# Low-temperature Magnetic Studies of a Linear Trimeric Nickel Compound: *abcjkl*-Hexa-aqua-*def;ghi*-hexakis[$\mu$-1,2,4-triazole-$N^1N^2$]-trinickel(II) Hexanitrate Dihydrate

By **Denis J. Mackey** * and **Raymond L. Martin**, Research School of Chemistry, Australian National University, P.O. Box No. 4, Canberra, Australia 2600

Magnetic studies of the title compound show that the trimer has an $S = 1$ ground state with a negligible zero-field splitting (z.f.s.). The magnetic moment can be fitted to two sets of parameters: (*a*) $g = 2.069$, $J = 7.58$ cm$^{-1}$, $J_{31} = -24.59$ cm$^{-1}$, and $N\alpha = 2.46 \times 10^{-9}$ m$^3$ mol$^{-1}$; and (*b*) $g = 2.048$, $J = -8.78$ cm$^{-1}$, $J_{31} = 4.87$ cm$^{-1}$, and $N\alpha = 2.49 \times 10^{-9}$ m$^3$ mol$^{-1}$ where $J$ and $J_{31}$ refer to the exchange constants between adjacent and terminal nickel ions respectively. The second set of parameters seems intuitively more reasonable and the small z.f.s. and $g$ value in this case can be rationalized in terms of the composition of the triplet ground state.

THE interpretation of magnetic-exchange interaction in polynuclear transition-metal complexes is greatly facilitated if the ground state of the individual metal ions is orbitally non-degenerate. This is the case for octahedrally co-ordinated Ni$^{II}$ since the ground state in $O_h$ symmetry is $^3A_{2g}$. If the symmetry is lowered, the three-fold degeneracy of the state is removed by second-order spin–orbit coupling producing a doublet and a singlet in axial symmetry and three singlets in rhombic or lower symmetry. This zero-field splitting (z.f.s.) is generally in the range 0—2 cm$^{-1}$,[1,2] although values up to 5 cm$^{-1}$ are known.[3-5] No other energy levels are thermally accessible at ordinary temperatures and the $g$ values of the ground-state manifold are usually isotropic to better than 1%.[1] If the magnetic-exchange interactions are much larger than any zero-field splittings then the susceptibility of an individual ion is primarily determined by an approximately isotropic $g$ value and a small second-order Zeeman term ($N\alpha$) which is only important at high temperatures. The magnetic susceptibility of the complete cluster then depends only on the appropriate exchange integrals and the values of $g$ and $N\alpha$ for the individual ions. In the case of a linear trimer an analytical expression for the magnetic susceptibility can be readily calculated if one assumes that the values of $g$ and $N\alpha$ are the same for all the individual ions and that zero-field splittings are negligible. The magnetic susceptibility per nickel ion is given by (1) where $x = J/\boldsymbol{k}T$, $y = J_{31}/\boldsymbol{k}T$, and $K = g^2N\beta^2/3\boldsymbol{k}$. This equation was originally derived by Ginsberg *et al.*[6] and was used to interpret the magnetism of [Ni$_3$(pd)$_6$] (pd = pentane-2,4-dionate). The equation given in ref. 6 is incorrect although the results obtained were calculated from the correct expression.

$$\chi_{\mathrm{Ni}} = \frac{2\mu_0K}{3T}\left[\frac{42\mathrm{e}^{2(2x+y)} + 15\mathrm{e}^{2(y-x)} + 15\mathrm{e}^{2(x-y)} + 3\mathrm{e}^{2(y-3x)} + 3\mathrm{e}^{-2(x+y)} + 3\mathrm{e}^{-4y}}{7\mathrm{e}^{2(2x+y)} + 5\mathrm{e}^{2(y-x)} + 5\mathrm{e}^{2(x-y)} + 3\mathrm{e}^{2(y-3x)} + 3\mathrm{e}^{-2(x+y)} + 3\mathrm{e}^{-4y} + \mathrm{e}^{-2(2x+y)}}\right] + N\alpha \qquad (1)$$

The Hamiltonian used for calculating the magnetic susceptibility in equation (1) is (2)

$$\mathscr{H} = -2J[(\boldsymbol{S}_1\cdot\boldsymbol{S}_2) + (\boldsymbol{S}_2\cdot\boldsymbol{S}_3)] - 2J_{31}(\boldsymbol{S}_3\cdot\boldsymbol{S}_1) \qquad (2)$$

where the subscripts refer to the individual nickel ions which are numbered sequentially.

