Spin–Spin Interactions in Polynuclear Nickel(II) Complexes: A Susceptibility and Low-temperature Magnetisation Study of the Linear Trimer Hexakis(allylamine)hexakis-μ-benzotriazolyl-trinickel(II)–Triphenylphosphine Oxide (1/2) ‡

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The linear title compound $[Ni\{Ni(N_3C_6H_4)_3[N(C_3H_5)H_2]_3\}_2]\cdot 2PPh_3O$ has been studied using bulk magnetic susceptibility and magnetisation measurements in the range 2.0—300 K. The molecule has been found to have a spin-triplet ground state from an analysis of the high-temperature (>4.2 K) data and confirmed by the low-temperature (16—1.8 K) magnetisation results. The magnetic susceptibilities have been interpreted in terms of the Heisenberg–Dirac–Van Vleck isotropic exchange Hamiltonian. An antiferromagnetic interaction (J = 10 cm^{-1}) occurs between adjacent atoms bridged by the benzotriazolyl molecules, and a small ferromagnetic interaction between the terminal ions. The mechanism of these interactions is discussed and compared with those found in similar molecules.

THE magnitude and sign of magnetic exchange interactions between paramagnetic ions bridged by small heterocyclic molecules or molecular ions [1] depend upon the electronic structure of the paramagnetic ions, the orientation of the metal d orbitals with respect to the bridging ligand orbitals, and the electronic structure of the bridging molecules. In the case of bi- and polynuclear complexes bridged by five-membered heterocyclic rings those of copper(II) have been most extensively studied.[2-4] Pyrazolate,[2] imidazolate,[3,4] 1,2,4-triazole,[2] and 1,2,4-triazolate-bridged [2] copper(II) complexes show quite large antiferromagnetic coupling between the metal centres. A detailed study of imidazolate and related molecular-ion-bridged binuclear complexes has shown that the interaction strength can be correlated with the imidazole substituents in the order 2-methylimidazolate > imidazolate > benzimidazolate.[3] Less is known of analogous nickel(II) complexes. A study by Mackey and Martin [5] of the trimer bridged by neutral 1,2,4-triazole, $[Ni_3(N_3C_2H_3)_6][NO_3]_6$,[6] has shown antiferromagnetic interactions between nearest neighbours of 17.6 cm^{-1}. A previous study of this and related trimers by Groeneveld and co-workers [7] using a model including only nearest-neighbour interactions gave an interaction of 25 ± 1 cm^{-1}, the large value reflecting the neglect of terminal-ion interactions in the model used.

The low-temperature magnetic properties of the trimeric complex hexakis(allylamine)hexakis-μ-benzotriazolyl-trinickel(II)–triphenylphosphine oxide (1/2) have been measured as part of a study of linear trimeric nickel(II) complexes [8] to determine the magnitude and sign of the exchange interactions between the nickel(II) ions and to compare these with those found in the similar molecule bridged by the neutral 1,2,4-triazole molecule recently studied by Mackey and Martin.[5] The benzotriazolyl trimeric complex was first reported by Drapier and Hubert.[9] An X-ray analysis of the molecule showed [10] it to be a linear trimer of point-group symmetry $\bar{3}$. A central nickel ion is bridged by six benzotriazolyl groups to two terminal nickel ions and the remaining co-ordination sites of the terminal atoms are occupied by allylamine nitrogen atoms (*cf.* Figure 1). The two PPh_3O molecules are not co-ordinated to the metal ions. The neighbouring metal–metal separation is 3.73 Å and that between the terminal atoms 7.46 Å. In linear molecules such as this only the 'e_g' (d_{z^2}, $d_{x^2-y^2}$) orbitals will be involved in exchange pathways through the heterocyclic molecule or molecular ion.

