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Low-Temperature Magnetic Study of Hexaaquadihydroxobis(1,1,1-trifluoro-2,4,6-heptanetrionato)trinickel(II), a Linear Trinuclear Nickel(II) Triketonate

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The magnetic properties of $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ (TFDAA = 1,1,1-trifluoro-2,4,6-heptanetrionato) have been measured from 4.38 to 296 K and evaluated by using the Heisenberg–Dirac–Van Vleck Hamiltonian to determine the magnitude and nature of the magnetic coupling in this linear trimeric triketonate complex. The results indicate that adjacent nickel(II) ions are ferromagnetically coupled with a J_{12} value of 10 cm^{-1}. The terminal nickel(II) ions are antiferromagnetically coupled with a J_{13} value of -6 cm^{-1}. The best fit g value is 2.285, and the trimer has an $S' = 3$ ground state. The J_{12}, J_{13}, and g parameters are highly correlated. The magnetic coupling is discussed in terms of the trinuclear structure and related to similar complexes.

Introduction

During the past several years we have investigated the magnetic exchange interactions between various metal ions bound to ligands derived from 1,3,5-triketones. Binuclear complexes predominate with these ligands. In general, the two metal ions, bridged by the central ketonic oxygen, are separated by about 3.0–3.2 Å and the two dianionic triketonate ligands are essentially planar. However, during exploratory syntheses of nickel(II) complexes of fluorinated 1,3,5-triketonates, an unusual trinuclear complex was prepared.[2a] The synthesis proved reproducible under conditions that used a large excess of nickel(II) and the disodium salt of the ligand in methanol. Because there are relatively few magnetic studies of trinuclear nickel(II) complexes,[2b,3,4] we have undertaken a complete low-temperature magnetic characterization of the compound hexaaquadihydroxobis(1,1,1-trifluoro-2,4,6-heptanetrionato)trinickel(II), which we abbreviate Ni_3-$(TFDAA)_2(OH)_2(H_2O)_6$.

In the previous studies by Martin and his co-workers, the magnetic properties[2b,3] of $[Ni(acac)_2]_3$ and two triazole-bridged trinuclear nickel(II) complexes[4] proved to be considerably different. In $[Ni(acac)_2]_3$ the adjacent nickel ions exhibit weak ferromagnetic coupling ($J_{12} \approx 12.5$ cm^{-1}) and the terminal nickel ions exhibit weak antiferromagnetic coupling ($J_{13} \approx -4.5$ cm^{-1}).[5] In contrast, the magnetic properties[4] of the triazole trimer are best explained by antiferromagnetic coupling between the adjacent nickel ions ($J_{12} = -8.8$ cm^{-1}) and ferromagnetic coupling between the terminal nickel ions ($J_{13} = 4.9$ cm^{-1}). Thus the experimental magnetic studies indicate that the acetylacetonate complex has a ground-state spin of $S' = 3$, whereas the triazole complex has a ground-state spin of $S' = 1$. Preliminary magnetic results for $Ni_3(TFDAA)_2$-

Table I. Magnetic Properties of $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$[a]

T, K	$10^6 \chi_M'$, cgsu	$1/\chi_M'$, cgsu^{-1}	μ_{eff}, μ_B
296	4 770	210	3.36
214	6 720	149	3.39
201	7 080	141	3.37
195	7 430	135	3.41
157	8 960	112	3.35
144	9 890	101	3.37
133	10 410	96	3.38
105	13 550	73.8	3.37
93.5	15 170	65.9	3.37
82.1	17 130	58.4	3.35
77.0	18 510	54.0	3.37
73.5	19 140	52.2	3.36
64.6	21 940	45.6	3.37
59.9	26 870	37.2	3.59
49.4	36 130	27.7	3.78
42.6	40 680	24.6	3.72
41.7	41 610	24.0	3.73
37.1	46 790	21.4	3.73
33.0	52 700	19.0	3.73
27.4	63 180	15.8	3.72
16.7	110 900	9.02	3.85
12.1	147 800	6.77	3.78
9.42	193 400	5.17	3.82
6.00	281 100	3.56	3.67
4.38	363 900	2.75	3.57

[a] Calculated per nickel atom with a molecular weight of 235.0 and a diamagnetic correction of -83×10^{-6} cgsu.

$(OH)_2(H_2O)_6$ suggested that its magnetic exchange is similar to that found in $[Ni(acac)_2]_3$ and prompted the more complete, low-temperature magnetic characterization reported herein.

