Spin–Spin Interactions in Polynuclear Nickel(II) Complexes: Susceptibility and Low-temperature Magnetisation Studies of Tris[bis(pentane-2,4-dionato)nickel(II)]

By **Peter D. W. Boyd** * and **Raymond L. Martin**, Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T., Australia 2600

The magnetic susceptibility and magnetisation of the trinuclear complex $[Ni_3(pd)_6]$ (pd = pentane-2,4-dionate) have been reinvestigated in the range 1.8—300 K. Detailed magnetisation studies have been performed to low temperatures to evaluate the properties of the septet ($S = 3$) ground state of the molecule. The results have been analysed in terms of the Heisenberg–Dirac–Van Vleck isotropic exchange Hamiltonian including contributions from single-ion zero-field splittings. Ferromagnetic coupling between adjacent ions is confirmed, although the magnitude of both this interaction and the antiferromagnetic interaction between the terminal ions is found to be half that previously reported. This diminution is due to the effect of zero-field splitting on the low-temperature magnetic properties, the ground-state septet ($S = 3$) having a splitting of -1.3 cm^{-1}.

THE linear trinuclear molecule $[Ni_3(pd)_6]$ (pd = pentane-2,4-dionate) has been characterised both structurally and magnetically.[1,2] Particular interest was aroused by the discovery of a ferromagnetic intramolecular interaction between adjacent nickel(II) ions leading to a spin septet ($S = 3$) ground state for the trinuclear molecule. The co-ordination about each nickel ion is approximately octahedral, the trimer being formed by three neighbouring NiO_6 octahedra sharing faces. The two pentane-2,4-dionate ions which chelate the central nickel atom simultaneously bridge the pair of terminal nickel atoms. On the other hand, one of the two pd ions which chelate each terminal nickel atom also functions as a bridge to the central nickel atom. Paths for intramolecular superexchange are thereby provided.[2]

Previously,[2] a sharp decrease in the magnetic moment (μ) at <4.3 K was noted but not investigated in detail. It was suggested that this decrease was due to small zero-field splitting within the septet state or to a weak lattice antiferromagnetic interaction. We have reinvestigated the susceptibility and low-temperature magnetisation of this model complex with a view to seeking a more complete understanding of the lower spin manifolds, especially the septet ground state. In conjunction with this study, a more complete theoretical model has been developed of the magnetic properties of linear trimeric nickel(II) complexes at low temperatures and high magnetic fields.

THEORY

The single-ion ground states of six-co-ordinate nickel(II) ions are orbital singlets.[3] The isotropic exchange interaction between the metal ions in a linear trimer may be described [4,5] by the Heisenberg–Dirac–Van Vleck exchange Hamiltonian (1) where S_a, S_b are terminal ion spins and S_c

$$\mathscr{H}_{\mathrm{EXC}} = J[S_a \cdot S_c + S_b \cdot S_c] + J_{ab}S_a \cdot S_b \qquad (1)$$

that of the central metal ion. We have followed the suggestion of Griffith [6] of using $+JS_1 \cdot S_2$ for the isotropic exchange interaction instead of $-JS_1 \cdot S_2$ or $-2JS_1 \cdot S_2$ for simplicity. In the calculation of the magnetic properties of linear trimers that follows, we have neglected biquadratic exchange terms,[7] anisotropic exchange terms,[8] magnetic dipole–dipole interactions,[9] and asymmetric exchange terms.[10] All these interaction terms are expected to be small in the molecule. The magnetic dipole–dipole interaction is estimated to be of the order of 0.1 cm^{-1}.[9] Anisotropic exchange terms for ions having orbitally non-degenerate states are of the order of $(\Delta g/g)^2J$ and antisymmetric terms of the order of $(\Delta g/g)J$.[11] Δg For nickel complexes is generally <0.01, for example in the case of $Na[Ni(pd)_3]$ to within experimental error the g value was found to be isotropic.[12] Thus for the trimer studied here we estimate an upper limit for these two interactions of 0.001 and 0.1 cm^{-1} respectively. Biquadratic terms are generally thought to be of the order of the antisymmetric exchange terms; [11] however, in the studies of polynuclear nickel(II) complexes so far reported it has not been found necessary to include such interaction terms.[13]