In [Ni$_3$(pd)$_6$] adjacent nickel atoms are ferromagnetically coupled while the terminal nickel atoms are antiferromagnetically coupled. The trimeric cluster has an $S' = 3$ ground state but at low temperatures the experimental magnetic susceptibility is much less than the calculated value and this was originally interpreted as being due to antiferromagnetic interaction between clusters. However, recent work has indicated that it is due to an appreciable zero-field splitting of the $S' = 3$ ground state.[7]

---

[1] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon, Oxford, 1970, p. 499.

[2] J. Reedijk and B. Nieuwenhuijse, *Rec. Trav. chim.*, 1972, **91**, 553.

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

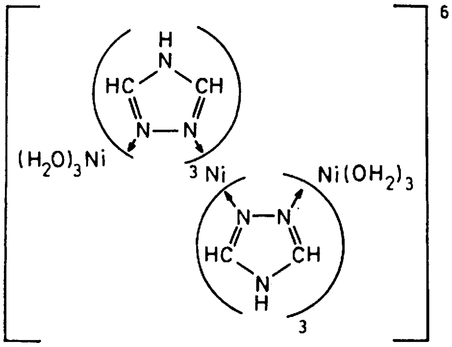
[4] D. J. Mackey, *J.C.S. Dalton*, 1977, 40.

[5] R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Amer. Chem. Soc.*, 1976, **98**, 3523.

[6] A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 1968, **7**, 932.

[7] P. D. W. Boyd and R. L. Martin, *J.C.S. Dalton*, in the press.

Unlike $[Ni_3(pd)_6]$ the complex *abcjkl*-hexa-aqua-*def*;*ghi*-hexakis[μ-1,2,4-triazole-$N^1N^2$]-trinickel(II) hexanitrate dihydrate, $[Ni\{Ni(N_3C_2H_3)_3(OH_2)_3\}_2][NO_3]_6\cdot 2H_2O$ (1), contains discrete centrosymmetric trinuclear cations so that the outer nickel atoms are equivalent by symmetry.[8] The magnetic susceptibility and e.s.r. spectrum of compound (1) were studied in order to investigate the ground state of the trinuclear ion and also to see whether the interpretation of the magnetic exchange was complicated by zero-field splitting. An interesting feature of a linear trimeric cluster of nickel ions is that the ground state is always paramagnetic when $J$ is positive while when $J$ is negative the ground state is diamagnetic only for $0.5 < J_{31}/J < 2$. Consequently, the ground state can often be investigated by e.s.r. and magnetization studies. Following ref. 6, the components of the trimer ground-state manifold will be labelled as $S'$ and $S^*$ where $S'$ is the total spin of the state and $S^*$ the total spin of the two terminal nickel ions.



(1)

## EXPERIMENTAL

Compound (1) was prepared as reported in the literature,[8] but the product was contaminated by a very fine pink compound which was completely insoluble in water and slowly precipitated from an aqueous solution of (1). The pink compound analyzed as $Ni_2L_7(NO_3)_4\cdot 3H_2O$ (L = 1,2,4-triazole). The formation of this material could be suppressed by the addition of nickel ions and large polycrystalline lumps of (1) were prepared by recrystallization of the crude material from an aqueous solution containing a 20% excess of $Ni^{2+}$ as the nitrate salt.

The average magnetic susceptibility was measured down to 2 K at magnetic field strengths from 1 to 5 T using equipment described previously.[9] The magnetization was calculated using a program written by Dr. P. D. W. Boyd and based on the equation of Vermaas and Groenveld.[10]

## RESULTS AND DISCUSSION

The temperature variation of the magnetic moment per nickel ion in (1) is shown in Figure 1 and indicates that the ground state of the trimeric cluster has $S' = 1$ with all the other levels being effectively depopulated at 10 K. From Figure 2 of ref. 6 this corresponds to either $J_{31}/J < -1.0$ ($J$ is positive) or $J_{31}/J < 0.5$ ($J$ is negative) and both these possibilities were investigated using a least-squares program. The effects of intercluster exchange and zero field splitting of the $S' = 1$ state would be most pronounced at low temperature and hence the experimental data were only fitted at >10 K. The parameters obtained from the least-squares program (Table 1) were then used to calculate the magnetic moment down to 2 K. These values are also shown in Figure 1 and it can be seen that the two possible sets of $J$ values give similar results although the fit is marginally better for parameter set 2. Intuitively, one would expect that exchange interactions would be greater between adjacent nickel ions and hence that $|J| > |J_{31}|$. For parameter set 1, $|J_{31}| \sim 3|J|$ and it is considered that this fit is less reasonable although it cannot be excluded as a possibility.