Experimental Section

The synthetic details and analytical data for $Ni_3(TDFAA)_2$-$(OH)_2(H_2O)_6$ are presented in a previous paper.[2a] The compound was synthesized three times over several months and was judged to be identical each time by spectral characterization, elemental analysis, and magnetic measurements.

The magnetic susceptibilities were measured on a standard Faraday balance between 77 K and room temperature at Wayne State University. Measurements between 4.3 and 296 K were obtained at the University of Missouri—Rolla on a Faraday balance that has been described earlier.[7] The moments were measured at eight applied fields between 1000 and 8000 G. All moments obtained above 6.0 K were independent of the applied field. At 6.00 and 4.38 K the moment was observed to decrease slightly with increasing applied field. The results were evaluated by using standard least-squares minimization computer programs and the standard Hamiltonian,[5] which leads to

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(2) (a) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1980**, *19*, 2949. (b) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Ibid.* **1968**, *7*, 932.

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(5) All coupling constants given in this paper are based on the Hamiltonian

$$H = -2J_{12}[(S_1 \cdot S_2) + (S_2 \cdot S_3)] - 2J_{13}(S_1 \cdot S_3)$$

where J_{12} represents the coupling between adjacent ions and J_{13} represents the coupling between the terminal ions. The notation follows that presented in ref 2 in which S_i represents the spin of an individual nickel ion, S' is the total spin of a state, and S^* is the total spin of the two terminal nickel ions. Coupling constants based on the alternative Hamiltonian suggested by Griffith[6] have been converted to the above Hamiltonian.

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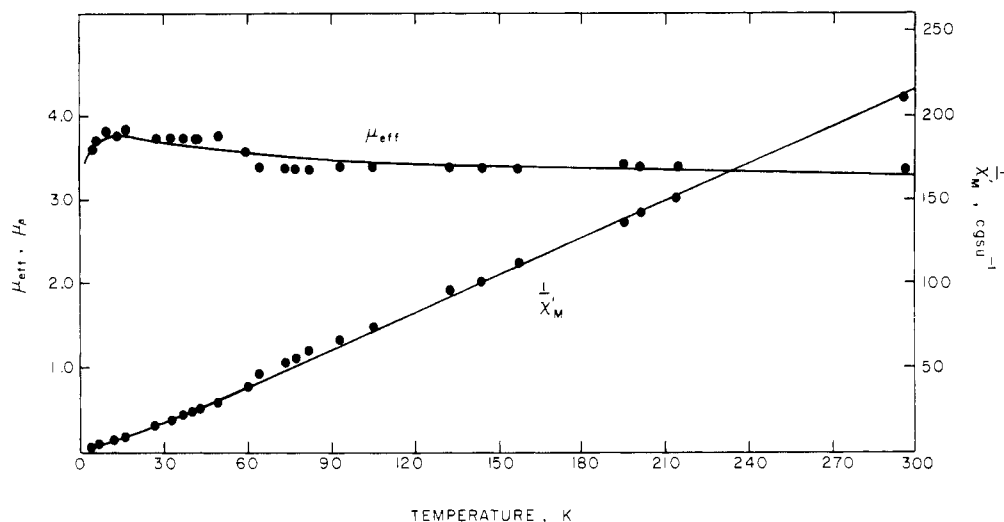
Figure 1. Magnetic moment and inverse susceptibility vs. temperature for $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$. The solid line is calculated for a g of 2.285, J_{12} of 10 cm^{-1}, J_{13} of -6 cm^{-1}, and δ of 8.6.
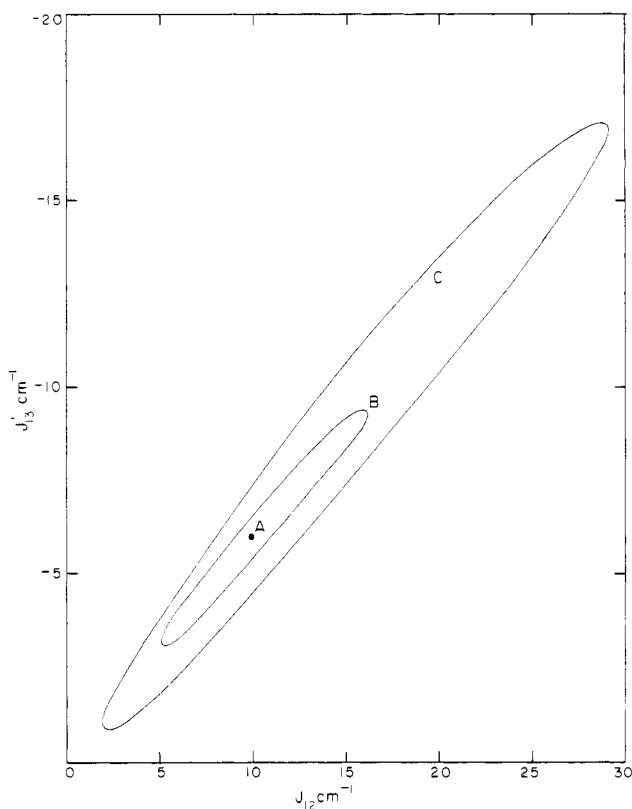