The spins of the metal atoms $S_a = S_b = S_c = 1$ couple to give states of total spin 3, 2, 2, 1, 1, 1, and 0. It is convenient to choose the coupling scheme in which the spins of the terminal atoms are first coupled to give the resultant S_{ab} which is further coupled with S_c to give the resulting total spin S of the trimer. The basis states of the trimer are thus $|(S_aS_b)S_{ab}S_cSM_s\rangle$, where M_s is the magnetic quantum number. The matrix elements of $\mathscr{H}_{\mathrm{EXC}}$ with respect to this basis may be conveniently evaluated using either irreducible tensor-operator formalism [6,14,15] or the method of Kambe which is equivalent in this coupling scheme.[2] The matrix elements are:

$$\langle S_{ab}S_cSM_s|J_{ab}S_a \cdot S_b|S_{ab}'S_cS'M_s'\rangle$$

$$= \delta_{ss'}\delta_{M_sM_s'}(-1)^{S_{ab}+2} \cdot 6 \begin{Bmatrix} 1 & 1 & 1 \\ 1 & 1 & S_{ab} \end{Bmatrix} J_{ab}$$

$$\langle S_{ab}S_cSM_s|JS_a \cdot S_c|S_{ab}'S_cS'M_s'\rangle$$

$$= \delta_{ss'}(-1)^{S_{ab}+S_{ab}'+S+4} \cdot 6[(2S_{ab}+1)(2S_{ab}'+1)]^{\frac{1}{2}} \begin{Bmatrix} S_{ab} & S_{ab}' & 1 \\ 1 & 1 & S \end{Bmatrix} \begin{Bmatrix} S_{ab} & S_{ab}' & 1 \\ 1 & 1 & 1 \end{Bmatrix} J$$

$$= \langle S_{ab}S_cS_sM|JS_bS_c|S_{ab}'S_cS'M_s'\rangle$$

It is worth noting that this coupling scheme gives only diagonal matrix elements in the exchange interaction whilst an alternative coupling scheme such as $|(S_aS_c)S_{ac}S_bSM_s\rangle$ would lead to off-diagonal matrix elements in the exchange interaction.[6]

Under the assumption of an isotropic Zeeman interaction, normally found in nickel(II) complexes, an expression for the magnetic susceptibility may be derived using the Van Vleck equation.[2] At lower temperatures and higher magnetic fields, the effect of single-ion zero-field splitting contributions within the various spin states, mixing of states *via* Zeeman matrix elements, and a breakdown of the Van Vleck approximation require the consideration of additional terms in the Hamiltonian as in (2) where $\mathscr{H}_{\mathrm{ZFS}}$ and $\mathscr{H}_{\mathrm{ZEE}}$ are the

$$\mathscr{H} = \mathscr{H}_{\mathrm{EXC}} + \mathscr{H}_{\mathrm{ZFS}} + \mathscr{H}_{\mathrm{ZEE}} \qquad (2)$$

where $\mathscr{H}_{\mathrm{ZFS}} =$

$$D_a[\boldsymbol{S}_{az^2} - \tfrac{1}{3}S_a(S_a + 1)] + D_a[\boldsymbol{S}_{bz^2} - \tfrac{1}{3}S_b(S_b + 1)] + D_c[\boldsymbol{S}_{cz^2} - \tfrac{1}{3}S_c(S_c + 1)]$$

and $\mathscr{H}_{\mathrm{ZEE}} = g_{a\parallel}(H_z\boldsymbol{S}_{az} + H_z\boldsymbol{S}_{bz}) + \boldsymbol{g}_{c\parallel}H_z\boldsymbol{S}_{cz} + g_{a\perp}(H_x\boldsymbol{S}_{ax} + H_y\boldsymbol{S}_{ay} + H_x\boldsymbol{S}_{bx} + H_y\boldsymbol{S}_{by}) + g_{c\perp}(H_x\boldsymbol{S}_{cx} + H_y\boldsymbol{S}_{cy})$

single-ion zero-field splitting and the Zeeman interaction terms. Axial symmetry about each nickel atom and alignment of the unique axes along the approximate three-fold axis of the linear trimer have been assumed.

