

Ferromagnetic Exchange in a Tetranuclear Nickel Complex

By J. E. ANDREW and A. B. BLAKE*

(Department of Chemistry, University of Hull)

THE first observation of ferromagnetic exchange in a discrete, polynuclear complex has recently been reported by Ginsberg, Martin, and Sherwood.¹ Nickel acetylacetonate, which is trimeric with Ni-O-Ni angles of 80—90°, was found to show the susceptibility-temperature behaviour expected for exchange-coupled ions with a positive value of the

exchange parameter for nearest-neighbour interactions. This is in agreement with the theoretical prediction² of ferromagnetic exchange between d^8 ions with a 90° M-O-M angle.

We have studied some tetranuclear compounds of nickel and cobalt which show the existence of such ferromagnetic exchange.

On the basis of molecular weight measurements, and spectral and magnetic evidence for six-fold co-ordination of the nickel ions, Schrauzer and Kohnle³ concluded that $[\text{Ni}(\text{O}-\text{C}_6\text{H}_4-\text{CHO})(\text{OCH}_3)_2\text{CH}_3\text{OH}]_4$ has a "cubane" type of structure, with nickel atoms and methoxy-groups at alternate corners of a distorted cube. The analogous cobalt compound was reported simultaneously by Bertrand and Caine.⁴ We have prepared these compounds, and the magnesium analogue, by the latter workers' method,⁴ and we find that the co-ordinated methanol can readily be replaced by ethanol or propan-2-ol by recrystallising from a mixture of chloroform and the appropriate alcohol. The three methanol solvates are isomorphous, as are the three ethanol solvates. The molecular weight of the nickel-ethanol solvate and the n.m.r. spectra of the magnesium compounds confirm the constitutions assigned to them. The nickel-ethanol solvate crystallises in space group $I4_1/a$, with $a = 22.17$, $c = 9.70$ Å, and four tetrameric molecules in the unit cell. This symmetry requires all atoms to occur in sets of four related by four-fold rotation-inversion axes, in agreement with the proposed structure.

The magnetic susceptibilities of the methanol and ethanol solvates of the nickel compound (corrected for diamagnetism of -120×10^{-6} c.g.s.u. and temperature-independent paramagnetism of 240×10^{-6} c.g.s.u.) obey the Curie-Weiss law $\chi = C/(T - \theta)$ between 80° and 300° K, and are independent of the field strength, with the following values of the parameters:

methanol solvate: $\mu = 3.25 \pm 0.05$ B.M., $\theta = 24 \pm 3^\circ$

ethanol solvate: $\mu = 3.30 \pm 0.05$ B.M., $\theta = 33 \pm 3^\circ$,

where μ is the effective magnetic moment at 300° K (cf. $\mu = 3.23$ B.M., $\theta \sim 26^\circ$ for $\text{Ni}_3(\text{acac})_6$)¹.

For a structure with four Ni^{2+} ions at the corners of a tetrahedron, with exchange represented by a term $-2J\sum_i \mathbf{S}_i \cdot \mathbf{S}_j$ in the Hamiltonian, the susceptibility is given by

$$\chi_M = \frac{4Ng^2\beta^2}{3kT} \frac{\sum_i a_i \exp(c_i x)}{\sum_i b_i \exp(c_i x)}$$

where $a_i = 5, 7, 5, 1, 0$; $b_i = 3, 7, 10, 6, 1$; and $c_i = 20, 12, 6, 2, 0$ for $i = 1, 2, 3, 4, 5$ respectively, and $x = J/kT$. Using a least-squares procedure, the best fit to the data is obtained with the following values of g and J :

methanol solvate: $g = 2.21$, $J = 5.8^\circ$ K,

ethanol solvate: $g = 2.17$, $J = 9.9^\circ$ K.

The experimental results and theoretical curves are shown as a graph of $1/\chi_M$ against T in the Figure.

