

## Single-crystal Magnetic Studies of Tris(ethylenediamine)nickel(II) Nitrate

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The magnetic anisotropy of  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  (en = ethylenediamine) has been determined from 4.58 to 300 K and the average susceptibility has been measured down to 2.01 K at field strengths ranging from 10 to 50 kG. The results are interpreted on a point-charge model for  $D_3$  symmetry using the parameters  $A_2^0 \langle r^2 \rangle = -630 \text{ cm}^{-1}$ ,  $\rho_4 = 7\,000 \text{ cm}^{-1}$ ,  $\alpha = 25^\circ$ ,  $F_2 = 1\,350 \text{ cm}^{-1}$ ,  $F_4 = 70 \text{ cm}^{-1}$ ,  $\zeta = 400 \text{ cm}^{-1}$ , and  $k = 1.0$ . The calculations show that a twist from octahedral toward trigonal-prismatic co-ordination has little effect on the magnetism. The magnetization and low-temperature anisotropy are consistent with the compound being weakly antiferromagnetic.

THE determination of magnetic anisotropy and magnetization greatly increases the value of magnetic-susceptibility measurements and in this paper we describe the magnetic properties of  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  (en = ethylenediamine) from 2 to 300 K. The compound grows as hexagonal crystals<sup>1</sup> and the high site symmetry ( $D_3$ ) of the nickel ion means there are no problems in calculating the molecular susceptibilities from the crystal susceptibilities since the two are identical. This is not the case for monoclinic crystals where one has to assume direction cosines before making the relevant tensor transformation.<sup>2</sup> The co-ordination about the nickel ion is considerably distorted from octahedral symmetry both by a compression along the three-fold axis and a twist toward trigonal-prismatic co-ordination. The effect of these two independent types of trigonal distortion on

magnetic properties has received some attention<sup>3-5</sup> and it has been reported that the trigonal twist was the more important in the  $[\text{V}(\text{urea})_6]^{3+}$  and  $[\text{Ti}(\text{urea})_6]^{3+}$  ions. The two effects can be separated by parameterizing the crystal field in terms of a point-charge model. Four variables (two radial and two angular parameters) are needed to describe the crystal field and, although this is one more than required by symmetry, calculations showed that, for small distortions, there was a simple relation between two of the parameters. The crystal-field potential and the definition of the parameters is described in the Appendix.

### EXPERIMENTAL

Large crystals of  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  were readily grown by slow evaporation of an aqueous solution. The crystals were

<sup>1</sup> L. N. Swink and M. Atoji, *Acta Cryst.*, 1960, **13**, 639.

<sup>2</sup> M. Gerloch and P. N. Quested, *J. Chem. Soc. (A)*, 1971, 2307.  
P. H. Davis and J. S. Wood, *Chem. Phys. Letters*, 1969, **4**, 466.

<sup>4</sup> B. N. Figgis and L. G. B. Wadley, *J.C.S. Dalton*, 1972, 2182.

<sup>5</sup> B. N. Figgis, L. G. B. Wadley, and M. Gerloch, *J.C.S. Dalton*, 1973, 238.

in the shape of hexagonal pyramids greatly elongated along the  $c$  axis. The hexagonal axis was located by  $X$ -ray crystallography. The average susceptibility was measured on an extensively modified Oxford Instruments Faraday magnetometer with redesigned supports for the microbalance and superconducting magnets. The system comprised a liquid-helium Dewar with a superconducting magnet assembly to provide the main and gradient fields, a variable-temperature insert for sample temperature control, a Sartorius microbalance for force measurements, and associated vacuum facilities. The main and gradient fields were independently variable, up to 60 kG and 1 000 G cm<sup>-1</sup>, respectively.\* Temperatures from 1.6 to 300 K could be achieved, the lowest temperatures by pumping on liquid helium. A Hewlett-Packard coupler-controller system was incorporated so that operation and data logging could be carried out automatically. The field strength of the main solenoid was calibrated by Oxford Instruments using proton and deuterium n.m.r. probes. The field gradient was calibrated with a sample of pure nickel using magnetization values reported in the literature.<sup>6</sup> There was a small interaction between the main field and field gradient and the latter was calibrated independently at all the field strengths used.

