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Magnetic Exchange in Transition Metal Complexes. V.[1a] Ferromagnetic Spin Coupling in a Tetranuclear Nickel(II) Cluster

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Three-dimensional single-crystal X-ray data show the tetrameric clusters of tetrakis[μ_3-methoxo-2,4-pentanedionatomethanolcobalt(II)] to have the "cubane" type molecular structure. The compound crystallizes as red needles (a = 21.79 (4) Å, b = 10.91 (2) Å, c = 20.21 (4) Å, and β = 121.7 (1)°) of monoclinic space group $C2/c$ with 4 tetramer units per unit cell; the calculated density of 1.43 g/cm³ agrees well with the experimental value of 1.40 (2) g/cm³. A total of 1557 unique nonzero reflections were visually estimated from precession camera photographs; least-squares refinement resulted in a conventional R value of 0.10. The Ni complex $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ is isostructural (a = 21.55 (4) Å, b = 10.88 (2) Å, c = 20.00 (4) Å, and β = 121.4 (1)°). The magnetic susceptibility of the Ni complex has been measured from 296 down to 1.63°K, and the field dependence of the susceptibility has been examined to 15.3 kOe at several temperatures below 20°K. The results demonstrate that the eight e_g electrons centered on the tetrad of nickel atoms are ferromagnetically coupled, the ground molecular spin state for the tetramer being S' = 4 (*i.e.*, eight spins parallel) and being fully populated by 21°K. The magnitude of the intramolecular Ni–Ni coupling constant is $J = +10°$ ($\equiv$7 cm^{-1}). The tetramer molecules in their ground state exhibit an additional intermolecular ferromagnetic coupling which gives rise to a Weiss constant $\theta = +0.8°$. This compound provides the second example of a polynuclear ferromagnet in which the level of maximum spin multiplicity has been fully populated by taking it to very low temperatures. It is the first example of a cluster complex found to exhibit both intra- and intermolecular ferromagnetic spin coupling.

Introduction

If potassium hydroxide in methanol is added to a solution of either cobalt(II) or nickel(II) acetylacetonate in boiling methanol, the tetrameric clusters $M_4(OCH_3)_4(acac)_4(CH_3OH)_4$ with M = Co or Ni separate from solution as large deep red or green crystals, respectively.[2,3] An X-ray single-crystal study[3] of the cobalt(II) tetramer, tetrakis[μ_3-methoxo-2,4-pentanedionatomethanolcobalt(II)], the details of which are reported in the present paper, shows that the cobalt and methoxy oxygen atoms occupy the alternate corners of a rather distorted cube—the so-called "cubane" arrangement (see Figure 3). Each methoxide group bridges three Co atoms with Co–O–Co angles of 94.6–98.6 (5)°. One acetylacetone chelate and one methanol ligand complete a distorted octahedron of oxygen atoms around each Co atom.

The nickel(II) tetramer, tetrakis[μ_3-methoxo-2,4-pentanedionatomethanolnickel(II)], is isostructural with the cobalt complex and has a room-temperature magnetic moment μ_{eff} = 3.3 BM per Ni atom, a value consistent with octahedrally coordinated divalent nickel. Since all the nickel atoms appear to be in an orbitally nondegenerate ground state, the tetrameric cluster provides an interesting opportunity to study spin–spin interactions in a crystal lattice composed of Ni_4 tetrahedra which are magnetically isolated from neighboring clusters by the peripheral ligands. The presence of Ni–O–Ni angles near 90° leads to the expectation that the unpaired e_g electrons will couple ferromagnetically, in which event the ground state of the tetramer should be associated with a "spin-only" magnetic moment of $\mu_{eff} = \sqrt{20}$ BM per Ni atom.[4]

The first observation of ferromagnetic exchange in a discrete, polynuclear cluster was reported by Ginsberg, Martin, and Sherwood[1a,5] in trimeric nickel(II) acetylacetonate. Andrew and Blake,[6,7] soon after, concluded that intramolecular ferromagnetic exchange was occurring in Schrauzer and Kohnle's[8] "cubane"-type tetramer $Ni_4(OCH_3)_4(salicyladehyde)_4(CH_3OH)_4$, although they were unable to extend their magnetic measurements below 80°K and so could not fully populate the level of maximum spin multiplicity. We report here susceptibility data as a function of temperature down to 1.6°K and as a function of field to 15.3 kOe for the present nickel "cubane" tetramer which confirms that the intramolecular Ni–Ni spin coupling is ferromagnetic. The susceptibility measurements also demonstrate the existence of an additional, much weaker, lattice ferromagnetism. $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ thus becomes the first example of a cluster complex found to exhibit *both* intra- and intermolecular ferromagnetic spin coupling.

Theory

The magnetic properties of tetranuclear clusters have been reviewed elsewhere.[4] For such compounds the spin–spin Hamiltonian

$$H = -2\sum J_{ij}\hat{S}_i\cdot\hat{S}_j \qquad (1)$$

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(1) (a) Part IV: A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **7**, 932 (1968). (b) Georgia Institute of Technology. (c) Bell Telephone Laboratories. (d) On leave at the Bell Telephone Laboratories (1967) from the Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Australia.

(2) J. A. Bertrand and D. Caine, *J. Amer. Chem. Soc.*, **86**, 2298 (1964).

(3) J. A. Bertrand and R. I. Kaplan, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-20.

(4) See, for example, R. L. Martin, "New Pathways in Inorganic Chemistry," Cambridge University Press, 1968, Chapter 9, p 175.

(5) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Chem. Commun.*, 856 (1967).

(6) J. E. Andrew and A. B. Blake, *ibid.*, 1174 (1967).

(7) J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1456 (1969).

(8) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 1727 (1964).

has eigenvalues which can be obtained by making use of the vector model.[9] The effects of nearest neighbor isotropic spin–spin interaction may be obtained by expanding the Hamiltonian to

$$H = -2J[\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_4\cdot\hat{S}_1 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_1\cdot\hat{S}_3] \quad (2)$$

where the spin–spin interaction constant is J for any Ni_2 pair in the Ni_4 tetrad. The expectation values of the spin angular momentum operators $\hat{S}_i$ (i = 1–4) are the same and we write it S. Then the characteristic value of $(\hat{S}_i\cdot\hat{S}_i) = S(S + 1)$. By taking $\hat{S}' = \hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \hat{S}_4$ we have

$$(\hat{S}'\cdot\hat{S}') = 4S(S + 1) + 2(\hat{S}_1\cdot\hat{S}_2) + 2(\hat{S}_2\cdot\hat{S}_3) + 2(\hat{S}_3\cdot\hat{S}_4) + 2(\hat{S}_4\cdot\hat{S}_1) + 2(\hat{S}_1\cdot\hat{S}_3) + 2(\hat{S}_2\cdot\hat{S}_4)$$

so that the Hamiltonian can be rewritten

$$H = -J[(\hat{S}'\cdot\hat{S}') - 4S(S + 1)] \quad (3)$$

The energy levels under this Hamiltonian are simply

$$E(S') = -J[S'(S' + 1) - 4S(S + 1)] \quad (4)$$

where the allowed values of S' are obtained by the addition rule for the spin vectors.