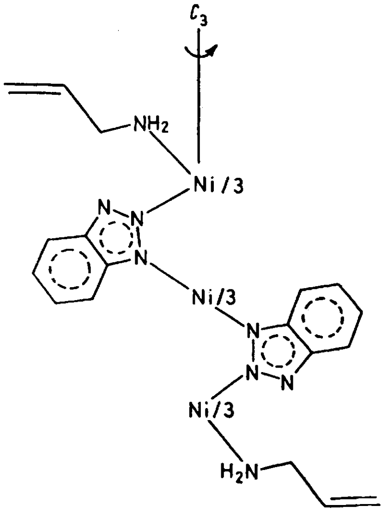

FIGURE 1 Schematic structure of hexakis(allylamine)hexakis-μ-benzotriazolyl-trinickel(II). Other benzotriazolyl molecules are related by the three-fold axis indicated

THEORY

The high-spin octahedral nickel(II) ions in C_3 symmetry have a ^3A ground state which may be split by a small zero-field splitting (z.f.s.) arising from mixing of the ^3A state with higher terms. The exchange interactions in a linear trimer comprised of ions with orbitally non-degenerate ground states may be described by the Heisenberg–Dirac–

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‡ *abcjkl*-Hexakis(allylamine)-*def*;*ghi*-hexakis(μ-benzotriazolyl-N^1N^2)-trinickel(II)–triphenylphosphine oxide (1/2).