The magnetic anisotropy was measured by the Krishnan critical-torque method<sup>7</sup> at field strengths from 850 to 4 500 G. The current through a 4-in Humphries electro-magnet was controlled by a Hewlett-Packard 6274B power supply and could be set to *ca.* 0.1% using a fine helipot. The field strength at seven predetermined settings was measured with an n.m.r. probe and the field strength was found to be reproducible to better than 0.2%. Quartz fibres were supplied by Heraeus Schott in diameters ranging from 5 to 50  $\mu$ m. Lengths of *ca.* 1 m were used and 20- or 30- $\mu$ m fibres were found to be the most useful. A modified Oxford Instruments modular helium Dewar was used, two thermocouples being built into the system and the reference junctions being redesigned. The temperature was controlled to within 0.1 K (0.05 K at lower temperatures) by an Artronix 5301E temperature controller. The output of the Chromel-Fe(Au) thermocouple was recorded by a Newport Series 2400 digital microvoltmeter.

The control and measurement of sample temperature in these two systems was the main source of difficulty in making accurate measurements. In both assemblies, the sample must be suspended freely and thermal equilibration with the controlled surroundings is achieved only by exchange gas contact. Exchange gas pressure was particularly important in the anisotropy apparatus and optimum stability occurred when the sample chamber was maintained at a constant 7 Pa pressure of helium gas. At higher pressures, there was considerable interference from convection currents in the exchange gas. The relatively low pressure caused the time required, particularly at low temperatures, for the oscillations to die down to increase after the crystal had flipped. The crystal was viewed from the top of the cryostat using a mirror system and hence the setting angle of any crystal could be measured accurately. The fibres were calibrated using a number of large crystals (*ca.* 100 mg) of 1,3,5-triphenylbenzene, assuming  $\Delta\chi_b$  to be  $174 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>.<sup>7</sup> As expected, the torsional constant

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

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

of the fibre was found to be independent of field in the range  $850 < H < 4\,500$  G. The effect of temperature on the torsional constant of the fibre was checked by measuring the anisotropy of 1,3,5-triphenylbenzene at 295 K with and without liquid nitrogen in the helium can, the results agreeing to within 0.1%. In the former case, much of the fibre would have been at *ca.* 77 K and hence it was concluded that temperature gradients along the fibre had a negligible effect. However, the anisotropy ( $\Delta\chi_b$ ) of 1,3,5-triphenylbenzene increased unexpectedly by 4% on cooling from 295 to 77 K and remained constant from 77 to 4.6 K. This was attributed to differential thermal expansion of the orthorhombic crystal altering the orientation of the benzene rings and increasing the anisotropy. A similar increase in anisotropy was found for [Mg(antipyrene)<sub>6</sub>][ClO<sub>4</sub>]<sub>2</sub> (antipyrene = 2,3-dimethyl-1-phenyl- $\Delta^3$ -pyrazolin-5-one) although the shape of the curve of anisotropy against temperature was quite different from that of 1,3,5-triphenylbenzene. For accurate measurements, it would seem that diamagnetic calibrants containing aromatic rings should be used only at temperatures close to that at which the absolute anisotropy was determined.

In both instruments, the thermocouples (and carbon resistor) were calibrated by suspending a gallium arsenide diode in the sample position under identical running conditions of exchange gas pressure (*ca.* 130 Pa for the Faraday balance). The diode was supplied and calibrated by Lakeshore Cryogenics and the e.m.f. was read on a Fluke 8375A digital multimeter to an accuracy of  $\pm 100$   $\mu$ V corresponding to a temperature resolution of *ca.* 0.05 K. In the anisotropy apparatus it was not possible to control the temperature below 6.5 K with sufficient accuracy, although measurements could be made at the lowest temperature attainable, *viz.* 4.58 K. Independent runs on various samples were reproducible to 0.01 B.M. in the Faraday balance and to better than 1% in the anisotropy apparatus.

Diamagnetic corrections to  $\bar{\chi}$  were applied using tabulated values<sup>8</sup> and the diamagnetic anisotropy was measured on the isomorphous zinc compound for which ( $\chi_{\perp} - \chi_{\parallel}$ ) was found to be  $1.0 \times 10^{-5}$  cm<sup>3</sup> mol<sup>-1</sup>. Unless otherwise stated, all magnetic moments were calculated † using the equation  $\mu = 2.828(\chi T)^{\frac{1}{2}}$ .