Figure 2. Correlation plot between J_{12} and J_{13} at a g value of 2.285. Point A represents the best fit. Any set of values within curve B or C will fit the experimental results to ± 0.1 or ± 0.2 μ_B, respectively.

the expression for the magnetic susceptibility per nickel ion presented by Ginsberg et al.[2b] and corrected by Mackey and Martin.[4] Our analysis used a temperature-independent paramagnetic term, $N\alpha$, of zero and did not include any zero-field splitting.

Results and Discussion

The magnetic susceptibility and magnetic moment per nickel ion measured between 296 and 4.38 K are presented in Table I. The inverse susceptibility vs. temperature plot obtained for data above 77 K yields a slope of 0.73 $cgsu^{-1}$ K^{-1} and hence a Curie constant, C, of 1.37 cgsu K. Thus, from the relationship $C = N\beta^2 g^2[S(S + 1)]/3k$, with $S = 1$, the calculated value of g is 2.34. (A g value of 2.27 is obtained if a temperature-independent paramagnetic contribution to the susceptibility, $N\alpha = 250 \times 10^{-6}$ cgsu, is included.) This value
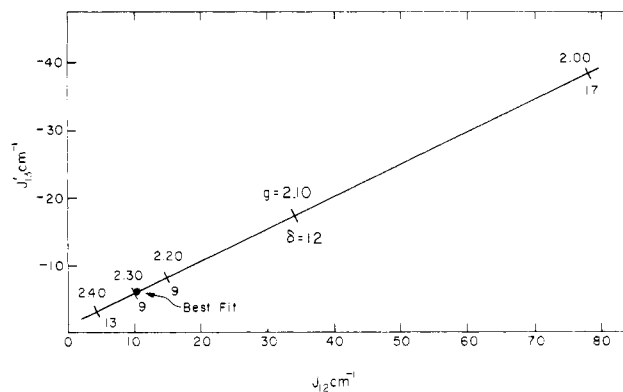

Figure 3. Correlation of g with the J_{12} and J_{13} values providing the best agreement with the experimental results as given by the residual value of δ.

should be considered an average value in the "paramagnetic region". The low-temperature data extrapolate to a Curie–Weiss Θ value of -0.4 K.

In order to determine the exchange coupling constants between the adjacent and terminal nickel ions, we have calculated the magnetic moment per nickel ion as a function of temperature, J_{12}, J_{13}, and g by using the expression given earlier.[2b,4,5] The minimized residual between the calculated and theoretical moments was calculated by

$$\delta = \sum_{i=1}^{n} |[\mu_{eff}(calcd)] - [\mu_{eff}(exptl)]^2|/n$$

where n is the number of data points. The best agreement between the calculated and experimental results was obtained for a value of g of 2.285, J_{12} of 10 cm^{-1}, and J_{13} of -6 cm^{-1} and yielded a residual δ value of 8.6. The experimental magnetic moments and inverse susceptibilities are compared with these calculated values in Figure 1. The range of values of J_{12} and J_{13} at a g value of 2.285, which are consistent with the experimental results, are plotted in Figure 2. The point A in this figure represents the best fit. Any set of J_{12} and J_{13} values within the B curve will reproduce the magnetic results to ± 0.1 μ_B. Any set of values within the C curve will reproduce the magnetic results to ± 0.2 μ_B. The results indicate that the error limits for the coupling constants are at least ± 5 cm^{-1} for J_{12} and ± 4 cm^{-1} for J_{13}, and the two parameters show a strong correlation with each other. The correlation of J_{12} and J_{13} with g is shown in Figure 3. Again there is a strong correlation and a fairly shallow minimum in g.
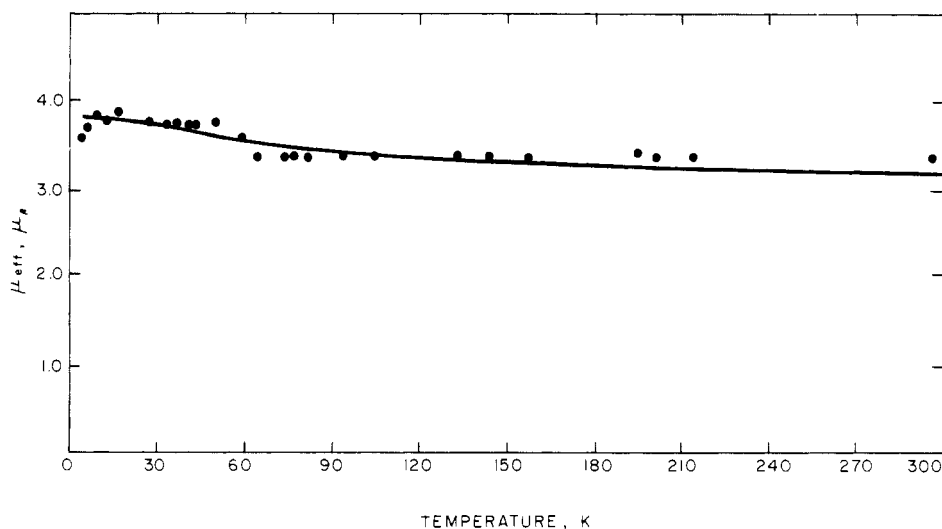
Figure 4. Magnetic moment vs. temperature for $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$. The solid line is calculated for a g value of 1.90, J_{12} of 8 cm^{-1}, J_{13} of 218 cm^{-1}, and δ of 10.6.