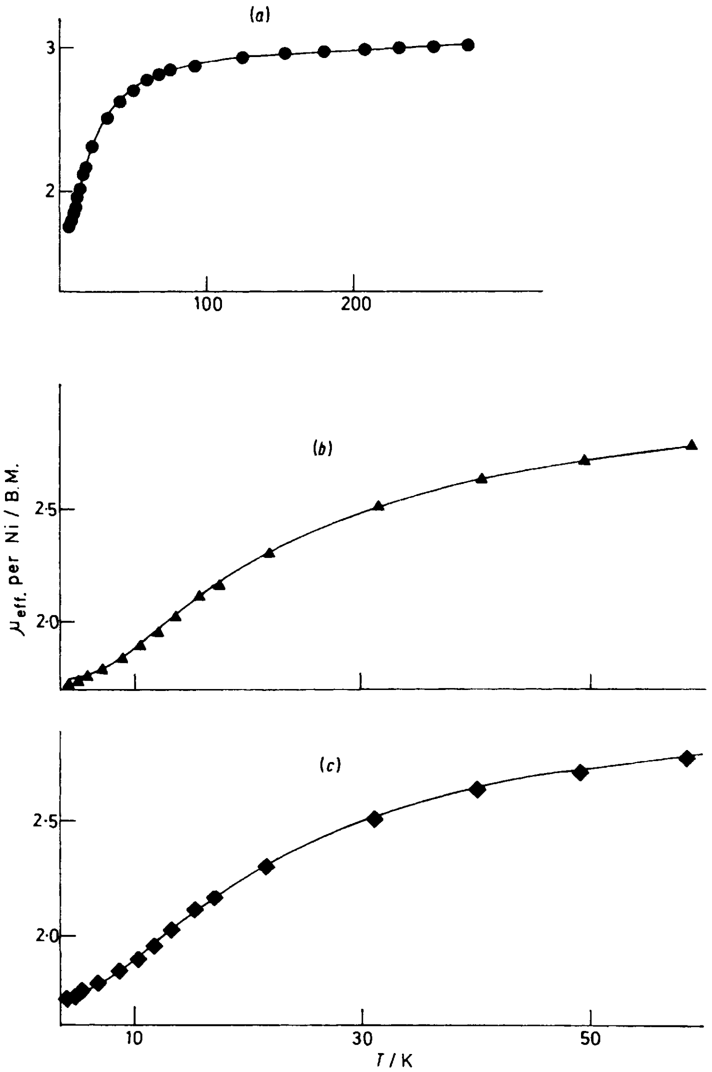

FIGURE 2 Temperature dependence of the magnetic moment ($\mu_{eff.}$ per ion) at 1 T. Experimental points are compared with the full curve calculated using equation (3) for the parameters: (a) $g = 2.128$, $J_{ab} = -7.5$ cm^{-1}, $J = 10.1$ cm^{-1}, and $N\alpha = 180 \times 10^{-6}$ cm^3 mol^{-1}; (b) $g = 2.160$, $J_{ab} = 0.0$ cm^{-1}, $J = 9.0$ cm^{-1}, and $N\alpha = 180 \times 10^{-6}$ cm^3 mol^{-1}; and (c) $g = 2.13$, $J_{ab} = -7.5$ cm^{-1}, $J = 10.1$ cm^{-1}, and $N\alpha = 180 \times 10^{-6}$ cm^3 mol^{-1}

Van Vleck (HDVV) isotropic exchange Hamiltonian [11,12] (1) where S_a, S_b are the spins of the terminal and S_c of the central nickel ion. Biquadratic exchange,[13] anisotropic exchange,[14] asymmetric exchange,[15] and magnetic dipole interaction [16] have not been considered for reasons outlined elsewhere,[8] the data being well described by $\mathcal{H}_{\text{exc}}$ in this case.

$$\mathcal{H}_{\text{exc}} = J(S_a \cdot S_c + S_b \cdot S_c) + J_{ab}S_a \cdot S_b \qquad (1)$$

Using the coupling scheme, $|(S_aS_b)S_{ab}S_cSM_s\rangle$, the energies of the total spin states $S = 3, 2, 2, 1, 1, 1,$ and 0 have been determined.[8,17,18] The Van Vleck approximation [11] is then used to calculate the susceptibility χ_{tri} ($=A/B$) of the trimer assuming an isotropic Zeeman interaction,[19,20] equations (2) and (3) where $K = 2g^2N\beta^2/3kT$, $x = J/kT$, and $y = J_{ab}/kT$.

$$A = K[42\exp(-2x - y) + 15\exp(x - y) + 15(y - x) + 3\exp(3x - y) + 3\exp(x + y) + 3\exp(2y)] \qquad (2)$$

$$B = [7\exp(-2x - y) + 5\exp(x - y) + 5\exp(y - x) + 3\exp(3x - y) + 3\exp(-x - y) + 3\exp(2y) + \exp(2x + y)] \qquad (3)$$

At low temperatures the Van Vleck approximation is no longer valid and it is necessary to calculate the magnetisation of the trimer rather than the susceptibility since the magnetisation is no longer linear with respect to the magnetic field. Calculations of this type including single-ion z.f.s. have recently been reported.[8] For the present molecule it is not necessary to include contributions from the single-ion z.f.s. when considering the low-temperature magnetic properties and, in fact, at very low temperatures the conventional Brillouin-function expressions for the magnetisation well describe the magnetic behaviour of the ground-state multiplet.[21]

EXPERIMENTAL

The complex crystallised from a solution of bis(triphenylphosphine)nickel(II) di-iodide and benzotriazole in allylamine as reported by Drapier and Hubert.[9] The elemental analyses were performed by the ANU Analytical Service Unit (Found: C, 60.7; H, 5.70; N, 18.8; Ni, 10.15; P, 3.40. Calc. for $C_{90}H_{96}N_{24}Ni_3O_2P_2$: C, 60.6; H, 5.40; N, 18.85, Ni, 9.85; P, 3.45%). The magnetic susceptibility from 4.2 to 300 K and magnetisations from 1.8 to 16 K were measured on a modified Oxford Instruments Faraday balance.[22] Magnetisations from 1 to 5 T were performed in Vaseline mulls of the complex to prevent crystallite-orientation effects at high magnetic field strengths.[8]

RESULTS

Figure 2(*a*) shows a plot of the magnetic moment ($\mu_{\text{eff.}}$ per ion) of the complex as a function of temperature from 2 to 300 K at 1 T. The moment drops with decreasing temperature from a value of 2.95 B.M.[*] at 280 K. The final value of the moment is consistent with a spin-triplet ground state. A non-linear least-squares fit of the high temperature (>4.2 K) data to equation (3) gave an excellent fit for the parameters $J_{ab} = -7.5$ cm^{-1}, $g = 2.128$, and $J = 10.1$ cm^{-1} ($N\alpha = 180 \times 10^{-6}$ cm^3 mol^{-1}, $R = 0.002\,7$, standard error = 0.007 B.M.). An alternative but less satisfactory fit was found for values of $J = -11.4$ cm^{-1} and $J_{ab} = 29.1$ cm^{-1} ($R = 0.01$, standard error = 0.03 B.M.). The magnitude of the terminal-ion interaction suggests this fit is unlikely.

