TABLE I

WEIGHTS, COLORS, AND ANALYSES OF METAL OXYFLUOROSULFATES

Compd	Wt, g	Wt of oxyfluorosulfate, g Calcd	Found	Oxyfluorosulfate	Color	Oxyfluorosulfate anal., %	Calcd	Found
$MnCO_3$	0.4680	0.6918	0.6952	$MnOSO_3F$	Brownish black	Mn	32.35	32.05
						S	18.82	18.68
						F	10.83	10.18
$CoCO_3$	0.4480	0.6549	0.6480	$CoOSO_3F$	Chocolate	Co	33.90	33.10
						S	18.39	18.00
						F	10.92	10.62
$NiCO_3$	0.4268	0.6245	0.6292	$NiOSO_3F$	Grayish black	Ni	33.79	33.00
						S	18.42	18.10
						F	10.96	10.64
Ag_2CO_3	0.6284	0.9790	0.9892	$Ag_2O(SO_3F)_2$	Black	Ag	50.23	49.80
Ag_2O	0.5264	0.9756	0.9740	$Ag_2O(SO_3F)_2$	Black	S	14.88	14.52
						F	8.86	8.24
Tl_2CO_3	0.5679	0.7740	0.7654	$TlOSO_3F$	Brown	Tl	63.99	62.54
						S	10.00	9.49
						F	5.95	5.35

Chemical Analysis.—Metals in the compounds were determined using standard methods.[9] Sulfur was determined as barium sulfate, while fluorine was determined using a fluoride ion sensitive electrode while titrating with thorium nitrate solution. Analytical results are given in Table I.

Discussion

The volatile products were found to be CO_2, $S_2O_5F_2$, O_2, unreacted $S_2O_6F_2$, and a trace of SiF_4. Probably the oxygen and pyrosulfuryl fluoride were formed by decomposition of part of the peroxydisulfuryl difluoride. The formation of oxyfluorosulfate from the carbonate of Mn, Co, or Ni can be represented by the general equation: $2MCO_3 + S_2O_6F_2 \rightarrow 2MO(SO_3F) + 2CO_2$ (M = Mn, Co, or Ni).

The oxyfluorosulfates of manganese, cobalt, nickel, and silver react with potassium iodide solution (made acidic with sulfuric acid) liberating both oxygen and iodine. To determine the number of oxidizing equivalents present per mole of the oxyfluorosulfate, it was necessary to measure both oxygen and iodine produced. To do this, a known weight of the salt was allowed to react with gas-free acidic solution of potassium iodide in a closed reactor. The vessel was then chilled to −183° and oxygen was pumped away. The loss in weight was that of the oxygen produced by the reaction. The amount of iodine was then determined by titration with standard sodium thiosulfate solution. Table II gives the results of these determinations and shows that each metal was reduced in oxidation state by one unit by reaction with acidic potassium iodide solution. Since the reduction would give Mn(II), Co(II), Ni(II), and Ag(I), it follows that oxyfluorosulfates contained Mn(III), Co(III), Ni(III), and Ag(II).

TABLE II

REACTIONS OF OXYFLUOROSULFATES WITH ACIDIC SOLUTION OF POTASSIUM IODIDE

Compd	Mol of salt $\times 10^3$	Mol of O_2 produced $\times 10^4$	Equiv of I_2 produced $\times 10^4$	Total equiv of $O_2 + I_2$ per mol of the salt
$MnOSO_3F$	5.98	14.18	5.75	1.04
$CoOSO_3F$	3.76	8.56	5.06	1.04
$NiOSO_3F$	4.39	10.81	5.01	1.09
$Ag_2O(SO_3F)_2$	0.83	3.75	1.70	2.01

Infrared spectra of the compounds were taken in the form of Nujol mulls between silver chloride disks. The instrument was a Beckmann IR 10 spectrometer. Since the compounds are good oxidizing agents, some of them may have reacted with Nujol. The spectra of $CoOSO_3F$ and $NiOSO_3F$ appeared to be of good quality. Peaks remaining after subtracting those for Nujol are listed in Table III. Spectra for salts of Mn, Ag, and Tl contained bands for S—F and S═O stretching in regions characteristic of fluorosulfates. Because of their rather poor quality in general, these spectra are not given.