The results presented in Figures 2 and 3 indicate the strong correlation that exists between these parameters and indicate that great care must be exercised in drawing conclusions about compounds based upon small changes in these parameters. There is, however, a clear indication of ferromagnetic coupling between the adjacent nickel ions and antiferromagnetic coupling between the terminal ions. There is *no* set of coupling constants that would be consistent with antiferromagnetic coupling between adjacent nickel ions and ferromagnetic coupling between terminal ions. Surprisingly, there is an adequate fit between the calculated and experimental results for a g value of 1.90 and $J_{12} = 8.0$ cm^{-1} and $J_{13} = 218$ cm^{-1}. In this fit, which is illustrated in Figure 4, the value of g is totally unjustified by experimental evidence and in comparison with other related compounds. Therefore, this result is not considered further herein. In this regard, it should be noted that when it is possible to fix the value of g from an independent measurement or by an approximation of it from the higher temperature "paramagnetic region" susceptibility data, the determination of the exchange coupling constants becomes relatively unambiguous.

The magnetic coupling in $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ is surprisingly similar to that reported[2b] for $[Ni(acac)_2]_3$, which has been interpreted as having parallel ferromagnetic spin coupling between adjacent nickel(II) ions and antiparallel antiferromagnetic spin coupling between the terminal nickel ions. In $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$, the gradual increase in μ_{eff} as the temperature is decreased to about 10 K leaves little doubt first that there is an important component of ferromagnetic exchange present and second that the ground state has a reasonably high spin multiplicity. At very low temperatures, the magnetic moment of both $[Ni(acac)_2]_3$ and $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ decrease. Boyd and Martin[3] have attributed this decrease in the acetylacetonate complex to a zero-field splitting of -1.3 cm^{-1} in an $S' = 3$ electronic ground state. Thus, although the magnitude of the magnetic susceptibilities differ somewhat, with the value for $[Ni(acac)_2]_3$ being larger at a given temperature, the overall features and trends are much the same. The slight increase in the moment of $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ at approximately 60 K may result from a small rearrangement or contraction in the molecule (perhaps accompanied by a phase change) with decreasing temperature.

The fit presented in Figure 1 corresponds to a value of g of 2.285. This value was not fixed but was obtained from the least-squares optimization of the g, J_{12}, and J_{13} values. This g value is very similar to the value obtained from the plot of

the inverse susceptibility vs. temperature (see above) in the "paramagnetic region" and therefore is a value justifiable on the basis of the experimental results. In addition, it is comparable to the EPR-measured g value in other six-coordinate nickel(II) complexes with oxygen donor atoms, e.g., $g = 2.25$[8] in $[Ni(H_2O)_6]^{2+}$ and $g = 2.20$[9] in $Na[Ni(acac)_3]$.