The matrix elements of $\mathscr{H}_{\mathrm{ZFS}}$ and $\mathscr{H}_{\mathrm{ZEE}}$ are calculated to be:

$$\langle S_{ab}S_cSM_s|H_{\mathrm{ZFS}}|S_{ab}'S_cS'M_s'\rangle = [30(2S + 1)(2S' + 1)]^{\frac{1}{2}}\begin{pmatrix} S & S' & 2 \\ -M_s' & M_s & 0 \end{pmatrix} \times$$

$$\Big\{[(2S_{ab} + 1)(2S_{ab}' + 1)]^{\frac{1}{2}}\begin{Bmatrix} S & S' & 2 \\ S_{ab}' & S_{ab} & 1 \end{Bmatrix}\begin{Bmatrix} S_{ab} & S_{ab}' & 2 \\ 1 & 1 & 1 \end{Bmatrix} \times [D_a(-1)^{M_s+2S'+S_{ab}+S_{ab}'+9} + D_b(-1)^{M_s+2S+2S_{ab}'+9}] + \begin{Bmatrix} 1 & 1 & 2 \\ S & S' & S_{ab} \end{Bmatrix}[D_c(-1)^{M_s+S'+S+S_{ab}+3}]\Big\}/3$$

and $\langle S_{ab}S_cSM_s|\mathscr{H}_{\mathrm{ZEE}}|S_{ab}'S_cS'M_s'\rangle$

$$= (-1)^{M_s+S'+1}\begin{pmatrix} S & S' & 1 \\ -M_s & M_s' & 0 \end{pmatrix} \times \mathrm{RM}\,1 \times H_z$$

$$+ (-1)^{M_s+S'+1}\left[\begin{pmatrix} S & S' & 1 \\ -M_s & M_s' & -1 \end{pmatrix} - \begin{pmatrix} S & S' & 1 \\ -M_s & M_s' & 1 \end{pmatrix}\right] \times \mathrm{RM}\,2 \times H_x/2^{\frac{1}{2}}$$

$$+ (-1)^{M_s+S'+1}i\left[\begin{pmatrix} S & S' & 1 \\ -M_s & M_s' & -1 \end{pmatrix} + \begin{pmatrix} S & S' & 1 \\ -M_s & M_s' & 1 \end{pmatrix}\right] \times \mathrm{RM}\,2 \times H_y/2^{\frac{1}{2}}$$

$$\mathrm{RM}\,1 = \boldsymbol{g}_{a\parallel}[\langle S\|T_a^{(1)}\|S'\rangle + \langle S\|T_b^{(1)}\|S'\rangle] + \boldsymbol{g}_{c\parallel}\langle S\|T_c^{(1)}\|S'\rangle$$

$$\mathrm{RM}\,2 = \boldsymbol{g}_{a\perp}[\langle S\|T_a^{(1)}\|S'\rangle + \langle S\|T_b^{(1)}\|S'\rangle] + \boldsymbol{g}_{c\perp}\langle S\|T_c^{(1)}\|S'\rangle$$

In general, matrix elements in $\mathscr{H}_{\mathrm{ZEE}}$ and $\mathscr{H}_{\mathrm{ZFS}}$ will exist not only within total spin multiplets but between them. For the case of the linear trimer $[\mathrm{Ni}_3(\mathrm{pd})_6]$, the septet ground state has matrix elements within the $S = 3$ manifold that may be described by a spin Hamiltonian ($S' = 3$) of the

$$\mathscr{H} = \beta\boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S}' + D[\boldsymbol{S}'^2 - \tfrac{1}{3}S'(S' + 1)] \qquad (3)$$

$$\text{where } D = (2D_a + D_c)/15$$
$$g_x = g_y = (2\boldsymbol{g}_{a\perp} + \boldsymbol{g}_{c\perp})/3$$
$$g_z = (2\boldsymbol{g}_{\parallel} + \boldsymbol{g}_{c\parallel})/3$$

form (3). Further matrix elements connect components of the $S = 3$ state to several other multiplets.