TABLE III

INFRARED SPECTRA OF OXYFLUOROSULFATES[a]

CoO-SO_3F	NiO-SO_3F	Assignment	CoO-SO_3F	NiO-SO_3F	Assignment
1246 vs	1246 vs	S–O asym str	607 s	615 s	S–O asym def
1081 vs	1088 vs	S–O sym str	560 s	560 s	S–O sym def
832 vs	820 vs	S–F str	504 s	505 s	

[a] Key: vs, very strong; s, strong.

The S—F band in fluorosulfates of copper and iron has been reported around 840 cm^{-1} and the salts are believed to be covalent in nature.[10] The S—F band in these oxyfluorosulfates is around 840 cm^{-1} which is more characteristic of covalently bonded fluorosulfates rather than ionic fluorosulfates like potassium fluorosulfate, the S—F frequency for which is 750[10] or 732 cm^{-1}.[11]

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research.

---

[8] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[9] A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1963.

[10] J. Gobeau and J. B. Milne, *Can. J. Chem.*, **45**, 2321 (1967).

[11] A. G. Sharpe, *J. Chem. Soc.*, 3761 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA 27514

The Low-Temperature Magnetic Susceptibility of Tetra-μ_3-methoxy-tetrakis[salicylaldehydato(ethanol)nickel(II)], a Complex with a Positive Exchange Coupling Constant

BY JAMES A. BARNES AND WILLIAM E. HATFIELD*

Received February 19, 1971

The existence of multimetallic molecules which exhibit intramolecular magnetic exchange has been well known for many years, but until recently all documented examples of intramolecular exchange have involved systems with a negative coupling constant, J, resulting in a singlet ground state. The copper acetate monohydrate dimer is perhaps the best known example of this type of behavior.[1] In the last few years, the existence of positive coupling constants for several multimetallic systems has been clearly demonstrated.[2-7] The first example of a positive J value to be identified was in the linear, trimeric complex bis(acetylacetonato)nickel(II), $Ni_3(acac)_6$.[2] This complex was characterized in terms of two coupling constants, one describing the interaction between adjacent nickel atoms and the other describing the coupling between the two terminal atoms of the linear trimer. The first constant was found to have a value of $+26\ cm^{-1}$, while the latter was found to equal $-7\ cm^{-1}$.

The second complex with a positive J to be reported[3,4] was tetra-μ_3-methoxy-tetrakis[salicyaldehydato(ethanol)nickel(II)]. The crystal structure of this complex has been reported[4] to contain four nickel atoms in a tetrahedron with each face occupied by a bridging methoxy group. The groups of four nickel atoms and four bridging oxygen atoms have exactly D_{2d} symmetry and are both within 1% of T_d symmetry. Ni-Ni separations are about 3.07 Å, Ni-O-Ni angles are 96.7-98.7°, and Ni-bridging O distances are 2.02-2.05 Å, while O-Ni-O angles are 80.9-82.5°. Each nickel atom in the Ni_4O_4 group is also bonded to an oxygen from the alcohol and the two oxygens from the salicylaldehyde.

Unfortunately, in their work,[3,4] Andrew and Blake were unable to extend their magnetic susceptibility measurements below 89°K. Thus while they were able to describe their experimental data in terms of a positive coupling constant, their $1/\chi_M$ *vs.* T curve did not show the low-temperature deviation from Curie-Weiss behavior which is characteristic of systems with positive coupling constants.[2] We have measured the magnetic susceptibility of this complex from 61.1 to 2.75°K. Our data clearly demonstrate this deviation from Curie-Weiss behavior and allow more complete discussion of the magnetic coupling present in this complex.

Experimental Section

$[Ni(CH_3O)(o\text{-}OC_6H_4CHO)(C_2H_5OH)]_4$ was prepared as previously reported.[4,8] *Anal.* Calcd: C, 46.7; H, 5.5. Found: C, 46.63; H, 5.48.

Comparison of the powder pattern data measured for this sample of $[Ni(CH_3O)(sal)(C_2H_5OH)]_4$ with the expected lines calculated from the reported crystal structure[4] confirmed the structure of our sample.