Further calculations were made to examine the uniqueness of the exchange parameters. Two-dimensional maps of the sum of the squares of the differences between the calculated and observed magnetic moments were calculated over a large range of values of g, J, and J_{ab}. It was found that the values of J and J_{ab} for the best fit were little altered by changes in the g value. However, maps of g *vs.* J for varying terminal-ion interactions, J_{ab}, showed that g and J_{ab} were highly correlated. That is, by an appropriate change in J_{ab} it was possible to find comparable fits to the experimental data for a new value of g and an only slightly changed value of J. This then leads to considerable uncertainty in the value of J_{ab}.

Figure 2(*b*) and (*c*) show calculated curves for optimised fits with $J_{ab} = 0.0$ and -7.5 cm^{-1} in the temperature range 4.2—60 K. It can be seen that there is little to distinguish between the two. A reason for this lack of sensitivity of fit to J_{ab} may be seen from a variation of the energies of the various spin states with changes in J_{ab}. In the range of $J_{ab} = -7.5$ to 0 cm^{-1} the ground-state triplet $|(11)211\,M_s\rangle$ and higher-lying quintet $|(11)212M_s\rangle$ are unchanged in energy separation whilst the singlet $|(11)110M_s\rangle$ and another triplet $|(11)111M_s\rangle$ move closer to the ground state. Over the temperature range where $\mu_{\text{eff.}}$ is rapidly changing the relative populations of the ground state and the quintet $|(11)212M_s\rangle$ dominate contributions to the moment. The final parameters for the description of the exchange interaction are $J = 10 \pm 1$ cm^{-1}, $J_{ab} = -8$ to 0, and $g = 2.13$—2.16.

Figure 3 shows a graph of the magnetisation data measured from 2.0 to 16 K where $\mu_{\text{eff.}}$ per ion has been plotted as a function of H/T. At lower temperatures, *viz.* from 4 K downwards, the curves at different fields merge and show the normal behaviour expected for a triplet state with small or no zero-field splitting.[21] The magnetisation, M, calculated from the Brillouin function for a triplet

$$M = Ng\beta SB_s(x),\ B_s(x) = \frac{(2S+1)}{S}\cdot\coth\frac{(2S+1)x}{2S} - \frac{1}{2S}\coth\frac{x}{2S} \quad (4)$$

state as in equation (4) where $S = 1$ and $x = g\beta SH/kT$, well describes the low-temperature (<4 K) behaviour. The full line in Figure 3 shows the calculated moment using the g value determined from fitting of the high-temperature susceptibility data. Above 4 K the nearest states above the ground triplet state $|(11)211M_s\rangle$ are the quintet $|(11)212M_s\rangle$ and singlet $|(11)110M_s\rangle$. Both these become significantly populated at higher temperatures. The populations of the upper states will be altered by large magnetic fields where shifts of up to 5 cm^{-1} may be expected compared with the separation of the spin multiplets of *ca.* 20 cm^{-1}. It is for this reason that the curves diverge at higher temperatures.