## RESULTS AND DISCUSSION

In the point-charge model used (see Appendix) the crystal field is expanded in terms of nearest-neighbour interactions only and the angles  $\theta$  and  $\alpha$  must be considered as parameters to be determined by experiment. In addition to the inherent limitations of a point-charge model, the angles  $\theta$  and  $\alpha$  will be affected by non-nearest neighbours,  $\pi$  bonding, asymmetric  $\sigma$  bonding, *etc.* The values of  $\theta$  and  $\alpha$  obtained from the crystal structure of [Ni(en)<sub>3</sub>][NO<sub>3</sub>]<sub>2</sub> are 57.18 and 26.34° respectively, and it might be expected that the magnetic anisotropy would at least reflect the sign of the distortions present in the molecule. The magnetic susceptibility is also a function of the radial parameters  $\rho_2$  and  $\rho_4$ , the interelectron repulsion parameters  $F_2$  and  $F_4$ , the spin-orbit coupling parameter  $\zeta$ , and the orbital-reduction parameter  $k$ . Rather than attempting to fit the results to all eight

<sup>6</sup> W. E. Gardner and T. F. Smith, *Progr. Vac. Microbalance Tech.*, 1972, **1**, 155.

<sup>7</sup> K. S. Krishnan and S. Banerjee, *Phil. Trans.*, 1935, **A234**, 265.

<sup>8</sup> A. Earnshaw, 'Introduction to Magnetochemistry,' Academic Press, New York, 1968.

parameters, the values of  $\rho_4$ ,  $F_2$ , and  $F_4$  were obtained from the spectrum reported by Dingle and Palmer.<sup>9</sup> The values used were  $\rho_4 = 7\,000\text{ cm}^{-1}$ ,  $F_2 = 1\,350\text{ cm}^{-1}$ , and  $F_4 = 70\text{ cm}^{-1}$ , but the calculated magnetic moments were little

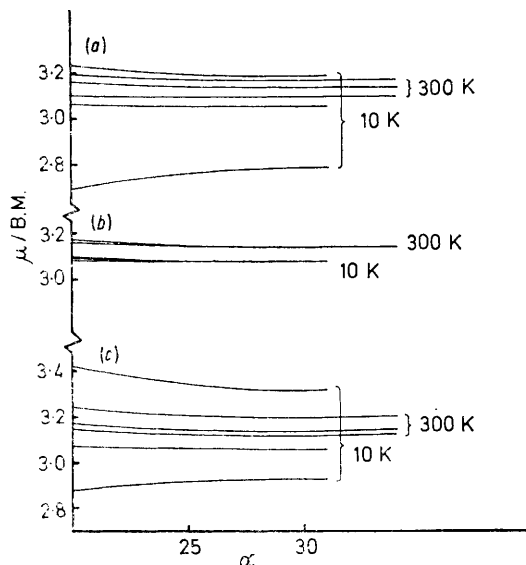


FIGURE 1 Variations of  $\mu_{\parallel}$ ,  $\mu_{\perp}$ , and  $\bar{\mu}$  with  $\alpha$  for  $F_2 = 1\,350\text{ cm}^{-1}$ ,  $F_4 = 70\text{ cm}^{-1}$ ,  $\rho_2 = 15\,000\text{ cm}^{-1}$ ,  $\rho_4 = 7\,000\text{ cm}^{-1}$ ,  $\zeta = 500\text{ cm}^{-1}$ , and  $k = 1.0$ : (a)  $\theta = 53^\circ$ ,  $\chi_{\perp} > \chi_{\parallel}$ ; (b)  $\theta = 54.736^\circ$ ; (c)  $\theta = 57^\circ$ ,  $\chi_{\parallel} > \chi_{\perp}$

affected by small (10%) changes in  $F_2$  and  $F_4$  provided  $F_2 - 5F_4$  was kept constant. Simple calculations<sup>10,11</sup> indicate that  $\rho_2 > \rho_4$  and in the present work  $\rho_2$  was varied from 7 000 to 30 000  $\text{cm}^{-1}$ .