Magnetic susceptibility measurements were made using a Foner-type vibrating-sample magnetometer[9] manufactured by Princeton Applied Research, Inc. Measurements were made on a sample contained in a sealed Lucite sample holder. Because of the field dependence of the susceptibility, which is discussed in detail in the next section, measurements were made at fields of 10,000, 7500, 5000, and 2500 G. The magnetometer was calibrated with a sample of Johnson, Matthey & Co. spectroscopically pure nickel. The calibration was confirmed by measurements on a sample of $Hg[Co(SCN)_4]$.[10] All data were corrected for diamagnetism of the sample holder assembly. Tem-

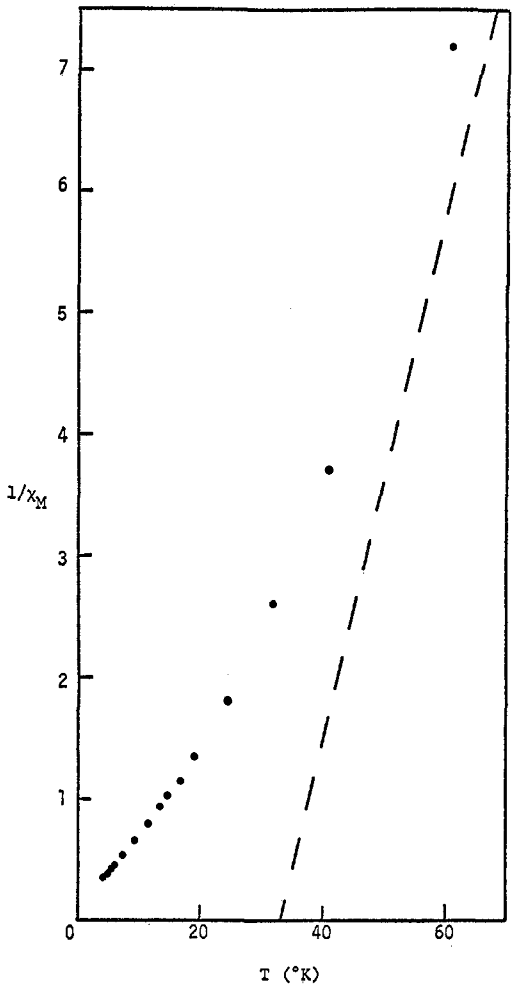

Figure 1.—The inverse of the magnetic susceptibility *vs.* temperature curve for $[Ni(CH_3O)(sal)(C_2H_5OH)]_4$. The dotted line is an extrapolation of the Curie-Weiss behavior exhibited by the complex at higher temperatures, as reported in ref 4.

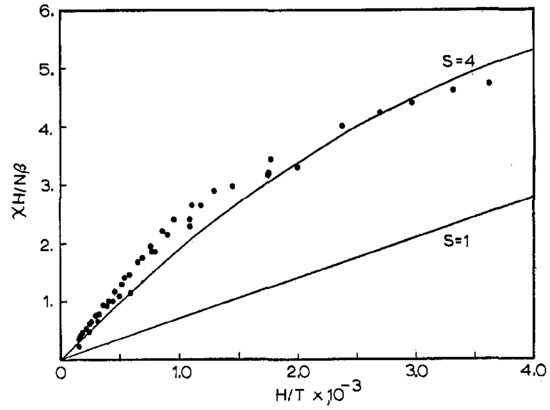

Figure 2.—Magnetization data for $[Ni(CH_3O)(sal)(C_2H_5OH)]_4$. The lines are the calculated Brillouin functions for a tetramer with $S = 4$ and for four noncoupled $S = 1$ spins.

---

(1) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(2) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Chem. Commun.*, 856 (1967); *Inorg. Chem.*, **7**, 932 (1968).

(3) J. E. Andrew and A. B. Blake, *Chem. Commun.*, 1174 (1967).

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

(5) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, unpublished results, quoted by R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968.

(6) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and R. Jones, *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

(7) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970); J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *ibid.*, 1593 (1970).

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

(9) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

(10) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

peratures below 4.2°K were obtained by pumping on the liquid helium coolant. Temperatures were measured with a calibrated, precision germanium resistance thermometer.

Results and Discussion

Magnetic susceptibility data are shown in Figures 1 and 2. Data have been corrected for the diamagnetism of the constituent atoms using Pascal's constants[11] (-120×10^{-6} cgsu/g-atom of nickel) and for the TIP of nickel ($+235 \times 10^{-6}$ cgsu/g-atom of nickel).

The measurements of the field-dependent magnetic susceptibilities are displayed in Figure 2, and the experimental data are compared there to the magnetization of an $S = 4$ spin state which is predicted by the Brillouin function

$$\langle \mu \rangle = 2SB_s(x) = 2S\left[\frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}\right)x - \frac{1}{2S}\coth\left(\frac{x}{2S}\right)\right]$$

where $x = 2S\beta H/kT$. The agreement between experiment and theory is sufficient to permit the conclusion that the $S = 4$ spin state is the ground state especially when contrasted with the calculated magnetization for a system containing four noninteracting nickel ions. The divergence between the calculated and experimental magnetizations probably reflects the neglect of zero-field splittings and other interactions between the magnetic clusters.