The tetranuclear cluster has a total spin degeneracy of $(2S + 1)^4 = 81$. This degeneracy is partially lifted by the isotropic Ni–Ni interactions to give the spin manifold shown in Figure 1 for positive (ferromagnetic) J. When the system is exposed to an external magnetic field (along the Z axis), the energy levels $E(S')$ are split further into $(2S' + 1)$ levels; *i.e.*, the first-order Zeeman term $gM_{S'}\beta H$ must be added to the energy, where g is the Lande splitting factor and $M_{S'}$ takes the values S', $(S' - 1)$, . . . , $(-S' + 1)$, $-S'$. The magnetic susceptibility of the tetranuclear cluster is obtained as the mean of the susceptibilities, $\chi(S')$, of the levels comprising the spin manifold, each weighted by its degeneracy and by the appropriate Boltzmann factor. After dividing by 4 to obtain the susceptibility, χ'_A, per gram-atom of Ni, the result is

$$\chi'_A = \frac{3K}{T}\left[\frac{5e^{20x} + 7e^{12x} + 5e^{6x} + e^{2x}}{3e^{20x} + 7e^{12x} + 10e^{6x} + 6e^{2x} + 1}\right] + N\alpha \quad (5)$$

where $x = J/kT$, $K = g^2N\beta^2/3k$, and $N\alpha$ is a correction added to take account of the temperature-independent paramagnetism.

Figure 2 shows a plot of eq 5 in the form of $\mu_{eff} = (3k\chi'_AT/N\beta^2)^{1/2}$ *vs.* the reduced temperature $kT/|J|$ for positive and negative J with $N\alpha = 0$. When $J/kT \rightarrow 0$, $\mu_{eff} \rightarrow \sqrt{2}g$; *i.e.*, the spin-only value of $\mu_{eff} = \sqrt{8}$ BM per Ni atom is obtained. If $J/kT \rightarrow \infty$, only the $S' = 4$ level is populated and $\mu_{eff} \rightarrow \sqrt{5}g$ corresponding to the spin-only value of $\mu_{eff} = \sqrt{20}$ BM per Ni atom. At sufficiently high temperatures ($T \gg J$), eq 5 reduces approximately to the Curie–Weiss law $\chi'_A(T - \Theta)$ = constant, with the Weiss constant being given by $\Theta \approx 4(J/k)$.

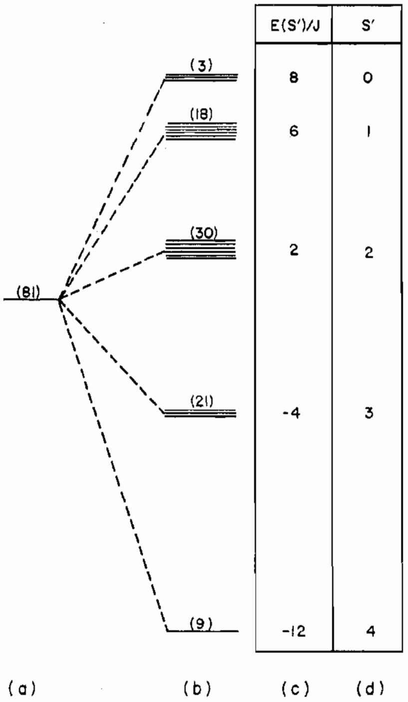

Figure 1.—Energy level scheme for a tetrahedron of weakly interacting Ni^{2+} ions ($t_{2g}^6e_g^2$): (a) total spin degeneracy of ground state; (b) effect of spin–spin interaction of form $-2J\hat{S}_i\cdot\hat{S}_j$ with J positive; (c) energy of spin levels $E(S')/J$; (d) values of S'.

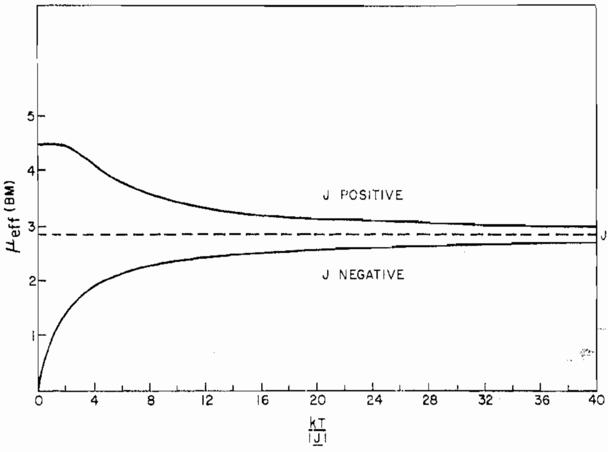

Figure 2.—Theoretical dependence of μ_{eff} (BM) per Ni atom for a tetrahedral Ni_4 cluster upon the reduced temperature $kT/|J|$ for g = 2.00.

Andrew and Blake[6,7] have also derived the susceptibility expression (eq 5) for a cluster with four Ni^{2+} ions at the corners of a tetrahedron but the numerator of their equation is too small by a factor of 3 due to a misprint. Their data listed in Table V are derived from the correct susceptibility expression (private communication from A. B. B.).

Experimental Section

Preparations.—The complex $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ was synthesized by dissolving nickel(II) acetylacetonate (0.007 mol) in 350 ml of refluxing methanol. Potassium hydroxide (0.007

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(9) K. Kambe, *J. Phys. Soc. Jap.*, **5**, 48 (1950).

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$

Atom	x	y	z	B, Å^2
Co1	0.0852 (1)[a]	0.0237 (3)	0.2992 (2)	3.08 (6)
Co2	0.0023 (1)	0.2219 (3)	0.1729 (2)	3.04 (6)
O1	−0.0008 (5)	0.0299 (12)	0.1822 (7)	2.53 (23)
O2	0.0733 (6)	0.2118 (12)	0.2897 (7)	2.65 (24)
O3	0.1586 (8)	0.0489 (17)	0.4219 (9)	5.44 (37)
O4	0.0962 (7)	0.2046 (17)	0.1600 (8)	4.30 (32)
*R1*O1[b]	0.1628 (6)	0.0281 (14)	0.2708 (7)	3.48 (27)
*R1*O2	0.0985 (7)	−0.1581 (15)	0.3152 (9)	4.27 (33)
*R2*O1	0.0065 (7)	0.4038 (15)	0.1618 (9)	4.41 (35)
*R2*O2	−0.0747 (7)	0.2095 (15)	0.0569 (8)	4.15 (31)
C1	0.0015 (9)	−0.0494 (24)	0.1284 (12)	4.11 (45)
C2	0.1343 (9)	0.2958 (20)	0.3268 (12)	3.45 (38)
C3	−0.2170 (19)	−0.0138 (37)	0.0200 (23)	9.03 (92)
C4	0.0952 (12)	0.1874 (29)	0.0864 (14)	5.46 (57)
*R1*C1	0.2040 (11)	−0.0624 (23)	0.2760 (13)	4.35 (46)
*R1*C2	0.1471 (10)	−0.2251 (24)	0.3139 (12)	4.30 (44)
*R1*C3	0.2601 (12)	−0.0382 (27)	0.2557 (15)	5.34 (52)
*R1*C4	0.1985 (11)	−0.1821 (25)	0.2953 (14)	4.85 (50)
*R1*C5	0.1472 (14)	−0.3613 (29)	0.3343 (17)	6.52 (69)
*R2*C1	−0.0237 (11)	0.4658 (26)	0.1002 (14)	4.46 (45)
*R2*C2	−0.0969 (11)	0.3010 (23)	0.0087 (14)	4.42 (46)
*R2*C3	−0.0023 (13)	0.6044 (30)	0.1100 (17)	6.30 (68)
*R2*C4	−0.0746	0.4194 (26)	0.0241 (15)	5.47 (56)
*R2*C5	−0.1550 (14)	0.2639 (31)	−0.0754 (17)	7.45 (73)