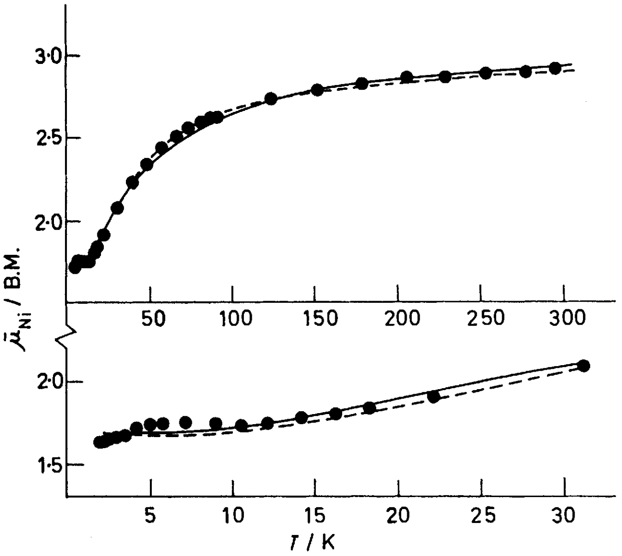


FIGURE 1 Average magnetic moment per nickel ion as a function of temperature. The calculated curves are for parameter set 1 (——) and 2 (– – – –) of Table 1; (●), experimental values

The magnetization of (1) from 2 to 20 K is shown in Figure 2 and it is apparent that at low temperatures the magnetic moment is a simple function of $H/T$. This implies that only one level is occupied and that the z.f.s. is negligible compared with the splitting produced by the applied magnetic field. The low-temperature results are in good agreement with those calculated on the

TABLE 1

Parameters used in fitting the magnetic moment of compound (1) between 300 and 10 K

| | Set 1 | Set 2 |
|---|---|---|
| $g$ | 2.069 | 2.048 |
| $J/\text{cm}^{-1}$ | 7.58 | −8.78 |
| $J_{31}/\text{cm}^{-1}$ | −24.59 | 4.87 |
| $N\alpha/\text{m}^3\ \text{mol}^{-1}$ | $2.46 \times 10^{-9}$ | $2.49 \times 10^{-9}$ |
| Standard deviation/B.M.* | 0.021 | 0.018 |

* 1 B.M. ≈ $9.27 \times 10^{-24}$ A m².

---

[8] C. W. Reimann and M. Zocchi, *Acta Cryst.*, 1971, **B27**, 682.

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

[10] A. Vermaas and W. L. Groenveld, *Chem. Phys. Letters*, 1974, **27**, 583.

assumption of an isolated state having $S' = 1$, $g = 2.05$, and essentially no z.f.s. The $g$ value for this lowest-lying level is in reasonable agreement with the values obtained from fitting the magnetic moment at higher temperatures (2.069 and 2.048 for parameters set 1 and 2 respectively). The e.s.r. spectrum of a polycrystalline sample of (1) increased dramatically in intensity at $<10$ K, and at 2.5 K a three-line spectrum was obtained which was in agreement with the lowest-lying triplet state having a z.f.s. which was comparable with the microwave quantum (*ca.* 0.3 cm$^{-1}$).

At $>10$ K the experimental magnetic moment is significantly higher than can be explained on the basis of an isolated spin triplet with $g = 2.05$, and is due to the presence of one or more low-lying states of higher spin multiplicity. From Table 1 of ref. 6 it is possible to calculate the energies of all the components of the trimer ground-state manifold and these are shown in Figure 3. The great similarity in energies of the lowest-lying states having the same total spin multiplicity accounts for the ambiguity in the description of the magnetic-exchange interactions. In both cases, there is a low-lying $S' = 2$ state at *ca.* 35 cm$^{-1}$ and it is this level which causes the experimental magnetic moment to increase at $>10$ K as it became populated.