The magnitude of the z.f.s. within the ground triplet may be expressed in terms of the contributions of the single-ion zero-field splitting as in equation (5), where the zero-field

$$D = (D_a + D_b - D_c)/12 \quad (5)$$

splitting has the form $D[S_z^2 - (1/3)S(S+1)]$.[8] The splitting within the ground triplet would then be small if the single-ion splittings of the terminal and central atoms are of comparable magnitude and an order of magnitude smaller than the single-ion z.f.s. In similar mononuclear nickel(II) complexes co-ordinated by six heterocyclic nitrogen atoms zero-field splittings of the order of 0.5 cm^{-1} or less are found [23] with similar g values to those reported here. It would be expected then that, within the ground-state triplet of the trimer, splittings would be of the order of 0.05 cm^{-1} or less. The fact that the behaviour of the low-temperature magnetisation can be described by the Brillouin function confirms this. Preliminary e.s.r. measurements in the temperature range 4.2—30 K on the powdered trimer show a considerable number of transitions in the range 0—1 T many of which are temperature dependent.

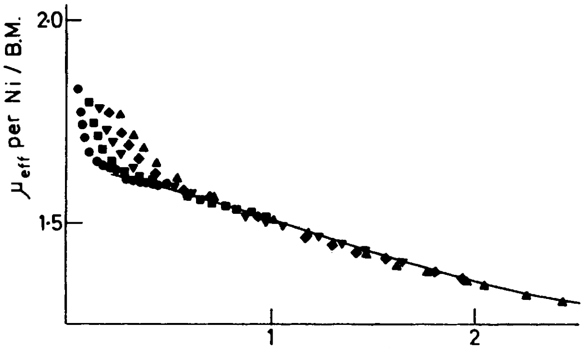

FIGURE 3 Magnetic moment ($\mu_{\text{eff.}}$ per ion) as a function of H/T for $H = 1$ (●), 2 (■), 3 (▼), 4 (♦), and 5 (▲). The full curve is that calculated from the Brillouin function, equation (4) with $g = 2.128$

DISCUSSION

Analysis of magnetic susceptibility measurements in terms of an isotropic exchange model show that in the present linear trimer the adjacent nickel(II) ions are coupled antiferromagnetically (10.1 cm^{-1}). The orientation of the metal-ion d orbitals in the complex allows superexchange pathways involving either the $d_{x^2-y^2}$ or d_{z^2} orbitals. In the point-group symmetry of the binuclear unit of adjacent ions the $d_{x^2-y^2}$ orbital (or d_{xy}

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[*] Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2; 1 eV ≈ 1.60 × 10^{-19} J.

depending on choice of axis) transforms as part of an E representation and the d_{z^2} as an A representation. Superexchange pathways are then possible *via* suitable combinations of the metal orbitals and ligand orbitals.[24]

Recent calculations by Hoffmann and co-workers[25] have demonstrated a relation between the energies of the metal orbitals in homonuclear dimeric complexes ($\phi_1 \approx d^{\mathrm{A}}{}_{x^2-y^2} + d^{\mathrm{B}}{}_{x^2-y^2}$, $\phi_2 \approx d^{\mathrm{A}}{}_{x^2-y^2} - d^{\mathrm{B}}{}_{x^2-y^2}$, $\phi_3 \approx d^{\mathrm{A}}{}_{z^2} + d^{\mathrm{B}}{}_{z^2}$, $\phi_4 \approx d^{\mathrm{A}}{}_{z^2} - d^{\mathrm{B}}{}_{z^2}$) and the exchange-interaction parameter from a configuration-interaction calculation involving the dimer metal d orbitals. For the case of dimers containing nickel(II) ions equation (6) is applicable where K_{ij} and J_{lm} are the

$$J = \tfrac{1}{2}\left(K_{ac} + K_{ad} + K_{bc} + K_{bd}\right) - \frac{1}{4}\left[\frac{(E_1 - E_2)^2}{J_{aa} - J_{ac}} + \frac{(E_3 - E_4)^2}{J_{bb} - J_{bc}}\right] \quad (6)$$

appropriate exchange and coulomb integrals.[25] Orbital energies E_1, E_2, E_3, and E_4 are the energies of molecular orbitals ϕ_1, ϕ_2, ϕ_3, and ϕ_4 and were estimated from extended-Hückel calculations. For the dimeric unit of neighbouring ions in the present complex such calculations are not practical, and the two ions are not strictly identical due to differing co-ordination.