[a] Numbers in parentheses here and elsewhere in this paper indicate the estimated standard deviation in the least significant digits. [b] *R1* and *R2* refer to the chelate rings.

mol) was added dropwise to the refluxing solution over a period of 1 hr. After 2 hr at reflux, the solution was filtered while hot. Large green crystals of the complex separated as the filtrate cooled *Anal.* Calcd for $NiC_7H_{14}O_4$: C, 38.0; H, 6.3. Found: C, 38.8; H, 5.8. The molecular weight and association values were determined in chloroform at 37° using a Mechrolab Model 301A vapor pressure osmometer. Molecular weights of 975 (0.025 M), 840 (0.050 M), and 789 (0.100 M) correspond to association numbers of 4.5, 3.8, and 3.6, respectively.

Crystals of $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$ were prepared by the addition of potassium hydroxide (0.01 mol), dissolved in 25 ml of methanol, to a refluxing methanolic solution of cobalt(II) acetylacetonate (0.01 mol in 50 ml); the red crystals which separated from the refluxing solution were filtered and dried. *Anal.* Calcd for $CoC_7H_{14}O_4$: C, 38.0; H, 6.3. Found: C, 38.0; H, 5.7.

Preliminary Crystal Studies.—A needlelike crystal of $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$ with approximate dimensions 0.10 × 0.20 × 0.80 mm was sealed inside a Lindemann glass capillary. The crystal was mounted on a precession camera with the long dimension (a) of the crystal parallel to the spindle axis (the shortest dimension of the crystal corresponds to the b axis). The unit cell dimensions at room temperature, obtained from zero-level precession photographs using zirconium-filtered molybdenum radiation (λ 0.7107 Å), are a = 21.79 (4) Å, b = 10.91 (2) Å, c = 20.21 (4) Å, and β = 121.7 (1)°. The calculated density of 1.43 g/cm^3, based on 4 tetramers per cell, agrees well with the experimental value of 1.40 (2) g/cm^3 obtained by the flotation method in a mixture of carbon tetrachloride and hexane.

From zero and upper level precession photographs, systematic absences were noted; for all reflections, $h + k = 2n + 1$ were absent, and for the $h0l$ level, $l = 2n + 1$ were also absent. Although space groups C2/c and Cc are both consistent with these absences, C2/c was assumed and the successful refinement of the structure has confirmed that choice.

A crystal of the nickel compound was mounted on a glass rod and precession photographs were taken; the unit cell dimsenions obtained from those photographs are a = 21.55 (4) Å, b = 10.88 (2) Å, c = 20.00 (4) Å, and β = 121.4 (1)°. All of the photographs showed the same systematic absences as the cobalt crystal and all reflections on the $hk0$, $h0l$, $hk1$, and $h1l$ levels had the same relative intensities as the corresponding reflections from the cobalt crystal.

Collection of Intensity Data.—Intensity data were collected on the precession camera, using the cobalt crystal used for the space group determination; zirconium-filtered Mo Kα radiation was again used. A total of 1557 nonzero, unique reflections from the hkl (l = 0 to −3) and hkl (k = 0–3) levels were visually estimated from exposures of 0.5, 5, and 50 hr. Lorentz–polarization corrections were computed; no corrections for absorption were made (μ = 13 cm^{-1}, maximum error in F estimated as 5%).

Magnetic Measurements.—Susceptibility measurements were made on polycrystalline samples of $Ni_4(OCH_3)_4(acac)_4(CH_3OH_4)$ between 1.6°K (pumped helium) and room temperature, with a null-coil pendulum magnetometer,[10] using the techniques described previously.[1a] The field dependence of the susceptibility was determined to 15.3 kOe at several temperatures from 1.6 to 20°K.

Results

Solution of the Structure.—Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer; programs employed included Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy ORFLS and ORFFE least-squares and function and error programs, and various locally written programs.

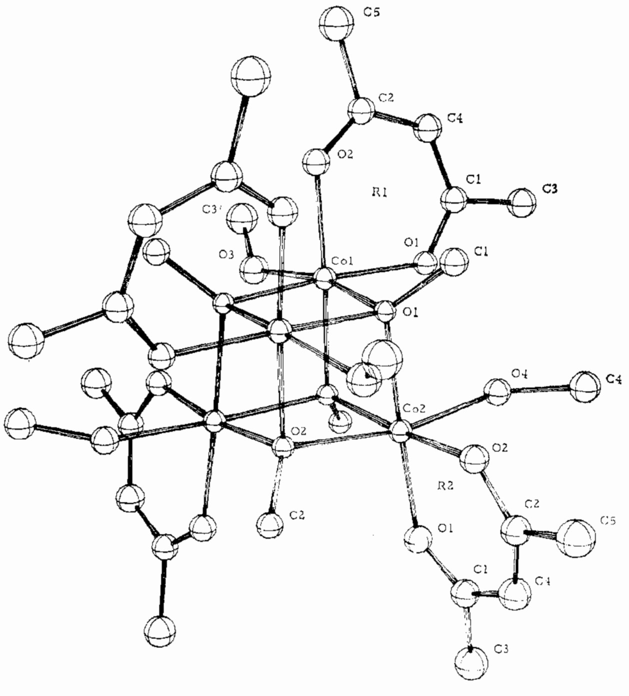

Figure 3.—Molecular structure of $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$. *R1* and *R2* on the figure denote chelate rings 1 and 2; the *R1* and *R2* designations are not repeated at the atoms of the rings.

