contribution from the change in coordination number would occur.[2a] This may contribute, at least in part, to the difference observed in Table IV between dimer and polymer complexes.

A recent matrix isolation investigation[11] in the far-infrared region for $CoCl_2$ appears to give parallel results to those obtained for the $CoL_2Cl_2$ complexes. In the dimeric $(CoCl_2)_2$ molecule (CN = 4), the Co–Cl bridge-

bond stretchings are observed at 323 and 289 cm$^{-1}$, and the terminal CoCl stretching is found at $\sim$432 cm$^{-1}$. Thus, the $\nu_b$CoCl (dimer)/$\nu_t$CoCl(dimer) is about 0.74. In monomeric $CoCl_2$ (CN = 2), the asymmetric $\nu_{CoCl}$ is found at 492 cm$^{-1}$ (the symmetrical vibration is not observed in the infrared region). The ratio of $\nu_b$CoCl (dimer)/$\nu_t$CoCl(monomer) is 0.62 and is observed to be less than the ratio $\nu_b$CoCl(dimer)/$\nu_t$CoCl(dimer).

# Interpretation of the Magnetic Properties of Pfeiffer's Cation, Cr₄(OH)₆(en)₆⁶⁺

BY M. T. FLOOD,[1a] C. G. BARRACLOUGH,[1b] AND HARRY B. GRAY

Magnetic susceptibility data for [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O are reported from 300 to 4.2°K. The observed antiferromagnetic behavior is satisfactorily accounted for on the basis of the Heisenberg–Dirac–Van Vleck spin–spin coupling model derived from a rhomboid arrangement of the four interacting chromium(III) atoms.

## Introduction

The interpretation of the temperature dependence of the magnetic susceptibility of "Pfeiffer's cation," Cr₄(OH)₆(en)₆⁶⁺, has been a subject of recent interest. Susceptibility measurements on [Cr₄(OH)₆(en)₆]I₆·4H₂O from room temperature to 77°K were originally interpreted[2a] using as a model a trigonal-planar array of four chromium(III) atoms. Although from analogy to Werner's[2b] Co[(OH)₂Co(NH₃)₄]₃⁶⁺ a trigonal-planar model is reasonable, it was subsequently pointed out[3] that the experimental magnetic data down to 77°K could be better explained by a tetrahedral array of four equivalent chromium(III) atoms.

The tetrahedral model, however, failed when susceptibility measurements on [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O were carried out from room to liquid helium temperature; these data were presented in a preliminary communication along with the results of an X-ray structural study, which revealed a rhomboid arrangement of the four chromiums.[4] In this paper we present a full report of the magnetic susceptibility data for [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O and an associated theoretical interpretation on the basis of the Heisenberg–Dirac–Van Vleck spin–spin coupling model.[5]

## Experimental Section

**Preparation of [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O.**—Crude [Cr₄(OH)₆(en)₆](SO₄)₃ was prepared according to the method of Pfeiffer.[6]

To the solid sulfate, a small quantity of water was added to form a paste. Concentrated hydrochloric acid was then added dropwise with mixing until the solid completely dissolved. After filtration, solid reagent grade sodium azide was added to the solution with stirring. A red precipitate of [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O formed almost immediately. The solid was washed with absolute ethanol and dried with ethyl ether. It was then dissolved in a minimum quantity of water and reprecipitated by adding solid sodium azide. After washing with water and absolute ethanol and drying with ethyl ether, the azide salt was dissolved again in a minimum amount of water and then diluted with half the original amount of water necessary to dissolve the compound. To the solution solid sodium azide was added and allowed to dissolve; then the solution was cooled to about 5°. After several hours, dark red crystals formed on the sides of the container. These were washed with water, absolute ethanol, and ether, and then air dried. A single-crystal X-ray diffraction study has shown[4] the exact formulation of the crystalline compound to be [Cr₄(OH)₆(en)₆](N₃)₆·4H₂O.

**Spectral Measurements.**—Visible spectra were obtained with a Cary Model 14 RI recording spectrophotometer. At liquid nitrogen temperatures, a dewar constructed in these laboratories was used. A sample of [Cr₄(OH)₆(en)₆][B(C₆H₅)₄]₆ for low-temperature study was obtained by adding a concentrated aqueous solution of sodium tetraphenylboron to an aqueous solution of the azide salt. The low-temperature (77°K) medium employed was a frozen solution of 2-methyltetrahydrofuran (freshly distilled from LiAlH₄) and methanol (degassed) in the volume ratio of 2:1, respectively.