Some qualitative features of the exchange mechanism may be discussed in terms of the electronic structure of the bridging molecular ion. Figure 4 shows the relative energies of the highest occupied molecular orbitals (h.o.m.o.s) of the benzotriazolyl ion calculated using the CNDO/2 method.[26] For comparison molecular-orbital energies of the neutral 1,2,4-triazole are also shown although it must be remembered that in the metal complexes their absolute positions will differ. Kahn and co-workers[27] have shown that for heterobinuclear complexes the exchange interaction J is composed of a ferromagnetic term and antiferromagnetic terms where $J_{\mathrm{AF}} \propto \sum_i S_i(\Delta_i^2 - \delta_i^2)^{\frac{1}{2}}$, S_i is the overlap of the two magnetic orbitals, Δ is the bonding–antibonding energy splitting of the dimer molecular orbitals, and δ is the difference in energy between the two single-ion d orbitals. For both the benzotriazolyl ion and neutral 1,2,4-triazole there are many possible exchange pathways *via* σ and π ligand molecular orbitals. The π m.o. of the heterocyclic molecules may combine with either of the metal d orbitals (A or E symmetry) whilst the σ m.o. may combine with either the A or E metal orbital depending upon the symmetry of the ligand m.o. Further, the relative stabilisation of the bonding and antibonding combinations of the metal orbitals will depend upon whether the bridging molecule's occupied m.o.s are bonding or antibonding.

Experimentally, the J value for triazole is greater than for benzotriazolyl for the nearest-neighbour interactions. This difference will be a combination of (*i*) the relative energies of the isolated m.o.s of nickel(II), (*ii*) the efficiency of m.o. formation *via* the bridge orbitals, and (*iii*) the relative energies of metal and ligand orbitals that will combine to form the dimer m.o.s. It is expected that δ_i would be larger for the benzotriazolyl complex and, together with the greater stabilisation of the ligand m.o. system in the aromatic molecule, would lead to smaller antiferromagnetic interactions in the benzotriazolyl case.

Further understanding of the exchange mechanism could be achieved if the analogous carbazole, benzocarbazole, and 1,2,3-triazole complexes could be synthesised.

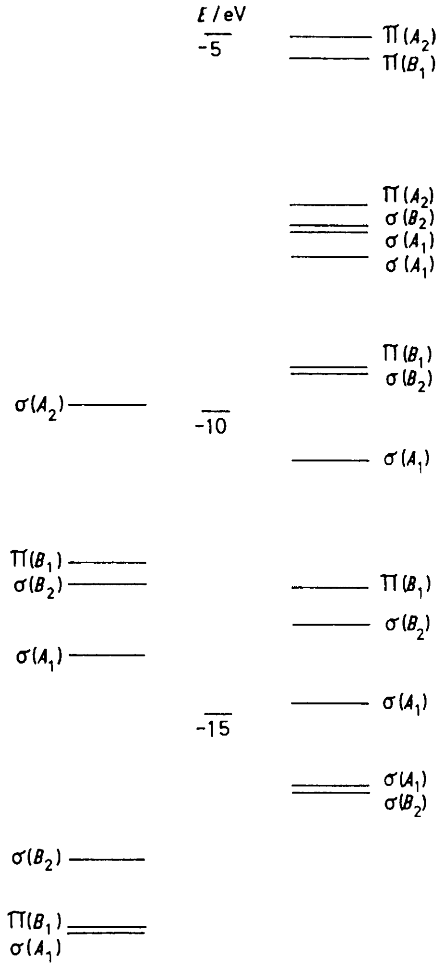

FIGURE 4 Energies of the higher occupied σ and π molecular orbitals of the benzotriazolyl anion and 1,2,4-triazole molecule

We thank the Queen Elizabeth II Fellowships Committee for the award of a Fellowship (to P. D. W. B.) and Mr. Peter Barlow for technical assistance.

[0/535 *Received*, 10*th April*, 1980]

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