Similarly, within a given spin manifold, spin Hamiltonians may be used to describe the properties of the multiplet. In the case of the next two highest states which will be considered here, namely $|(11)112M_s\rangle$ and $|(11)011M_s\rangle$, $D = (D_c - D_a)/3$, $g_x = g_y = (\boldsymbol{g}_{a\perp} + \boldsymbol{g}_{c\perp})/2)$, and $g_z = (\boldsymbol{g}_{c\parallel} + \boldsymbol{g}_{c\parallel})/2$, and $D = D_c$, $g_x = g_y = \boldsymbol{g}_{c\perp}$, and $g_z = \boldsymbol{g}_{c\parallel}$ respectively. Matrix elements connect components of these two states to other higher multiplets also. The form of the zero-field splitting within each multiplet is the same as that expected for magnetic dipole–dipole and anisotropic exchange interactions.

Powder average magnetisations are calculated using the basic thermodynamic formula (4).[16,17] The matrix including exchange interactions, Zeeman terms, and zero-field splitting terms was diagonalised to obtain E_{p} values and the derivatives were calculated using the Hellman–Feynman Theorem.[18,19] The integral was evaluated numerically. Figure 1 shows the effect of zero-field splitting on the bulk magnetisations at 2 K.

$$\bar{M} = \frac{-N}{4\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\{\Sigma[(\partial E_{\mathrm{p}}/\partial H)\exp(-E_{\mathrm{p}}/\boldsymbol{k}T)]/\Sigma\exp(-E_{\mathrm{p}}/\boldsymbol{k}T)\}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \qquad (4)$$

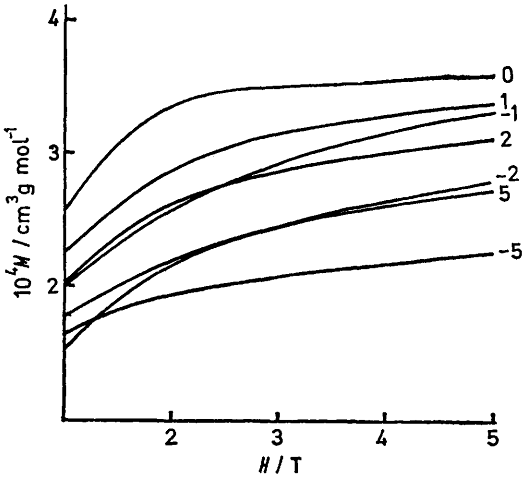

FIGURE 1 Effect of single-ion zero-field splitting on magnetisation, $\bar{M}$, at 2 K as a function of magnetic field for a linear nickel(II) trimer. The numbers on the curves are values of D/cm^{-1}

EXPERIMENTAL

The complex $[\mathrm{Ni}_3(\mathrm{pd})_6]$ was prepared as previously reported.[20] Susceptibility and magnetisation measurements were performed using a modified Oxford Instruments Faraday balance.[21] Susceptibility measurements were carried out in the temperature range 4.2—89 K at 1 T and from 89 to 300 K at 4 T. Magnetisations were determined in the range 1.8—19 K, in fields of 1—5T, in Vaseline mulls of the complex. It was necessary to use this mulling technique since strong magnetic and large anisotropies present in the powdered crystals lead to a partial orientation of the crystallites. The extent of this orientation presumably depends on the crystallite shape and size and the magnetic anisotropy of the individual crystals. The quantity of the complex present in the mull was found by a comparison of the low-field values of the magnetisation of the mull and the powdered sample. Typically, the comparison was performed at about eight temperatures in the range 4—20 K. The estimated error in the magnetisation measured in this way is $< 1\%$ based on a comparison of the measured magnetisation at 1 T in the range 4—20 K with that calculated for the mull.