The most surprising result to arise from the present work is that for  $20^\circ < \alpha < 30^\circ$  there was little variation in the calculated magnetic susceptibilities for reasonable values of the other parameters. In Figure 1 it can be seen that even for  $\alpha = 20^\circ$  the anisotropy at 10 K is only 0.01 B.M. for  $\theta = \theta_{\text{oct.}}$ . In the presence of either a trigonal elongation or compression, the change in anisotropy at 10 K with  $\alpha$  was more marked, but it is still very small compared with similar changes in  $\theta$ . At 300 K the change in anisotropy with  $\alpha$  was negligible although  $\bar{\mu}$  increased as the octahedron was twisted. Since  $\alpha$  appears only in the fourth-order part of the crystal-field potential, it might be anticipated that the magnetic anisotropy would be dominated by the  $Y_2^0$  spherical harmonic in the potential. For small distortions, as in the present case, this is found to be true since the anisotropy is independent of  $\rho_2$  (within 0.5%) for  $7\,000 < \rho_2 < 30\,000\text{ cm}^{-1}$  provided that  $\rho_2(3 \cos^2\theta - 1)$  remains constant. This result has been found before in the rare-earth antipyrene iodides and is best illustrated in the cerium compound.<sup>11</sup> In the present case, the phenomenon was much more pronounced and is probably due to the larger values of  $\rho_2$  and the absence of sixth-order terms in the crystal-field potential. The crystal field can therefore be described by  $A_2^0\langle r^2 \rangle$ ,  $\rho_4$ , and  $\alpha$  where  $A_2^0\langle r^2 \rangle = \frac{5}{2}\rho_2 - (3 \cos^2\theta - 1)$ .<sup>11</sup> Since  $\alpha$  is relatively unimportant, it was

set at  $25^\circ$  and the number of crystal-field variables was reduced to one since  $\rho_4$  was taken to be  $7\,000\text{ cm}^{-1}$ .

When the calculated anisotropy was plotted against  $\theta$  for various values of  $\rho_2$  and  $\zeta$ , it was found that  $\chi_{\parallel}$  was always greater than  $\chi_{\perp}$  for  $\theta > \theta_{\text{oct.}}$  and the experimental anisotropy was therefore due to a trigonal compression as is found in the crystal structure. The value of  $\bar{\mu}$  was independent of  $A_2^0\langle r^2 \rangle$  for small distortions but was dependent on  $\zeta$ . For distortions of a few degrees  $\Delta\chi$  was proportional to  $\theta - \theta_{\text{oct.}}$  for a wide range of values of  $\rho_2$ ,  $\zeta$ , and temperature, but the value of  $\theta$  required to fit the experimental anisotropies was independent of temperature only for  $\zeta = 400\text{ cm}^{-1}$ . For  $\zeta = 300\text{ cm}^{-1}$  the experimental values of  $\Delta\chi$  at 300 and 50 K could only be reproduced by a 16% increase in  $A_2^0\langle r^2 \rangle$  as the temperature was decreased. For  $\zeta = 500\text{ cm}^{-1}$ , a decrease of ca. 16% was needed. This value of  $\zeta$  agrees with that obtained<sup>12</sup> for  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  and also reproduces the experimental value of  $\bar{\mu}$  for  $50 < T < 300\text{ K}$ . The corresponding value of  $A_2^0\langle r^2 \rangle$  was  $-630\text{ cm}^{-1}$  and the excellent agreement between theory and experiment for  $T > 50\text{ K}$  is shown in Figures 2 and 3. A comparable fit could also be obtained using  $\alpha = 22.5^\circ$  and  $A_2^0\langle r^2 \rangle = -600\text{ cm}^{-1}$ .

The ground state of the nickel ion in  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  is formally a spin triplet with a small amount of orbital contribution due to spin-orbit mixing with higher states, and the magnetic moment is increased to ca. 0.25 B.M. above the spin-only value. In this case both  $\bar{\mu}$  and  $\Delta\chi$  decrease monotonically with decreasing  $k$  and the experimental

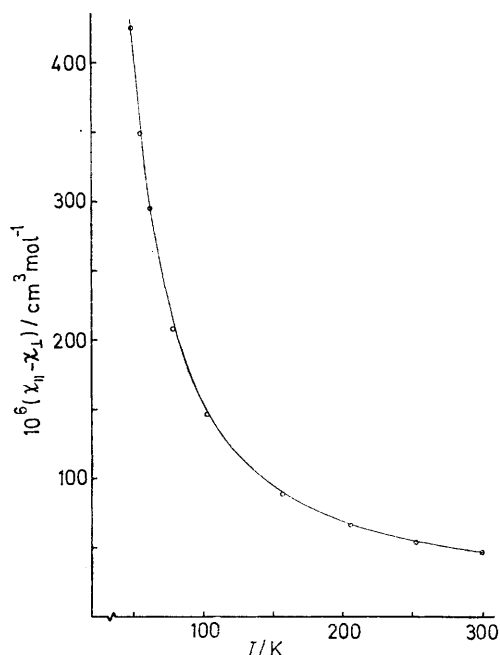


FIGURE 2 Calculated anisotropy for  $F_2 = 1\,350\text{ cm}^{-1}$ ,  $F_4 = 70\text{ cm}^{-1}$ ,  $\rho_4 = 7\,000\text{ cm}^{-1}$ ,  $A_2^0\langle r^2 \rangle = -630\text{ cm}^{-1}$ ,  $\zeta = 400\text{ cm}^{-1}$ ,  $\alpha = 25^\circ$ , and  $k = 1.0$ . Experimental points are given as open circles