A three-dimensional Patterson function was computed; due to the superposition of Co–O vectors, the Co–Co vectors were not easily chosen. However, since the tetramer was required to occupy a site of twofold symmetry and since a cubane-type structure was expected, it was possible to assign, from the Patterson function, coordinates for the cobalt and oxygens of the cubane portion of the structure; successive cycles of structure-factor and electron density calculations were used to obtain coordinates for the remaining nonhydrogen atoms. Full-matrix least-squares refinement (each

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

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (ELECTRONS × 10) FOR $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$

L= 0			
H	K	FO	FC
0	4	351	394
0	10	23	30
0	12	60	52
1	3	48	36
1	5	413	369
1	7	74	75
1	9	69	70
1	11	80	70
1	13	12	9
2	2	112	114
2	4	148	145
2	6	50	47
2	8	23	19
2	10	28	34
2	12	32	31
3	3	115	117
3	5	130	132
3	7	65	78
3	9	66	70
3	11	59	53
3	13	21	20
4	2	60	53
4	4	29	18
4	6	131	124
5	1	59	73
5	3	27	29
5	5	25	17
5	7	111	111
5	9	25	19
5	11	45	43
5	13	24	23
6	0	76	69
6	2	87	73
6	4	12	3
6	6	138	145
7	1	105	110
7	7	94	79
7	9	19	18
7	11	51	46
7	13	26	24
8	0	146	151
8	2	98	101
8	4	26	34
8	6	65	67
8	8	22	13
9	3	50	51
9	5	91	92
9	7	38	41
9	9	31	31
9	11	52	36
9	13	23	19
10	0	275	287
10	2	44	41
10	4	85	88
11	1	143	166
11	5	181	186
11	7	39	32
11	9	37	43
11	11	62	42
12	0	364	349
12	2	23	23
12	4	146	157
12	12	30	30
13	1	119	107
13	3	41	47
13	5	152	150
13	7	37	43
13	9	51	51
13	11	50	44
14	0	173	188
14	2	45	42
14	4	102	87
14	6	33	39
14	8	26	9
14	12	17	21
15	3	32	23
15	5	62	56
15	7	44	55
15	9	34	28
15	11	27	31
16	2	82	79
16	6	56	52
17	1	41	43
17	3	53	49
17	7	37	44
17	9	28	18
17	11	36	21
18	2	58	56
18	6	41	41
19	3	29	28
19	7	29	34
20	0	53	50
20	2	41	44
21	5	22	26
21	7	25	12
22	0	57	53
22	4	27	32
23	1	38	36
23	3	28	22
23	5	34	32
24	0	55	53
24	4	26	35
L=-1			
H	K	FO	FC
-24	2	15	16
-23	1	29	39
-23	5	29	28
-22	2	16	16
-22	6	33	36
-21	1	20	32
-21	3	14	16
-21	5	30	25
-20	6	19	17
-19	1	16	18
-19	3	28	38
-19	7	25	23
-19	9	18	3
-18	4	23	27
-18	6	16	11
-18	8	39	31
-17	1	27	41
-17	3	39	46
-17	7	34	41
-17	9	19	15
-16	4	48	48
-16	6	16	4
-16	8	50	53
-16	10	16	5
-15	1	51	58
-15	3	78	78
-15	7	39	44
-15	9	20	17
-14	2	18	32
-14	4	65	60
-14	6	35	53
-14	8	32	27
-14	10	43	38
-13	1	114	126
-13	3	42	39
-13	5	72	73
-13	9	16	11
-13	11	34	35
-12	2	91	103
-12	4	36	43
-12	6	160	165
-12	10	78	73
-11	1	179	175
-11	3	29	41
-11	5	152	134
-11	7	26	31
-11	9	50	55
-11	11	55	52
-10	2	32	25
-10	4	35	46
-10	6	152	157
-10	8	24	21
-10	10	89	91
-9	1	119	128
-9	3	65	90
-9	5	68	76
-9	7	23	30
-9	9	15	7
-9	11	33	33
-8	2	43	49
-8	4	62	57
-8	6	33	28
-8	8	53	50
-8	10	39	38
-8	12	31	27
-8	14	19	13
-7	1	61	56
-7	3	45	58
-7	5	20	17
-7	7	46	52
-7	9	30	33
-6	2	10	7
-6	6	25	25
-6	8	38	31
-6	12	57	52
-5	1	23	23
-5	3	81	77
-5	7	103	93
-5	9	23	11
-5	11	36	31
-5	13	26	23
-4	2	9	2
-4	4	154	157
-4	8	116	100
-4	12	62	52
-3	1	170	186
-3	3	143	150
-3	7	64	75
-3	13	26	17
-2	2	150	155
-2	4	188	187
-2	6	185	183
-2	8	85	76
-2	10	74	61
-1	3	100	90
-1	5	166	165
-1	7	53	60
-1	9	40	36
-1	11	78	76
-1	13	20	3
0	2	81	68
0	4	34	42
0	6	189	222
0	10	139	140
0	14	33	34
1	3	104	79
1	5	310	306
1	7	83	90
1	9	57	49
1	11	287	101
2	2	65	66
2	6	182	199
2	8	16	10
2	10	107	110
2	14	28	26
3	3	108	105
3	5	143	140
3	11	27	31
4	2	94	92
4	4	213	206
4	6	29	27
4	8	106	104
4	10	48	44
4	12	43	40
5	1	27	47
5	3	21	74
5	7	87	86
5	11	22	17
5	13	26	20
6	2	15	14
6	4	116	118
6	6	19	10
6	8	63	74
6	12	62	53
7	1	87	81
7	3	54	42
7	5	19	19
7	7	47	37
7	9	45	31
7	11	32	28
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15	5	34	34
15	6	57	52
15	7	67	60
15	8	21	21
15	9	24	28
17	4	39	37
17	5	24	27
17	7	39	41
17	13	20	18
19	5	17	23
19	7	21	25
23	0	30	36
25	0	29	26
K= 2			
H	L	FO	FC
-30	22	27	21
-28	12	19	17
-28	14	24	15
-26	12	27	28
-26	14	33	34
-26	18	19	18
-24	4	42	39
-24	6	19	28
-24	10	47	49
-24	12	54	64
-24	14	46	52
-24	18	27	32
-24	20	27	28
-22	5	27	23
-22	7	33	29
-22	8	29	29
-22	10	52	59
-22	12	58	61
-22	13	18	24
-22	16	55	55
-22	18	59	68
-22	20	37	46
-22	24	27	25
-20	5	37	30
-20	6	26	26
-20	11	25	22
-20	12	17	27
-20	13	52	62
-20	16	75	66
-20	18	65	61
-20	24	39	44
-18	6	24	34
-18	8	31	33
-18	10	35	37
-18	12	37	45
-18	13	40	48
-18	14	29	24
-18	16	17	18
-18	18	24	18
-18	19	35	34
-18	22	26	25
-18	24	33	39
-16	4	28	32
-16	6	60	67
-16	8	114	106
-16	9	22	25
-16	10	47	42
-16	12	49	50
-16	13	15	19
-16	14	38	41
-16	16	28	20
-16	19	38	40
-14	4	94	103
-14	5	15	18
-14	6	102	113
-14	8	126	131
-14	9	25	33
-14	10	68	76
-14	12	118	107
-14	14	85	79
-14	16	41	42
-14	18	25	32
-14	19	23	19
-14	20	38	38
-12	4	123	120
-12	5	19	15
-12	6	82	83
-12	7	64	65
-12	9	83	84
-12	10	146	137
-12	12	150	141
-12	14	61	67
-12	16	43	51
-12	18	76	78
-12	20	54	59
-12	22	36	36
-10	4	82	75
-10	5	65	56
-10	6	34	19
-10	7	82	92
-10	8	54	55
-10	9	41	41
-10	10	103	89