RESULTS AND DISCUSSION

Figure 2 shows a plot of the magnetic moment as a function of temperature from 1.8 to 300 K. The curve rises from a value of *ca.* 3.3 B.M.* at 300 K to a maximum of 4.11 B.M. at 7.5 K and then drops sharply as the temperature is decreased still further. Magnetisation data are shown in Figure 3 where $\mu_{eff.}$ of the trimer has been plotted against H/T. It can be seen that, even at 10 K, the magnetic moment is field dependent and that non-linear effects are important in the description of the magnetisation. The susceptibility data are in agreement with those measured by Ginsberg *et al.*[2] although the scatter of their data at lower temperatures, obtained with a pendulum magnetometer, is considerably greater than the Faraday-balance data reported here. The magnetisations were lower than those previously reported presumably due to the crystallite-orientation effect described above.

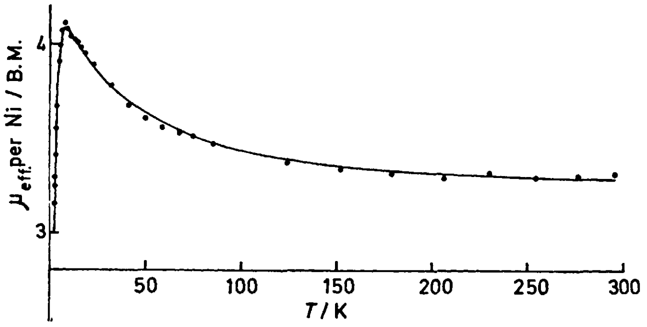

FIGURE 2 Temperature dependence of the magnetic moment ($\mu_{eff.}$ per ion) at 10 Kg. Experimental points (●) are compared with values (full lines) calculated using the full magnetisation calculation up to 20 K and the susceptibility expression above for the parameters $g = 2.175$, $J = -25$ cm^{-1}, $J_{ab} = 9$ cm^{-1}, $N\alpha = 230 \times 10^{-6}$ cm^3 mol^{-1}, and $D = -1.3$ cm^{-1}

The susceptibility expression [2] for the nickel trimer is unable to describe the magnetic behaviour of [Ni$_3$(pd)$_6$] at all temperatures especially at *ca.* <20 K. Using the method of Ginsberg *et al.*,[2] a term $(T + \theta)$ was substituted in the denominator for T and an approximate fit obtained for the parameters $g = 2.07$, $J = -56$ cm^{-1}, $J_{ab} = 22$ cm^{-1}, $\theta = 0.2$ K, and $N\alpha = 230 \times 10^{-6}$ cm^3 mol^{-1} in agreement with ref. 2. Besides the poor fit (R 0.102, standard error 0.062 B.M.), the g value obtained appeared to be well outside those found for octahedral nickel(II) complexes.[12,22] A vastly improved fit with parameters $g = 2.175$, $J = -25$ cm^{-1}, $J_{ab} = 9$ cm^{-1}, and $N\alpha = 230 \times 10^{-6}$ cm^3 mol^{-1} could be obtained (R 0.006, standard error 0.024 B.M.), together with a more satisfactory value of g, by omitting from consideration data at <20 K.