results would then require a small increase in the absolute values of  $(\zeta/\rho_4)$  and  $A_2^0\langle r^2 \rangle$ . There is no simple interpretation of the parameter  $k$ ,<sup>13</sup> and since a good fit was obtained with reasonable values of  $\zeta$  and  $\rho_4$  and the ligand is not  $\pi$  bonded the value of  $k$  was left as 1.0.

<sup>12</sup> C. J. Ballhausen and A. D. Liehr, *Mol. Phys.*, 1959, **2**, 123.

<sup>13</sup> M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

<sup>9</sup> R. Dingle and R. A. Palmer, *Theor. Chim. Acta*, 1966, **6**, 249.

<sup>10</sup> M. Gerloch, J. Lewis, G. G. Phillips, and P. N. Quedsted, *J. Chem. Soc. (A)*, 1970, 1941.

<sup>11</sup> M. Gerloch and D. J. Mackey, *J. Chem. Soc. (A)*, 1970, 3040.

Using the parameters above, the zero-field splitting ( $D$ ) is calculated to be  $-0.65 \text{ cm}^{-1}$  ( $D$  is defined as positive when the singlet level is lowest). This agrees with the work of

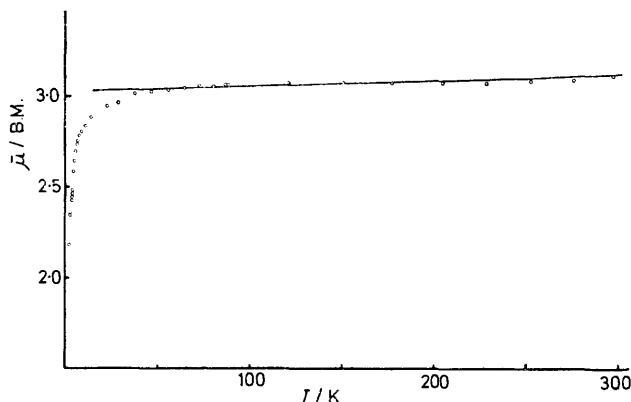


FIGURE 3 Calculated average magnetic moment for  $F_2 = 1350 \text{ cm}^{-1}$ ,  $F_4 = 70 \text{ cm}^{-1}$ ,  $\rho_4 = 7000 \text{ cm}^{-1}$ ,  $A_2^0\langle r^2 \rangle = -630 \text{ cm}^{-1}$ ,  $\zeta = 400 \text{ cm}^{-1}$ ,  $\alpha = 25^\circ$ , and  $h = 1.0$ . Experimental points are given as open circles

Carlin and his co-workers<sup>14</sup> who found that  $|D| < 1.3 \text{ cm}^{-1}$  at 14 K. Calculations of the magnetization from 2 to 20 K and 10 to 50 kG indicate that a zero-field splitting of  $-0.65 \text{ cm}^{-1}$  should have little effect and that  $\bar{\mu}$  should be a simple function of  $H/T$  as is observed<sup>15</sup> in  $[\text{Ni}(\text{en})_3][\text{SO}_4]$ . The large discrepancy between theory and experiment is shown in Figure 4. The magnetization calculations also indicate that  $\bar{\mu}$  (at 10 kG) should change very little between 5 and 50 K in marked contrast to the experimental results. These results, together with the increasing discrepancy between observed and calculated values of  $\Delta\chi$  as the temperature is decreased from 50 K (Figure 5), are taken as indirect evidence of the antiferromagnetism reported previously.<sup>14</sup>