Repeated attempts to grow suitable single crystals of Ni_3-$(TFDAA)_2(OH)_2(H_2O)_6$ for X-ray structure determination have failed. However, several factors support a generalized structure similar to I or II. First, recrystallization of Ni_3-

I

II
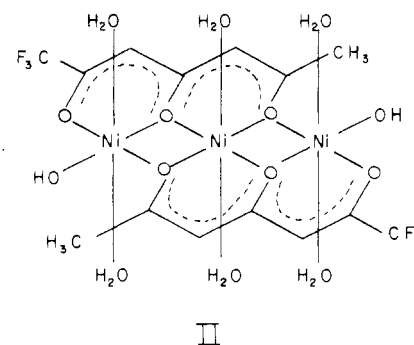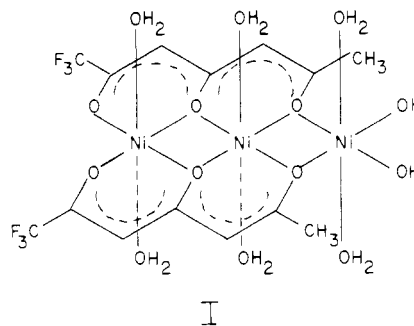
$(TFDAA)_2(OH)_2(H_2O)_6$ from pyridine yields crystals of the simple binuclear triketonate $Ni_2(TFDAA)_2(py)_4$, the structure of which has been reported.[2a] The formation of this binuclear complex would be particularly easily accomplished from structure I. Second, the infrared and visible spectra of Ni_3-$(TFDAA)_2(OH)_2(H_2O)_6$ are consistent with "normal" six-

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coordinate nickel(II) with oxygen donor atoms. Third, both I and II represent the planar, dianionic coordination of the triketonate ligand that we have observed to be exclusively the case for first-row transition-metal ions in our previous work.[2a,10,11] Fourth, there is ample literature precedence for type I complexation to form binuclear complexes[12] from mononuclear Schiff base chelates. Thus, although the structural details are not known with certainty, it is reasonable to assume that the three nickel(II) ions are in a linear array each with

two bridging ketonic type oxygen atoms. In other words, there is a shared edge between adjacent pseudooctahedra in the complex.

The magnetic properties of $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ are quite unexpected in view of the results obtained for the binuclear nickel(II) 1,3,5-triketonates. These complexes, which contain two nickel(II) pseudooctahedra sharing a common edge, exhibit antiferromagnetic exchange between the adjacent nickel ions with exchange constants, J, from about -10 to -30 cm^{-1}.

Registry No. $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$, 80502-89-2.

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Stabilities of Structures Related to the High-Pressure Form of GeP, Which May Be Derived from Rock Salt by Bond Breaking

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There are four different structures with a rock salt size cell which contain square-pyramidal coordination at each center and where the pseudo-fourfold rotors point in the same direction. One of these corresponds to the high-pressure form of the nine-electron compound GeP. We show how band structure calculations correctly predict this as the lowest energy structure and how the yellow form of TlI is by far the most stable arrangement among these structures for 10-electron compounds. The band structure energies of these systems can be successfully modeled by considering the energetics associated with variation of the apical–basal bond angle in five-coordinate square-pyramidal molecules. The chemical and electronic reasons behind this stability sequence may thus be simply understood.

Introduction

We have recently described a simple technique by which we may make progress in understanding why solid-state materials adopt the structures they do.[2] First, we enumerate the number of symmetry inequivalent ways we may distort a symmetrical parent structure to a daughter. Second, we calculate, via band structure computations, the energies of these alternatives and compare them with observed structure types. Last, we look for chemical reasons behind these energetics and hence qualitative arguments as to structural stability and preferences. One series which has succumbed to our treatment is the generation of structures related to those of arsenic or black phosphorus from that of rock salt (Figure 1) by scission of three mutually orthogonal linkages at each atomic site of the latter.[3] It turns out that there are 36 different ways of producing universal trigonal-pyramidal coordination in a cell of this size. Only a few of these are actually found in reality, and the reasons behind the adoption of the stable possibilities are fascinating ones.[4]

Electronically the distortion of the eight-electron rock salt structure to that of arsenic (or its derivative structure exhibited

by GeTe) or black phosphorus (or its derivative structure exhibited by GeS) is understandable along lines which are established for viewing molecular geometries.[5] The extra two electrons per formula unit (for 10-electron GeS, GeTe) would have to occupy high-energy orbitals at the rock salt geometry. On distortion, as three linkages around each center are broken, these orbitals drop dramatically in energy to become lone-pair orbitals in the new structure. In this paper we are interested in the somewhat smaller group of structures which may be derived from rock salt by breaking a single linkage around each center and are typified by the high-pressure modification of the nine-electron species GeP[6] (Figure 2).

Structural Enumeration

In previous papers[3,7] using our theoretical philosophy we have made use of powerful combinatorial techniques, on the basis of Pólya's theorem,[8] to derive the number of structurally related arrangements. For the present system however it is very easy just to write down the seven possibilities based on a rock salt-sized cell and square-pyramidal coordination at each site. These are shown in Figure 3 and divide naturally

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