The magnetisation data at <3.5 K are due only to the ground-state septet ($S = 3$). To account for the magnetisation of the septet it was assumed that $g_{a\parallel} = g_{c\parallel} = g_{a\perp} = g_{c\perp} = g$, and that $D_a = D_c$. It was then found that the data were accounted for by a zero-field splitting parameter $D = -1.3$ cm^{-1} in the spin-Hamiltonian formalism (3). If the temperature was increased to >3.5 K the magnetisation deviated from that of the septet due to thermal occupation of the low-lying quintet $|(11)112M_s\rangle$ and triplet $|(11)01M_s\rangle$ states lying at 7 and 23 cm^{-1} higher in energy, respectively. In an analysis of the measured moments up to 19 K it was found that these three states were the only ones significantly occupied. Using the g value and exchange parameters obtained from fitting the high-temperature data, good agreement with the three-state model was obtained provided that single-ion zero-field splitting was included. The fully fitted plot of $\mu_{eff.}$ for the trimer against H/T is shown in Figure 3. A fit of the susceptibility expression neglecting single-ion zero-field splitting down to 20 K and the exact magnetisation calculation at <20 K is given in Figure 2. Thus, it is found that in [Ni$_3$(pd)$_6$] there is a ferromagnetic interaction between neighbouring nickel(II) ions of -25 cm^{-1} and an antiferromagnetic interaction of 9 cm^{-1} between the terminal nickel(II) ions. The magnitudes of these two values are about half those reported previously, *viz.* -52 and 14 cm^{-1}. The reduction in magnitude of these interactions shows the importance of including zero-field splitting effects in the analysis of low-temperature susceptibility and magnetisation properties.

In spite of the diminished magnitude of the exchange integrals, the general conclusions of Ginsberg *et al.* remain valid. Antiferromagnetic interactions between adjacent nickel atoms are expected to be small for paths of the type $e_g\|2s\|e_g$, whilst ferromagnetic terms may arise from orthogonalities of the type $e_g\|p_x \perp p_y\|e_g$ or the less favourable $e_g\|p_x\|(t_{2g} \perp e_g)$. A similar ferromagnetic interaction has been observed in a linear trimeric nickel(II) complex [Ni{tren(sal)$_3$}NiNi{tren(sal)$_3$}] where the terminal nickel ions are connected to the central nickel ion by three shared phenolic oxygens.[23]

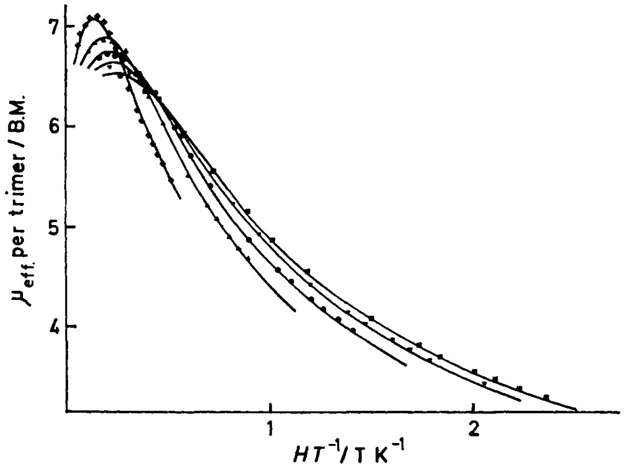

FIGURE 3 The magnetic moment ($\mu_{eff.}$ per Ni$_3$ unit) as a function of H/T for fields of 10 (♦), 20 (▲), 30 (●), 40 (▼), and 50 Kg (■). Full curves are calculated using the 'three-state' model with parameters $g = 2.175$, $J = -25$ cm^{-1}, $J_{ab} = 9$ cm^{-1}, $N\alpha = 230 \times 10^{-6}$ cm^3 mol^{-1}, and $D = -1.3$ cm^{-1}

The antiferromagnetic exchange between the terminal

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

ions is still surprising since it involves the interaction of the two ions *via* four atoms. However, extended interactions of this type appear to be possible when the orbitals of the ions [24,25] and intervening atoms are correctly orientated; in this case, between the well developed π-systems of the pd ligand and the half-full $d_{x^2-y^2}$ orbitals of the terminal nickel ions.

The zero-field splitting within the septet state of -1.3 cm^{-1} suggests that single-ion zero-field splitting is of the order of $-5D/3 = -2.17$ cm^{-1}. This value is well within measured zero-field splittings for analogous nickel(II) complexes such as Na[Ni(pd)$_3$] where $D = -2.19$ cm^{-1} or Na[Ni(pd)$_3$]·dioxan where $D = -1.87$ cm^{-1}.[12,22] The second complex is rhombically distorted, however, with $E = -0.083$ cm^{-1}.

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