-10	12	137	132
-10	13	52	50
-10	14	31	31
-10	15	54	56
-10	16	83	76
-10	18	75	76
-10	20	29	40
-10	24	38	43
-8	4	148	158
-8	6	108	97
-8	7	64	58
-8	8	138	137
-8	9	31	29
-8	10	23	22
-8	11	22	28
-8	12	17	11
-8	13	106	99
-8	15	43	47
-8	16	60	65
-8	18	67	69
-8	20	34	35
-8	21	25	19
-8	24	33	41
-6	6	174	178
-6	7	45	43
-6	8	113	113
-6	9	26	24
-6	10	83	82
-6	12	41	46
-6	13	90	89
6	14	48	44
-6	15	25	32
-6	19	38	31
-6	21	18	19
-6	24	27	34
-4	6	86	71
-4	8	120	110
-4	12	108	98
-4	14	73	69
-4	16	31	36
-4	18	24	21
-4	19	43	41
-4	20	31	15
-4	21	26	17
-2	6	125	117
-2	7	29	34
-2	8	141	127
-2	9	61	47
-2	10	93	89
-2	12	121	121
-2	14	42	48
-2	16	36	33
-2	18	35	32
-2	19	18	17
-2	20	49	49
0	6	174	182
0	7	14	15
0	8	122	104
0	9	87	78
0	10	93	102
0	11	23	18
0	12	141	132
0	14	57	57
0	18	65	65
0	20	38	48
2	4	82	83
2	5	37	34
2	7	100	85
2	8	56	66
2	9	49	59
2	10	77	92
2	11	25	38
2	12	84	85
2	14	33	26
2	15	38	34
2	16	43	46
2	18	53	64
2	20	27	31
4	4	183	169
4	5	78	83
4	6	42	34
4	7	93	105
4	8	81	75
4	9	25	35
4	10	30	42
4	11	22	22
4	12	40	54
4	13	56	53
4	15	44	46
4	18	27	26
6	4	32	40
6	6	124	128
6	8	127	121
6	10	40	54
6	11	31	30
6	12	17	15
6	13	40	44
6	14	48	38
6	16	27	24
8	4	123	121
8	6	138	140
8	8	57	65
8	10	27	9
8	12	63	61
8	14	53	57
10	4	83	86
10	6	70	73
10	8	30	22
10	9	18	9
10	10	36	35
10	12	63	68
10	14	33	35
12	4	17	4
12	6	25	18
12	9	26	29
12	10	27	27
12	12	43	39
12	18	26	23
14	4	28	41
14	5	22	22
14	7	38	34
14	9	19	19
16	4	26	32
16	8	28	25
18	6	39	36
18	8	34	37
20	6	34	37
K= 3			
H	L	FO	FC
-25	4	25	26
-25	5	21	27
-25	6	36	33
-25	7	29	21
-25	10	20	27
-25	12	34	38
-25	14	28	26
-25	15	28	25
-25	19	20	20
-25	25	20	10
-23	5	20	25
-23	8	34	27
-23	9	19	15
-23	10	58	53
-23	11	33	34
-23	12	38	48
-23	13	43	45
-23	16	27	22
-23	18	33	33
-23	19	27	33
-23	20	27	24
-23	21	19	29
-21	4	34	29
-21	6	27	25
-21	8	18	17
-21	9	29	25
-21	10	26	23
-21	11	41	34
-21	13	41	44
-21	14	36	24
-21	16	58	49
-21	17	45	42
-21	18	41	36
-21	19	46	48
-21	21	19	19
-21	24	20	24
-19	5	18	26
-19	6	31	30
-19	8	39	38
-19	10	30	25
-19	16	30	28
-19	17	35	34
-19	19	25	32
-19	22	27	26
-19	23	23	27
-19	24	28	35
-19	25	31	30
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-17	9	54	59
-17	12	22	24
-17	13	51	50
-17	14	23	13
-17	15	46	37
-17	19	17	23
-17	22	26	27
-15	4	45	39
-15	5	51	50
-15	6	81	70
-15	7	52	43
-15	8	65	53
-15	9	38	41
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-15	12	15	21
-15	13	50	54
-15	15	35	42
-15	16	42	41
-15	19	51	55
-15	21	31	33
-15	25	28	15
-13	4	67	59
-13	5	102	96
-13	6	71	70
-13	7	83	78
-13	10	76	73
-13	11	51	42
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-13	14	50	56
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-13	17	25	36
-13	18	23	31
-13	19	47	45
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-13	21	17	20
-13	25	28	26
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-11	5	16	20
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-11	7	23	21
-11	8	51	40
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-11	10	117	104
-11	11	72	67
-11	12	96	97
-11	13	76	75
-11	14	37	42
-11	15	38	37
-11	16	47	45
-11	17	31	31
-11	18	64	68
-11	19	37	37
-11	20	38	46
-11	21	25	31
-11	25	28	25
-9	4	22	18
-9	5	22	15
-9	6	30	37
-9	7	66	71
-9	8	17	21
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-9	10	68	60
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-9	16	84	65
-9	17	46	42
-9	18	58	60
-9	19	50	56
-9	20	24	24
-9	21	36	37
-9	25	28	31
-7	7	88	86
-7	8	15	7
-7	10	83	81
-7	11	23	17
-7	12	53	63
-7	13	55	61
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-7	16	36	38
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-7	22	26	27
-7	25	28	27
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-5	10	97	102
-5	11	14	9
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-5	13	65	56
-5	14	39	39
-5	15	32	34
-5	16	34	43
-5	17	16	13
-5	19	17	20
-5	21	18	12
-3	8	57	64
-3	9	88	83
-3	10	35	36
-3	11	50	45
-3	12	100	100
-3	13	47	52
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-1	8	37	38
-1	9	11	17
-1	10	76	64
-1	11	78	82
-1	12	80	72
-1	13	65	64
-1	14	26	24
-1	15	42	42
-1	18	25	33
-1	19	45	51
-1	21	19	26
1	6	28	45
1	7	29	39
1	9	17	20
1	10	91	80
1	11	37	41
1	12	55	69
1	13	27	30
1	14	51	50
1	15	24	17
1	16	35	27
1	17	40	39
1	18	26	37
1	19	38	40
3	5	26	23
3	6	50	50
3	7	34	23
3	8	17	16
3	9	38	24
3	15	25	20
3	16	45	49
3	18	27	39
3	20	20	16
5	4	71	80
5	5	45	48
5	6	30	38
5	7	94	81
5	8	57	46
5	9	33	35
5	10	54	58
5	11	28	35
5	12	27	40
5	13	17	9
5	15	29	20
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7	6	85	77
7	7	69	64
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7	10	48	45
7	13	45	39
7	14	19	19
7	15	34	29
9	4	67	58
9	5	53	63
9	6	35	39
9	7	33	32
9	8	48	50
9	11	32	26
9	12	47	49
9	13	39	42
9	14	20	33
9	15	20	17
11	4	65	70
11	5	44	50
11	6	30	33
11	7	25	21
11	8	26	24
11	10	33	35
11	11	19	25
11	12	40	46
11	13	20	25
13	10	28	32
15	4	53	65
15	6	27	21
17	4	31	33
17	7	41	30