The molar susceptibility data were interpreted using the theoretical equation for this system[12]

$$\chi = [4Ng^2\beta^2/kT]\left[\sum_i(a_i\exp(c_ix))/\sum_i(b_i\exp(c_ix))\right] \quad (1)$$

where $x = J/kT$; and $a_i = 5, 7, 5, 1, 0$; $b_i = 3, 7, 10, 6, 1$; $c_i = 20, 12, 6, 2, 0$ for $i = 1, 2, 3, 4, 5$. The use of a single coupling constant is reasonable in light of the almost T_d symmetry of the system. The experimental data were fitted to this equation using a weighted least-squares fitting program. The term $\Sigma_i[(\chi_{i\text{calcd}} - \chi_{i\text{exptl}})T_i]^2$ was minimized instead of the more common deviation without the temperature weighting factor. This modification is necessary in systems such as the present one if susceptibility data from a wide range of temperatures are to be of equal importance in the curve-fitting process. This fitting process and the general shape of the $1/\chi$ *vs.* T curve confirm that $J = 4$–8 cm^{-1} when g is any reasonable number. Unfortunately the field dependence of the magnetic moment below about 15°K makes it very difficult to calculate a single set of g and J values that will describe the data over the whole temperature range measured. In addition, weak lattice magnetic interactions may be expected to be operative and become increasingly important at low temperatures.

The nature of the field dependence of the susceptibility in the present system is extreme. In the present system the total spin is $S = 4$, and when $J > 0$, the first-order Zeeman splitting of the ground state results in nine separate energy levels. Thus, even in the absence of zero-field splittings, the energy span of the ground state is $8g\beta H$, so that at 10,000 G, the ground-state Zeeman levels span several wave numbers.

Reducing the field strength at which measurements were made helped to reduce the field dependence problem, but we were unable to lower field dependence effects below observable limits without using impractically weak magnetic fields. Therefore, while the data chosen for further discussion represent the best available, they are not ideal.

The $1/\chi_M$ *vs.* T curve for the tetramer is shown in Figure 1. The data between 4.26 and 17°K are those measured at 2500 G. Above 17°K, field effects seem to be small. Data between 17 and 61.1° were measured with the magnetometer at 10,000 G. Data between 2.75 and 4.2°K are not included; they were measured at 10,000 G and therefore exhibit significant field dependence.

Values for χ_M^{cor} were fitted to eq 1 in several groups. The best fit for the data above 80°K was found when $g = 2.145$ and $J = 7.46$ cm^{-1}. These numbers are slightly different from those reported by Andrew and Blake.[3,4] Their values, $g = 2.17$ and $J = 6.88$ cm^{-1}, were apparently calculated using a normal least-squares fitting technique; they represent a slightly poorer fit than the present calculation. (The minimized sum of squares of deviations for our values is slightly better than that calculated with the parameters suggested by Andrew and Blake.)

Unfortunately the fitting process was not as satisfying when measurements between 9.55 and 61.10°K were included in the data set. (Data between 4.26 and 7.55°K were not used because of the presence of field effects even at a field strength of 2500 G.) The best fit for the 302–9.55°K data set was obtained when $g = 2.387$ and $J = 4.97$ cm^{-1}. The weakness of this fit is demonstrated by the fact that the sum of squares of the deviations is larger than those calculated only for the high-temperature data, but these parameters describe all of the data much better than did the parameters calculated from the high-temperature data alone; when the latter parameters are used to fit the whole data set, the sum of squares of the deviations rises by a factor of 4.

Though there is some uncertainty as to the exact value of the magnetic parameters, it is clear that the sign of J is positive. The presence of a positive coupling constant is confirmed dramatically by the characteristic deviation of the $1/\chi$ *vs.* T plot from Curie–Weiss behavior as is shown in Figure 1.

It is of interest to note that in the tetramer $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$, the nickel spins are also ferromagnetically coupled[13] with $J = +7$ cm^{-1}.

Acknowledgments.—This research was supported in part by the National Science Foundation under Grant GP-7400 and by the Materials Research Center of the University of North Carolina through Contract SD-100 with the Advanced Research Projects Agency. We wish to thank Mr. Guy W. Inman for experimental assistance.

---

(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

(12) This equation, as reported in ref 3 and 4, was in error by a factor of 3. This error was not present in the calculations reported in these references.

(13) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971).