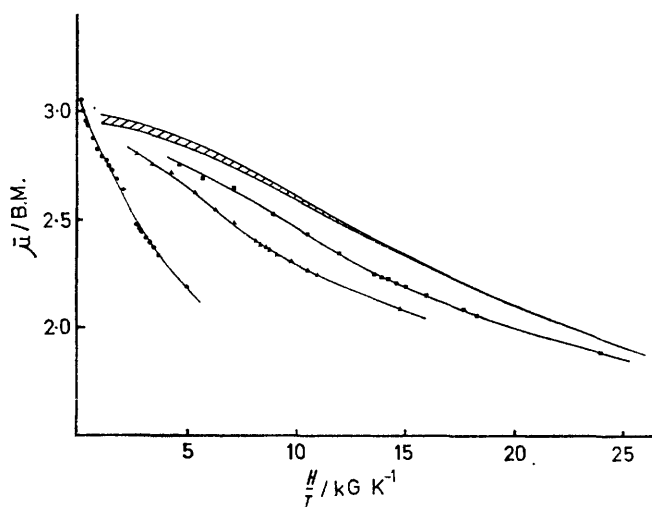


FIGURE 4 Experimental magnetization curves at 10 (●), 30 (▲), and 50 kG (■). The upper curves give the range of calculated moments for  $g_{\parallel} = g_{\perp} = 2.12$  and  $0 \leq D \leq 1 \text{ cm}^{-1}$  (doublet level lowest)

The magnetization curves in Figure 4 could be explained by a value of  $|D| \gg 0.65 \text{ cm}^{-1}$  and it could be argued that at

low temperatures the distortion of the nickel ion is increased. If this were true, then the calculated anisotropy (for  $D = -0.65 \text{ cm}^{-1}$ ) would be much smaller than the experimental values at low temperature. From Figure 5 it is seen that the reverse is true and hence it is presumed that  $D$  does not increase below 14 K.

The magnetization calculations show that the value of  $\bar{\mu}$

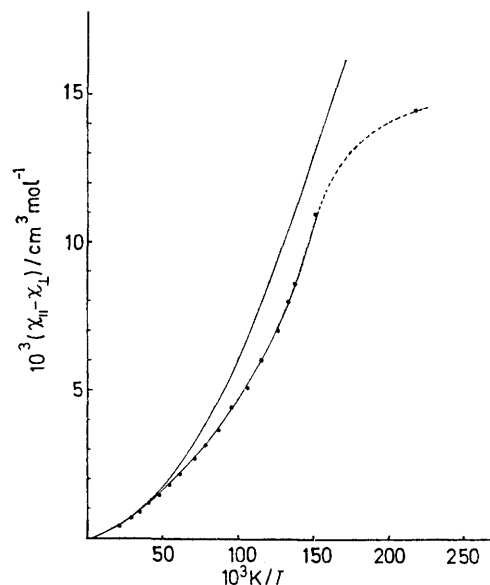


FIGURE 5 Upper curve, calculated anisotropy for  $F_2 = 1350 \text{ cm}^{-1}$ ,  $F_4 = 70 \text{ cm}^{-1}$ ,  $\rho_4 = 7000 \text{ cm}^{-1}$ ,  $A_2^0\langle r^2 \rangle = -630 \text{ cm}^{-1}$ ,  $\zeta = 400 \text{ cm}^{-1}$ ,  $\alpha = 25^\circ$ , and  $h = 1.0$ ; lower curve, experimental values

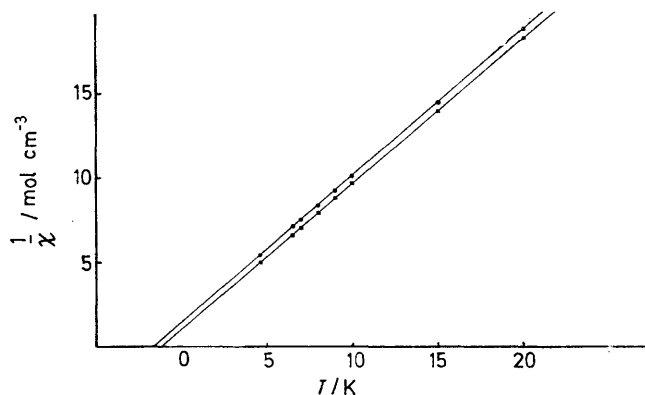


FIGURE 6 Experimental values of reciprocal susceptibility parallel (■) and perpendicular (●) to the  $c$  axis ( $\chi_{\parallel} > \chi_{\perp}$ )

( $H \rightarrow 0$ ) is within 0.01 B.M. of  $\bar{\mu}$  ( $H = 10 \text{ kG}$ ) above 6.5 K and is only 0.04 B.M. larger at 2 K. The anisotropy at low temperatures was measured at 850 G and hence the relation (1) is valid in the present case provided that the value of  $\bar{\chi}$

$$3\bar{\chi} = \chi_{\parallel} + 2\chi_{\perp} \quad (1)$$

<sup>14</sup> A. J. Van Duyneveldt, A. Van der Bilt, J. P. C. Vreugdenhil, and R. L. Carlin, *Chem. Phys. Letters*, 1974, **26**, 100.