reflection assigned unit weight) of individual layer scale factors, individual isotropic temperature factors, and atomic coordinates for the 24 atoms of the asymmetric unit (80 parameters) converged to a conventional R value $(\Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|)$ of 0.10. Final atomic parameters are given in Table I and the final F_o and F_c values are compared in Table II; selected intramolecular distances and angles are given in Table III and the molecular structure is indicated in Figure 3. The complex $Ni_4(OCH_3)_4(o\text{-}OC_6H_4CHO)_4(CH_3OH)_4$ has recently been found[7] to have a similar structure.

Magnetic Measurements.—Our measurements of the field-independent susceptibility of $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ between 1.6 and 300°K are given in Table IV as χ'_A, the susceptibility expressed per Ni atom. A diamagnetic correction[11] ($\chi_d = -88.8 \times 10^{-6}$ cm^3 g-atom^{-1}) is included. Above 13°K, these measurements were made at a field strength of 15.3 kOe. Below 13°K, the susceptibilities at 15.3 kOe were field dependent, and the values reported in Table IV were determined at lower field strengths (less than 5kOe), at which no field dependence could be detected. The results are shown in Figure 4 as plots of $(\chi'_A)^{-1}$ and $\mu_{eff} = 2.8273[\chi'_A T]^{1/2}$ *vs.* T.

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[11] P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience, New York, N. Y., 1956, pp 78, 92.

TABLE III

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN $Co_4(OCH_3)_4(acac)_4(CH_3OH)_4$

Atoms	Distance, Å	Atoms	Distance, Å
Co1–Co1′	3.16 (1)	O1–C1	1.41 (3)
Co1–Co2	3.10 (1)	O2–C2	1.46 (2)
Co1–Co2′	3.12 (1)	O3–C3′	1.38 (4)
Co2–Co2′	3.17 (1)	O4–C4	1.49 (3)
Co1–O1	2.11 (1)	*R1*O1–*R1*C1	1.30 (3)
Co1–O1′	2.06 (1)	*R1*C1–*R1*C4	1.39 (3)
Co1–O2	2.06 (1)	*R1*C2–*R1*C4	1.43 (3)
Co2–O2	2.04 (1)	*R1*O2–*R1*C2	1.30 (2)
Co2–O2′	2.14 (1)	*R1*C1–*R1*C3	1.50 (3)
Co2–O1	2.11 (1)	*R1*C2–*R1*C5	1.54 (4)
Co1–O3	2.15 (2)	*R2*O1–*R2*C1	1.26 (3)
Co2–O4	2.20 (2)	*R2*C1–*R2*C4	1.43 (3)
Co1–*R1*O1	2.05 (1)	*R2*C2–*R2*C4	1.36 (3)
Co1–*R1*O2	2.01 (2)	*R2*O2–*R2*C2	1.30 (3)
Co2–*R2*O1	2.00 (2)	*R2*C1–*R2*C3	1.56 (4)
Co2–*R2*O2	2.05 (2)	*R2*C2–*R2*C5	1.55 (3)

Atoms	Angle, deg	Atoms	Angle, deg
Co1–O1–Co1′	98.4 (6)	O_4–Co2–*R2*O2	96.5 (6)
Co2–O2–Co2′	98.6 (5)	*R2*O1–Co2–*R2*O2	89.8 (7)
Co1–O1–Co2	94.6 (5)	Chelate Ring 1	
Co2–O1–Co1′	97.0 (5)	Co1–*R1*O1–*R1*C1	127 (1)
Co1–O2–Co2	98.3 (5)	*R1*O1–*R1*C1–*R1*C3	118 (2)
Co1–O2–Co2′	95.8 (5)	*R1*O1–*R1*C1–*R1*C4	125 (2)
O1–Co1–O1′	81.5 (6)	*R1*C3–*R1*C1–*R1*C4	117 (2)
O1–Co1–O2	82.5 (5)	*R1*C1–*R1*C4–*R1*C2	125 (2)
O1′–Co1–O2	84.5 (5)	*R1*C4–*R1*C2–*R1*C5	120 (2)
O1–Co1–*R1*O1	93.5 (6)	*R1*C4–*R1*C2–*R1*O2	125 (2)
O1–Co1–*R1*O2	100.4 (6)	*R1*C5–*R1*C2–*R1*O2	115 (2)
O1′–Co1–O3	88.9 (6)	*R1*C2–*R1*O2–Co1	127 (1)
O3–Co1–*R1*O1	95.5 (6)	Chelate Ring 2	
O3–Co1–*R1*O2	89.1 (7)	Co2–*R2*O1–*R2*C1	128 (2)
*R1*O1–Co1–*R1*O2	89.9 (6)	*R2*O1–*R2*C1–*R2*C3	115 (2)
O2–Co2–O2′	81.0 (5)	*R2*O1–*R2*C1–*R2*C4	125 (3)
O2–Co2–O1	83.3 (5)	*R2*C3–*R2*C1–*R2*C4	119 (2)
O2′–Co2–O1	81.5 (5)	*R2*C1–*R2*C4–*R2*C2	124 (3)
O2′–Co2–*R2*O1	100.3 (6)	*R2*C4–*R2*C2–*R2*C5	119 (3)
O2–Co2–*R2*O1	97.6 (6)	*R2*C4–*R2*C2–*R2*O2	128 (2)
O2–Co2–O4	86.9 (5)	*R2*C5–*R2*C2–*R2*O2	113 (2)
O4–Co2–*R2*O1	88.4 (6)	*R2*C2–*R2*O2–Co2	124 (1)

TABLE IV

EXPERIMENTAL VALUES OF THE FIELD-INDEPENDENT SUSCEPTIBILITY PER Ni ATOM OF $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ BETWEEN 1.6 AND 296°K WHERE $\mu_{eff} = 2.8273(\chi'_A T)^{1/2}$

T, °K	$10^6\chi'_A$,[a] cm^3 g-atom^{-1}	μ_{eff}, BM	T, °K	$10^6\chi'_A$,[a] cm^3 g-atom^{-1}	μ_{eff}, BM
1.63	2,582,000	5.80	123.5	12,800	3.56
4.25	832,800	5.32	136.5	11,000	3.46
7.4	427,900	5.03	158.5	9,160	3.41
13.3	228,000	4.92	187.0	7,580	3.37
21.0	141,000	4.86	206.5	6,790	3.35
24.6	116,000	4.78	221.5	6,300	3.34
32.2	83,100	4.62	228.0	6,080	3.33
43.5	55,700	4.40	241.5	5,680	3.31
52.5	42,500	4.22	258.0	5,270	3.30
64.0	32,000	4.04	272.0	4,950	3.28
84.0	20,600	3.72	296.0	4,630	3.31
105.5	15,500	3.61			

[a] Diamagnetic correction -88.8×10^{-6} cm^3 g-atom^{-1}.

Figure 5 shows the magnetization curve determined at 1.63°K. The ordinate in this plot, $\langle\mu\rangle$ per tetramer, is the component along the field direction of the magnetic moment per tetramer molecule.