In the foregoing discussion it has been assumed that the zero-field splittings of the three-nickel ions were negligible and that their $g$ values were the same. Although the $g$ value of the ground-state $S' = 1$ level appears to be the same as that obtained from the high-temperature fit to the magnetic moment, the $g$ value seems anomalously low. For example, the related ions $[Ni(pyrazole)_6]^{2+}$, $[Ni(imidazole)_6]^{2+}$, and $[Ni(OH_2)_6]^{2+}$ have $g$ values of 2.19,[2] 2.20,[2] and 2.25 [1] respectively.[1] A more probable explanation of the small z.f.s. and the $g$ values of the ground state is that both are linear combinations of appropriate single-ion values. It is possible to set up the complete $27 \times 27$ matrix for the trimer ground-state manifold and also to obtain effective $g$ values and z.f.s. for each state in terms of the single-ion values.[7] It was assumed that the trimer had axial symmetry, and within the limits of the present discussion this seems justified from the $X$-ray structure determination.[8] The z.f.s. of an $S' = 1$ state is then equal to $D$ where the splitting is produced by the operator $DS_z^2$ acting within the triplet state. The analytical expressions are given in Table 2 for the two possible ground states (1, 0) and (1, 2). If the ground state is (1, 0) then the $g$ value should be the same as that of the central metal ion and, by analogy with the pyrazole and imidazole compounds mentioned previously, one would expect a value of *ca.* 2.2 and not 2.05. Although there is only a slight distortion of the central nickel ion and hence the possibility of a small z.f.s., a more likely explanation is that the ground state is (1, 2) since the small z.f.s. could then arise from a partial cancellation of much larger zero-field splittings of the opposite sign for the central and terminal nickel ions. Similarly, the small $g$ value could occur if the $g$ values of the central and terminal nickel ions were much greater than 2.05 but with the value for the central being the larger.

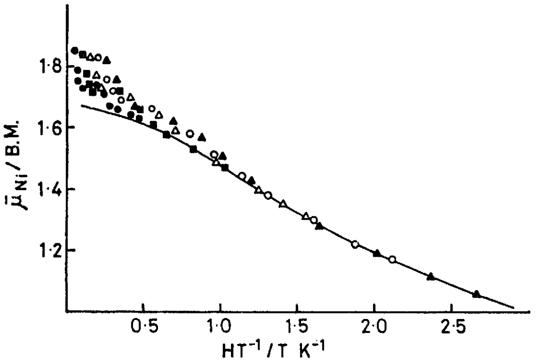


FIGURE 2 Experimental values of the magnetic moment per nickel ion at field strengths of 1 (●), 2 (■), 3 (△), 4 (○), and 5 T (▲). The curve is calculated for an isolated triplet state having $g = 2.05$ and no z.f.s.

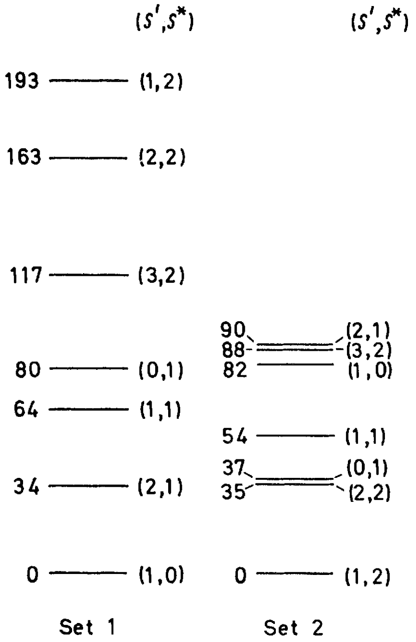


FIGURE 3 Calculated energies (cm$^{-1}$) of the ground-state manifold of compound (1) using the parameters given in Table 1. The labels $S'$ and $S^*$ refer to the total spin of the state and the total spin of the two terminal nickel ions respectively

TABLE 2

Ground-state $g$ values and zero-field splittings expressed as linear combinations of the single-ion values. Axial symmetry is assumed and the letters in parentheses refer to terminal (T) or central (C) ions

| Ground state | (1, 0) | (1, 2) |
|---|---|---|
| $g$ | $g$ (C) | $\frac{3}{2}g$ (T) $- \frac{1}{2}g$ (C) |
| $D$ | $D$ (C) | $\frac{7}{10}D$ (T) $+ \frac{1}{10}D$ (C) |

We thank Dr. P. D. W. Boyd for many fruitful discussions and for supplying data on the complete trimer calculations prior to publication, and Dr. R. Bramley for recording the e.s.r. spectrum.

[7/866 *Received*, 17*th May*, 1977]