<sup>15</sup> D. J. Mackey and S. V. Evans, unpublished work.

(4.58 K) is corrected for the slight effect of magnetization. Figure 6 shows a plot of temperature against reciprocal susceptibility parallel and perpendicular to the  $c$  axis. The parallel Weiss constant (1.2 K) is in good agreement with the value of the parallel Néel temperature (1.30 K) obtained by Carlin and his co-workers.<sup>14</sup> Using the relation  $\bar{\mu} = 2.828[\chi(T + 1.8)]^{1/2}$  the average moment is found to be  $3.08 \pm 0.02$  B.M. for the range  $4.2 < T < 300$ . A full discussion of the magnetization of  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  in the presence of a zero-field splitting and an antiferromagnetic interaction will be left to a future paper.

**Conclusions.**—It was hoped that the point-charge model would enable us to separate the radial and angular parts of the crystal-field potential and, in particular, to obtain an estimate of  $\rho_2$  independent of site symmetry thus leading to a 'spectrochemical series' based on second-order radial parameters.<sup>16</sup> This may not be possible in general since for  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$  the calculated magnetic susceptibilities, zero-field splittings, and  $g$  values are identical for  $A_2^0 \langle r^2 \rangle = -630 \text{ cm}^{-1}$  and  $7\,000 < \rho_2 < 30\,000 \text{ cm}^{-1}$ . On the other hand, the present model provides more insight into the relative importance of the two types of trigonal distortion than a model parameterized in terms of various free-ion matrix elements or coefficients of spherical harmonics. The relative insensitivity to a trigonal twist seems reasonable since  $\alpha$  does not occur in the  $Y_2^m$  part of the crystal-field potential and occurs only as an off-diagonal contribution to the matrix elements of  $Y_4^m$ . This is equivalent to a second-order contribution to the trigonal splittings as has been discussed by Schäffer,<sup>17</sup> and suggests that  $\alpha$  should be relatively unimportant for any electronic configuration. The results of Davis and Wood<sup>3</sup> on  $[\text{Ti}(\text{urea})_6]^{3+}$  and Figgis and Wadley<sup>4,5</sup> on  $[\text{Ti}(\text{urea})_6]^{3+}$  and  $[\text{V}(\text{urea})_6]^{3+}$  are not in agreement with this hypothesis but there are a number of shortcomings in these investigations. Davis and Wood measured only average susceptibilities while Figgis and Wadley used a model based on a perturbation of the ground-state orbital triplet ( $O_h$ ) term. The latter model, apart from the limitations imposed by a restricted basis set, would be seriously in error for the large splittings found in the urea complexes. Even a splitting of  $50 \text{ cm}^{-1}$  in excited states can lead to large discrepancies between simple perturbation theory and a complete calculation, as has been shown in magnetic studies of  $\text{Cs}_2[\text{UCl}_6]$ .<sup>18</sup> There are also numerical errors in the crystal-field potential and in the matrix elements given in the appendices of refs. 4 and 5 so that the reported agreement between the simple model and a more complete crystal-field treatment would seem to be fortuitous.

#### APPENDIX

In general, a crystal field of  $D_3$  symmetry contains imaginary terms but by choosing the  $z$  axis along the three-fold axis and the  $y$  axis along a two-fold axis the potential becomes real. In a point-charge crystal-field calculation the six point-charge ligands have the following co-ordinates:

<sup>16</sup> M. Gerloch and R. C. Slade, 'Ligand Field Parameters,' Cambridge University Press, 1973.

<sup>17</sup> C. E. Schäffer, *Proc. Roy. Soc.*, 1967, **A297**, 96.

<sup>18</sup> B. N. Figgis and D. J. Mackey, *Austral. J. Chem.*, 1974, **27**, 2053.

<sup>19</sup> H. Eyring, J. Walter, and G. E. Kimball, 'Quantum Chemistry,' John Wiley, 1967, p. 371.