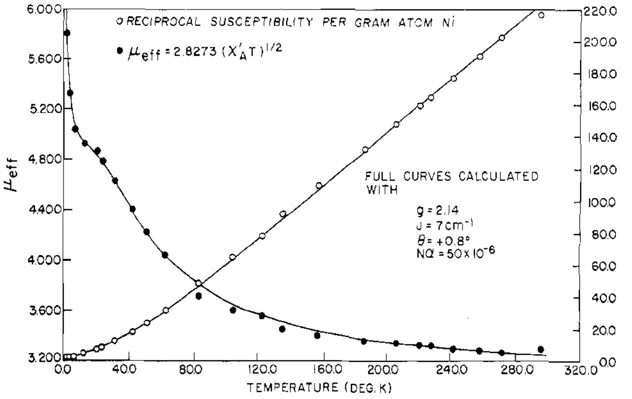

Figure 4.—Temperature dependence of μ_{eff} (BM) per Ni atom and $1/\chi'_A$ for $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$.

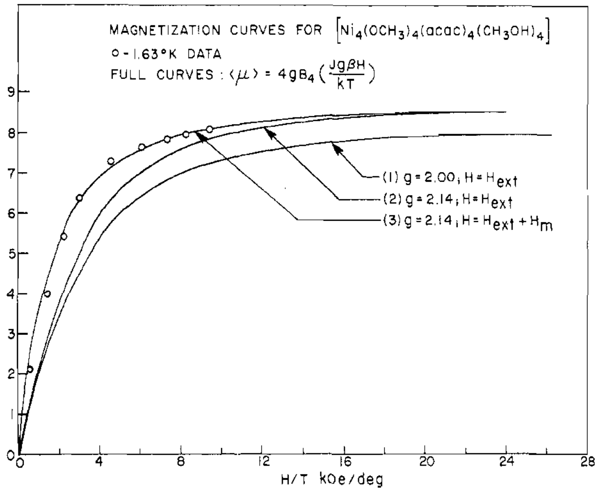

Figure 5.—Magnetization curves for $Ni_4(OCH_3)_4(acac)_4$-$(CH_3OH)_4$. Full curves are calculated Brillouin functions. The circles are experimental data taken at 1.63°K.

Discussion

At 296°K, μ_{eff} = 3.31 BM per Ni atom, a value in the range observed for octahedrally coordinated nickel(II) complexes with a $^3A_2$ ground state arising from the configuration $t_{2g}^6e_g^2$. This suggests that the spin coupling between the four nickel atoms is extremely weak and that all the levels of the Ni_4 spin manifold have been populated in accord with the Boltzmann distribution at room temperature. As the temperature is lowered, μ_{eff} increases steadily showing an inflection between 10 and 25°K and having the value 4.86 BM at 21°K. At lower temperatures μ_{eff} continues to increase, reaching 5.80 BM at 1.63°K.

Comparison with the theoretical curves in Figure 2 indicates that J must be positive; *i.e.*, the unpaired e_g electrons of the four Ni atoms are ferromagnetically coupled. However, rather than showing a low-temperature plateau when μ_{eff} has reached the range for the spin-aligned state (an S' = 4 state of the tetramer, in which all eight e_g spins are coupled parallel, corresponds to a μ_{eff} of 4.70–4.92 BM for g = 2.1–2.2), the experimental curve merely exhibits an inflection and then continues rising with decreasing temperature. We attribute the low-temperature increase in μ_{eff} to a weak

TABLE V

COMPARISON OF MAGNETIC PARAMETERS FOR FERROMAGNETIC POLYNUCLEAR NICKEL(II) CLUSTERS

Compd	Structure type	Temp range studied, °K	g	J, cm^{-1}	J_{31}, cm^{-1}	θ for intercluster interaction, deg	Ref
$Ni_3(acac)_6$	Linear trimer	0.365–296	2.06	26	−7	−0.2	1a, 5
$Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$	"Cubane" tetramer	1.63–296	2.14	7	. . .	+0.8	This work
$Ni_4(OCH_3)_4(sal)_4(CH_3OH)_4$[a]	"Cubane" tetramer	80–300	2.21	4	. . .	b	6, 7
$Ni_4(OCH_3)_4(sal)_4(C_2H_5OH)_4$[a]	"Cubane" tetramer	80–300	2.17	7	. . .	b	6, 7
$Ni(OCH_3)Cl$	Interconnected "cubane" tetramer	80–300	2.22	3	. . .	b	13
$Ni(OCH_3)Cl(CH_3OH)$	Interconnected "cubane" tetramer	80–300	2.23	11	. . .	b	13
$Ni(OCH_3)Cl(CH_3OH)_2$	"Cubane" tetramer	80–300	2.25	8	. . .	b	13
$Ni(OCH_3)Br(CH_3COCH_3)_2$	"Cubane" tetramer	80–300	2.15	4	. . .	b	13

[a] Sal = o-OC_6H_4CHO. [b] Not studied at low enough temperature to detect intercluster interaction.

lattice ferromagnetic interaction between the tetramer molecules in the $S' = 4$ state. In support of this hypothesis we note that the susceptibility data from 1.63 to 21.0°K follow a Curie–Weiss law with a Weiss constant $\Theta = +0.8°$ and a slope which gives an effective magnetic moment of 4.78 BM per Ni atom; the latter corresponds to an $S' = 4$ state of the tetramer molecules with $g = 2.14$.

The magnetization data in Figure 5 provide further support for the existence of a weak ferromagnetic interaction between the tetramer molecules in their spin-aligned ground state. The solid curves in Figure 5 are plots of the Brillouin function

$$\langle\mu\rangle = gS'B_{S'}(x) = gS'\left[\frac{2S'+1}{2S'}\coth\left(\frac{2S'+1}{2S'}\right)x - \frac{1}{2S'}\coth\frac{x}{2S'}\right] \qquad (6)$$

where $x = (H/T)(Jg\beta/k)$. Curves 1 and 2 were calculated, respectively, for $g = 2.00$ and 2.14 with H in eq 6 taken as the applied external magnetic field H_{ext}. Evidently, $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ is more easily magnetized than a paramagnetic (*i.e.*, $H = H_{ext}$) tetramer with $g = 2.00$ or 2.14. It is also clear from Figure 5 that simply increasing g will not enable eq 6 to fit the magnetization data. In curve 3, the effect of interaction between the tetramer molecules was introduced by setting[12] $H = H_{ext} + H_m$ where H_m is the molecular field. In the classical molecular field theory[12] H_m is assumed to be proportional to the magnetization M, so that

$$H_m = N_wM = N_wN\beta\langle\mu\rangle \qquad (7)$$

The molecular field constant N_w is related to the Weiss constant by the equation

$$N_w = \frac{3k\Theta}{Ng^2\beta^2S'(S'+1)} \qquad (8)$$

For $\Theta = +0.8°$ and $g = 2.14$, eq 7 and 8 give $H_m = 390\langle\mu\rangle$. This relation was used in calculating curve 3, which is in excellent agreement with the experimental results.

In order to permit eq 5 to take account of the interaction between the tetramer molecules, T in the coefficient $3K/T$ was replaced by $T - 0.8$. The least-squares best fit of this modification of eq 5 to the experimental susceptibilities is found for $g = 2.14$, $J = 10°$ ($\equiv 7$ cm^{-1}), and $N\alpha = 50 \times 10^{-6}$ cm^3 g-atom^{-1}. Figure 4 shows the comparison between experiment and theory; the agreement is good. The use of $N\alpha$ as an adjustable parameter in the fitting procedure does not materially affect the values obtained for g and J. Thus, if $N\alpha$ is fixed at 230×10^{-6} (the value we used for $Ni_3(acac)_6$[1a]) the best fit is obtained for $g = 2.13$ and $J = 10°$.

