]_2$ but the co-ordination around the nickel is almost exactly octahedral in both cases. The magnetic-susceptibility measurements suggest an elongation of the octahedron but the distortion needed is very small and is *ca.* 0.8° for $\rho_2 = 15\,000$ cm^{-1} and 0.4° for $\rho_2 = 30\,000$ cm^{-1}.

Our results do not necessarily imply that there is a crystallographically undetected elongation of the octahedron of oxygen atoms since the angle θ incorporates many effects such as π bonding, or perturbations of the crystal-field potential by the pyridine rings or the tetrafluoroborate anions. Nevertheless it is apparent that quite small distortion from exact octahedral symmetry can have significant effects on the magnetic properties. The mechanism for the suggested antiferromagnetism is not at all obvious, particularly since the structure indicates that the $[\mathrm{BF_4}]^-$ groups do not link the cations together by hydrogen bonds. The magnitude of the zero-field splitting explains the absence of an e.s.r. spectrum for this compound[21] at normal magnetic field strengths where the energy of the microwave radiation is *ca.* 0.3 cm^{-1}.

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