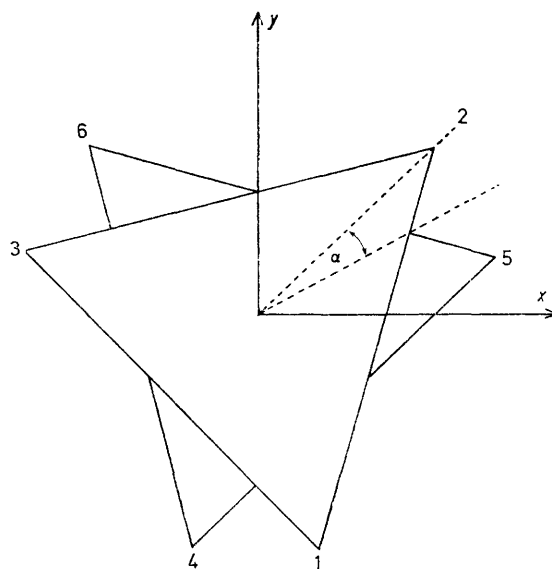


FIGURE 7 Definition of axes in  $D_3$  symmetry. The axes form a right-handed set

Point	$\theta_i$	$\phi_i$
1	0	$\frac{3\pi}{2} + \alpha$
2	$\theta$	$\frac{\pi}{6} + \alpha$
3	$\theta$	$\frac{5\pi}{6} + \alpha$
4	$\pi - \theta$	$\frac{3\pi}{2} - \alpha$
5	$\pi - \theta$	$\frac{\pi}{6} - \alpha$
6	$\pi - \theta$	$\frac{5\pi}{6} - \alpha$

Substituting in<sup>19</sup> equation (A1) and using  $V_{D_3} = \sum_{l=1}^k \frac{e z}{r_{ij}^l}$

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \cdot \frac{r_{<}^l}{r_{>}^{l+1}} \cdot Y_l^m(\theta_j, \phi_j) \cdot Y_l^{m*}(\theta_i, \phi_i) \quad (\text{A1})$$

we obtain equation (A2) for  $d$  electrons.

$$V_{D_3} = \frac{ze\gamma <^2}{r >^3} \left[ \frac{24\pi}{5} \cdot \left( \frac{5}{16\pi} \right)^{\frac{1}{2}} \cdot (3 \cos^2\theta - 1) Y_2^0 \right] \\ + \frac{ze\gamma <^4}{r >^6} \left[ \frac{24\pi}{9} \cdot \left( \frac{9}{256\pi} \right)^{\frac{1}{2}} \cdot [35 \cos^4\theta - 30 \cos^2\theta + 3] Y_4^0 \right. \\ \left. + \frac{24\pi}{9} \cdot \left( \frac{315}{64\pi} \right)^{\frac{1}{2}} \cdot \sin^2\theta \cos\theta \sin 3\alpha (Y_4^3 - Y_4^{-3}) \right] \quad (\text{A2})$$

If the axes are rotated around the  $z$  axis by  $\frac{\pi}{3}$ , the coefficient of  $(Y_4^3 - Y_4^{-3})$  changes sign. This latter potential then reduces to the form given by Davis and Wood<sup>3</sup> when  $\theta = \theta_{\text{oct}}$ . The potential is identical to that for  $D_{3d}$  symmetry<sup>10</sup> except for the factor  $\sin 3\alpha$ . For octahedral symmetry  $\theta_{\text{oct}} = \cos^{-1}(1/3)^{\frac{1}{2}} = 54.736^\circ$  and  $\alpha = 30^\circ$ . The two radial parameters  $\rho_2$  and  $\rho_4$  are defined as<sup>10,11</sup> in equation (A3) and are related to  $Dq$  and  $Cp$  by  $Dq = \frac{1}{6}\rho_4$  and  $Cp = \frac{2}{7}\rho_2$ . It is easy to show that  $G_2 \geq G_4$  and hence  $\rho_2 \geq \rho_4$ .

$$\rho_n = ze^2 G_n \text{ where } G_n = \int_0^\infty R^2(3d) \frac{r <^n}{r >^{n+1}} r^2 dr \quad (\text{A3})$$

The calculations were made by diagonalizing the complete  $45 \times 45$  matrix using a general computer program.<sup>20,21</sup> It should be noted that the equation for the matrix elements of spin-orbit coupling given in ref. 18 has a misprint; the

<sup>20</sup> D. J. Mackey, W. A. Runciman, and E. R. Vance, *Phys. Rev.*, 1975, **B11**, 211.

<sup>21</sup> M. Gerloch and D. J. Mackey, *J. Chem. Soc. (A)*, 1971, 2605.

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.<sup>22</sup>

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<sup>22</sup> A. Vermaas and W. L. Groenveld, *Chem. Phys. Letters*, 1974, **27**, 583.

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