In summary, we consider that our magnetic measurements strongly support the following conclusions. (1) The spins on the four Ni atoms in the $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ tetramer interact ferromagnetically with an exchange integral of 7 cm^{-1}. (2) The molecular ground state of the tetramer is fully populated by 21°K and has total spin $S' = 4$ corresponding to eight electrons with their spins parallel. (3) The tetramer molecules in their ground state interact ferromagnetically with a paramagnetic Curie point (Weiss constant) of +0.8°. $Ni_3(acac)_6$, the only other ferromagnetic cluster so far studied at low enough temperatures to fully populate the molecular ground state, also showed interactions between the cluster units, but in this case the interaction was antiferromagnetic.

Table V shows a comparison of the magnetic parameters that have been determined for ferromagnetic Ni clusters. Except for $Ni_3(acac)_6$ and $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$, measurements have been restricted to the range 80–300°K, so that intercluster interactions were not detected. It is of interest that all of the "cubane"-type clusters have similar exchange integrals (3–11 cm^{-1}) while the exchange integral for adjacent Ni atoms in $Ni_3(acac)_6$ is considerably larger. Andrew and Blake[7] have commented on this point.

The major contribution to J in these "cubane"-type tetramers is certainly that due to superexchange *via* methoxide bridging groups rather than to the direct overlap of Ni–Ni orbitals. The Ni–Ni distance along the side of the Ni_4 tetrahedron is considerably longer (3.1 Å) than the Ni–Ni distance in nickel metal (2.44 Å); in addition, it is the t_{2g} subset which is oriented correctly for direct Ni–Ni bonding in the cubane struc-

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(12) See, for example, A. H. Morrish. "The Physical Principles of Magnetism," Wiley, New York, N. Y., 1965, Chapter 6.

(13) A. G. Krüger and G. Winter, *Aust. J. Chem.*, in press.

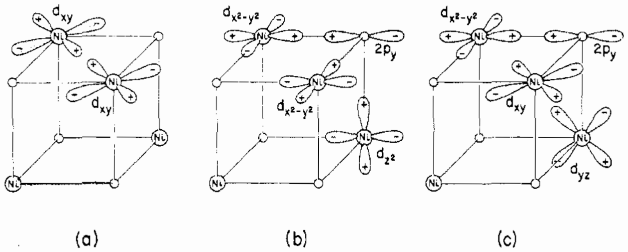

Figure 6.—(a) Orientation of t_{2g} (say, d_{xy}) orbitals along the edges of an Ni_4 tetrad. (b) Orientation of e_g orbitals of three Ni atoms with respect to a $2p_y$ orbital of the bridging methoxide group. (c) Orientation of a $2p_y$ orbital of a bridging methoxide group with respect to the e_g orbital of one Ni atom and t_{2g} orbitals of two other Ni atoms.

ture, but this subset has no unpaired electrons for participation in metal-metal bonding (see Figure 6a).

Following the more recent viewpoint of Anderson,[14,15] the ferromagnetic sign of the spin interaction constant J can be qualitatively rationalized from the symmetry relationships between the e_g and t_{2g} orbitals of the four nickel and the s and p orbitals of the four bridging methoxide groups. We assume here an idealized geometry with Ni–O–Ni angles of 90° with p_x, p_y, and p_z orbitals lying along the edges of the Ni_4O_4 cube (*i.e.*, true T_d symmetry). The predominant contributions to J are as follows.

(i) $d_{x^2-y^2}(Ni_I)$–$2p_y$(O)–$e_g(Ni_{II}, Ni_{III})$ Pathway (Figure 6b).—Unpaired spin density (say α) initially in $d_{x^2-y^2}$ on Ni_I is transferred into a $2p_y$ orbital of oxygen. Since the $2p_y$ orbital is orthogonal both to $d_{x^2-y^2}(Ni_{II})$ and $d_{z^2}(Ni_{III})$, the interatomic direct exchange term is ferromagnetic so that the e_g electrons of Ni_{II} and Ni_{III} will also have α spin.

(ii) $d_{x^2-y^2}(Ni_I)$–$2p_y$(O)–$t_{2g}(Ni_{II}, Ni_{III})$ Pathway (Figure 6c).—Since the $2p_y$ orbital is not orthogonal to either $d_{xy}(Ni_{II})$ or to $d_{yz}(Ni_{III})$, α spin can be transferred to these t_{2g} orbitals *via* the superexchange pathway. The intraatomic direct exchange term between the t_{2g} and e_g subsets centered on each of the nickel atoms II and III then ensures that the e_g orbitals of both have α spin.

(iii) $e_g(Ni_I)$–2s(O)–$e_g(Ni_{II}, Ni_{III})$ Pathway.—Since the e_g orbitals all mutually overlap with the spherically symmetrical 2s orbital of the bridging oxygen atom, this superexchange pathway will lead to antiferromagnetic coupling; *i.e.*, if Ni_I has α spin then β spin will reside on Ni_{II} and Ni_{III}. Taken over the whole Ni_4O_4 unit, J is negative and a ground state with $S' = 0$ would be favored.

(iv) $e_g(Ni_I)$–2s(O)–$t_{2g}(Ni_{II}, Ni_{III})$ Pathway.—Since the 2s orbital is orthogonal to the t_{2g} subset on the nickel atoms, this pathway also leads to a direct interatomic exchange term which is ferromagnetic.

The resultant magnitude and sign of J will be the sum of terms of the kinds (i) to (iv). The contribution by each pathway will be determined by the magnitude of the relevant overlap integrals, the Ni–O distance, the Ni–O–Ni angle, and the relative energies of the nickel and oxygen orbitals. In the present case, the combined effect of the ferromagnetic terms (i), (ii), and (iv) predominates over the single antiferromagnetic term (iii).

It is interesting that all of the polynuclear nickel ferromagnets whose crystal structures are known involve Ni–O–Ni angles which deviate considerably from the ideal value of 90°. In $Ni_3(acac)_6$ the bridge angles fall in the range 76–89°; in $Ni_4(OCH_3)_4$(salicylaldehyde)$_4$-$(C_2H_5OH)_4$ the range is 96.7–98.7°; in $Ni_4(OCH_3)_4$-$(acac)_4(CH_3OH)_4$ the range is 94.6–98.6°. This confirms that deviations from 90° of at least ±14° can be tolerated before the direct ferromagnetic exchange terms will cease to be dominant. Finally, we note from the limited information available (*cf.* Table V), the magnitude of J (3–26 cm^{-1}) is quite small; the marked temperature dependence of the effective magnetic moment arises because the total width of the spin manifold, $20J$, is comparable with kT at room temperature ($\sim$200 cm^{-1}).

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[14] P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959).

[15] P. W. Anderson in "Magnetism," Vol. 1, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1963, Chapter 2.