

Ferromagnetic Ni–Ni Interactions in Trimeric Bis(acetylacetonato)nickel(II)

By A. P. GINSBERG,* R. L. MARTIN,† and R. C. SHERWOOD

(*Bell Telephone Laboratories, Incorp., Murray Hill, New Jersey 07971*)

MANY compounds are being discovered in which paramagnetic transition-metal atoms are arranged in the crystal lattice as magnetically isolated exchange-coupled clusters. To date, the observed couplings have been antiferromagnetic. Here we report the first example in which ferromagnetic

spin-coupling in a magnetically isolated cluster is unambiguously demonstrated.

Bis(acetylacetonato)nickel(II) has been shown¹ to form linear trimeric molecules with nearly octahedral co-ordination of each nickel ion. This co-ordination results from the sharing of triangular

† On leave from the Department of Inorganic Chemistry, University of Melbourne, Australia.

faces of adjacent octahedra, an acetylacetonato-oxygen being situated at each apex of the linear triad of fused octahedra. The intramolecular Ni-Ni distances are 2.882 and 2.896 Å. There are no atomic bridges between molecules in the crystal lattice and the closest intermolecular Ni-Ni distance is so great [~ 8 Å] that intermolecular spin-spin coupling is expected to be very weak. The trimer molecules should therefore behave as if magnetically isolated from each other at all but the very lowest temperatures.

A sample of trimeric $\text{Ni}(\text{acac})_3$ was prepared by recrystallizing anhydrous $\text{Ni}(\text{acac})_2$ from n-hexane under dry nitrogen. The product analysed correctly and the d -spacings and intensities of its X-ray powder pattern lines closely matched those calculated from the lattice constants and structure factors reported in reference 1. Magnetic susceptibility measurements were made between 1.5° and 300° K with a null-coil pendulum magnetometer² on samples contained in a Teflon capsule and compressed by a tight-fitting Teflon piston. A magnetization curve determined at 1.59° K showed that for field strengths above about 2500 oersteds the susceptibility was field dependent. Measurements were therefore made at 2400 oersteds up to 10° K, at which point the susceptibility determined at 2400 oersteds was the same as that at our highest field strength, 15,300 oersteds. Measurements were continued at the latter field strength up to room temperature. The results are shown in the Figure in the form of a plot (circles) of $\mu_{\text{eff}} = 2.827(\chi'_A T)^{\frac{1}{2}}$ vs. T . χ'_A is the field-independent susceptibility per gram atom of Ni. A diamagnetic correction³ ($\chi_d = -106 \times 10^{-6}$) and a temperature-independent paramagnetism correction⁴ ($N\alpha = +230 \times 10^{-6}$) were included.

At 296° K, $\mu_{\text{eff}} = 3.23$ B.M. As the temperature is decreased, μ_{eff} gradually increases until at 4.3° K a maximum value of 4.1 B.M. is reached; below this temperature μ_{eff} decreases with decreasing temperature. An $S = 3$ state of the trimer (i.e., all six e_g -spins coupled parallel), corresponds to a μ_{eff} of 4.2 B.M. for $g = 2.1$. Hence, our results indicate that by 4.3° K the trimer molecules are largely in an $S = 3$ spin state, i.e., the spins on the three Ni atoms are ferromagnetically coupled. The decrease in moment below 4.3° K may be attributed to the combined effects of a small zero-field splitting of the $S = 3$ state and very weak residual lattice antiferromagnetism (a.c. susceptibility measurements[†] show that there is no Néel point in the susceptibility curve down to 0.365° K). To take account

of these minor effects on the low temperature measurements, we have recalculated the moments with the Curie-Weiss relation $\mu_{\text{eff}} = 2.827 [\chi'_A (T + 0.2)]^{\frac{1}{2}}$, where 0.2° is an estimated effective Weiss constant for points below 2° K. The results are shown in the Figure as open circles.

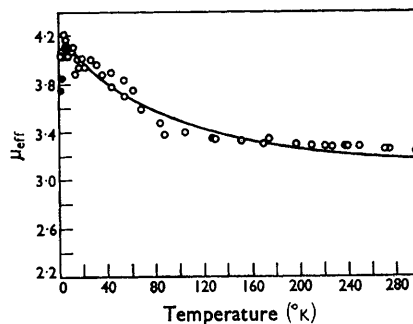


FIGURE. Effective magnetic moment (B.M.) per nickel atom of $[\text{Ni}_3(\text{acac})_3]$ between 1.5 and 300° K.

○ experimental data ($\theta = -0.2^\circ$); ● experimental data ($\theta = 0^\circ$). Full curve calculated with $g = 2.06$, $J_1 = +37^\circ$, $J_2 = -10.3^\circ$.

Comparison of the experimental results with the susceptibility equation for a linear trimer, derived by an extension of Kambe's theory,⁵ shows that the major features of the data may be accounted for with $g = 2.05$ and $J_1 \sim +30^\circ$ ($= +21 \text{ cm.}^{-1}$), where J_1 is the exchange integral between adjacent nickel atoms in the trimer. Agreement between theory and experiment is somewhat improved if a second exchange integral, J_2 , between the terminal Ni atoms of the trimer, is allowed to be different from zero. With this theory the curve of best fit is obtained with $g = 2.06$, $J_1 = +37^\circ$ ($= +26 \text{ cm.}^{-1}$), $J_2 = -10.3^\circ$ ($= -7 \text{ cm.}^{-1}$). The solid curve in the Figure is a plot of the theoretical equation.

The ordering of the spin levels necessitated by our results is as follows:

$$\begin{aligned} S' &= 1, S^* = 2 \\ S' &= 0, S^* = 1 \\ S' &= 2, S^* = 2 \\ S' &= 1, S^* = 1 \\ S' &= 1, S^* = 0 \\ S' &= 2, S^* = 1 \\ S' &= 3, S^* = 2 \end{aligned}$$

where S' is the total spin of the trimer and S^* is the total spin of the two terminal atoms. Although

[†] We thank G. W. Hull for these measurements.

the magnitude of the nearest neighbour Ni-Ni interaction is rather weak ($|J_1| = 26 \text{ cm.}^{-1}$) compared with, for example, that between pairs of copper atoms in the copper acetate dimer ($|J| \sim 150 \text{ cm.}^{-1}$), the overall width of the spin manifold is similar, being $10|J_1|$ for $[\text{Ni}_3(\text{acac})_6]$ but only $2|J|$ for $[\text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$.

The sign of the nearest neighbour Ni-Ni exchange

interaction is consistent with the 90° [Ni-O-Ni] ferromagnetic super-exchange mechanism dominating antiferromagnetic terms originating in direct overlap of nickel e_g -orbitals. These and other aspects of this unusual magnetic system will be presented in more detail elsewhere.

(Received, July 3rd, 1967; Com. 688.)

¹ G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

² R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, 1956, **103**, 572.

³ P. W. Selwood, "Magnetochemistry", 2nd edn., Interscience, New York, 1956, pp. 78, 92.

⁴ See, for example, C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw Hill, New York, 1962, p. 142.

⁵ K. Kambe, *J. Phys. Soc. Japan*, 1950, **5**, 48.