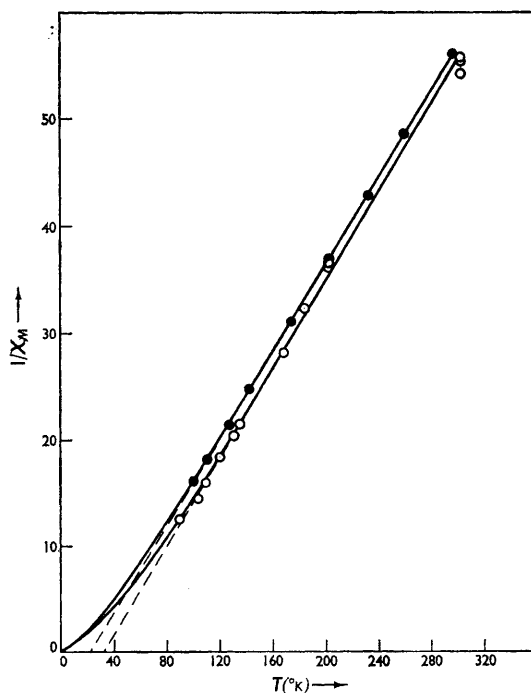


FIGURE. Reciprocal susceptibilities of $[\text{Ni}(\text{O}-\text{C}_6\text{H}_4-\text{CHO})(\text{OCH}_3)_2\text{ROH}]_4$ plotted against temperature: ●, experimental values for $\text{R} = \text{CH}_3$; ○, experimental values for $\text{R} = \text{C}_2\text{H}_5$. The solid lines are the theoretical curves of best fit.

There are two mechanisms other than intramolecular ferromagnetic exchange which might conceivably give rise to the observed increase in the effective magnetic moment $\mu_{\text{eff}} = 2.83\sqrt{\chi T}$ with decreasing temperature. The first is lattice ferromagnetism, which is highly unlikely in view of the apparent magnetic dilution and the absence of field dependence. The second is the possibility that there is an axial distortion so large that the spin-paired states of the individual nickel ions are appreciably populated in the temperature range studied. However, it is impossible to fit the data with this assumption, except with unreasonably large values of g (~ 2.9). We conclude that intramolecular ferromagnetic exchange is the true origin of the magnetic behaviour of these compounds.

The susceptibility of the ethanol solvate of the cobalt complex (corrected for diamagnetism) was

found to obey the Curie law down to 80° K, with a moment of 4.95 ± 0.05 B.M. For an isolated Co^{2+} ion in an approximately octahedral environment, spin-orbit coupling within the ${}^4T_{1g}$ term usually leads to pseudo-Curie-Weiss behaviour, with $\theta \sim -30^\circ$.⁵ For example, $\text{Co}(\text{O}\cdot\text{C}_6\text{H}_4\text{-CHO})_2(\text{H}_2\text{O})_2$ has $\mu_{\text{eff}} = 4.70$ B.M. at 300° K and an average θ of -25° . The zero value of θ in the present case, coupled with the relatively high moment, thus strongly suggests the presence of ferromagnetic interaction here also.

Goodenough² has discussed the various contributions to the exchange interaction between two d^n cations separated by an oxide or similar anion, in the cases where the M-O-M angle is 180° and 90°. He concludes that under normal conditions the 180° super-exchange will always be antiferromagnetic, being dominated by strong correlation super-exchange involving the anion $p\sigma$ orbital. For 90° super-exchange, however, the contribution from this orbital is weaker, and it vanishes altogether if the t_{2g} orbitals are full (as in d^8). In the

90° case there is also a moderately large *ferromagnetic* term arising from correlation of cation e_g electrons with electrons in two different anion $p\sigma$ orbitals. Delocalisation super-exchange (including direct overlap) contributes an additional antiferromagnetic term, which is probably smaller in the d^8 case than in the d^7 . The net result is that the 90° coupling between d^8 ions should be moderately ferromagnetic, while that between d^7 ions will be weaker but probably still positive. The behaviour of the nickel and cobalt complexes discussed above seems to be in agreement with these predictions.

In conclusion, it is necessary to remark that positive θ values have occasionally been reported for other nickel complexes, in particular for $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (24°).⁶ We have re-examined the latter, and find $\theta = -10^\circ$, in satisfactory agreement with the value of -6° obtained by Serres.⁷

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