**Magnetic Measurements.**—Magnetic susceptibilities were determined using a Princeton Applied Research FM-1 vibrating sample magnetometer using a liquid helium dewar obtained from Andonian Associates, Inc. Temperatures were measured on a Leeds and Northrup potentiometer using a copper–constantan thermocouple calibrated at low temperatures against a calibrated carbon resistor. Because of the insensitivity of the thermocouple to temperature changes at very low temperatures, accurate measurements were not possible in the temperature range 30–4.2°K. The liquid helium point, however, could be accurately determined by the final (and maximum) value of the susceptibility.

## Theoretical Section

The magnetic properties of the Cr₄(OH)₆(en)₆⁶⁺ cation (en = ethylenediamine) may be quantitatively inter-

(1) (a) National Science Foundation Fellow, Columbia University, 1964–1967. (b) On leave from University of Melbourne, Melbourne, Victoria, Australia.
(2) (a) R. A. D. Wentworth and R. Saillant, *Inorg. Chem.*, **6**, 1436 (1967); (b) A. Werner, *Ber.*, **47**, 3087 (1914).
(3) C. G. Barraclough, H. B. Gray, and L. Dubicki, *Inorg. Chem.*, **7**, 844 (1968).
(4) M. T. Flood, R. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 193 (1969).
(5) J. S. Smart in "Magnetism," G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1960, Chapter II.
(6) P. Pfeiffer, *Z. Anorg. Allgem. Chem.*, **58**, 286 (1908).

preted by allowing for spin–spin coupling between the Cr(III) ions within the molecule. The four chromium atoms are arranged in a rhombus as shown in I,



I
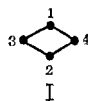
with Cr–Cr distances:[4]  Cr(1)–Cr(2) = 2.93 Å, Cr(1)–Cr(3) = 3.61 Å, and Cr(3)–Cr(4) = 6.55 Å. For this system the spin–spin coupling is assumed to be described by the Hamiltonian

$$\mathcal{H}_{spin} = -2J(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_4 + \hat{S}_2\cdot\hat{S}_4) - 2J_{12}\hat{S}_1\cdot\hat{S}_2$$

The very large distance between Cr(3) and Cr(4) makes it unlikely that any significant spin–spin interaction can occur between these atoms, so this interaction has been taken as zero. $\hat{S}_i$ denotes the spin operator for the $i$th atom, and $J$ and $J_{12}$ are interaction constants.

By extending the method used by Kambe[7] for a trinuclear cluster, the magnetic moment associated with the above Hamiltonian can readily be derived. Let

$$S^* = \hat{S}_1 + \hat{S}_2$$
$$S^+ = \hat{S}_3 + \hat{S}_4$$
$$S^T = S^* + S^+$$

Using the vector model the eigenvalues of the Hamiltonian are

$$E_{spin}(S^T, S^*, S^+, S) = -J\{S^T(S^T + 1) - S^+(S^+ + 1) - S^*(S^* + 1)\} - J_{12}\{S^*(S^* + 1) - 2S(S + 1)\}$$

$S^T$, $S^*$, $S^+$, and $S$ are the quantum numbers associated with the spin operators $S^T$, $S^*$, $S^+$, and $\hat{S}$.

For each of the four Cr(III) atoms $S = 3/2$, so both $S^*$ and $S^+$ can take the values of 3, 2, 1, and 0. Table I shows the allowed values of $S^T$, $S^*$, and $S^+$.

When an external magnetic field ($H$) is applied to the molecule along a direction which we arbitrarily define as the $Z$ axis, the Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_{spin} - g\beta S^T_z H$$

Here $S^T_z$ is the operator for the $z$ component of $S^T$ and $g$ is the Lande splitting factor associated with the total spin operator $S_i$. However, $S^T$ is just the linear sum of the individual $S_i$ so $g$ is equal to the $g$ value of the individual Cr(III) atoms.

The eigenvalues are now

$$E(S^T, S^*, M_sT) = E_{spin}(S^T, S^*, S^+) - g\beta M_sTH$$

where $M_sT$ can take the values $S^T$, $S^T - 1$, ..., $-S^T$. Putting these energies into the standard Van Vleck formula the result can be expressed as

$$\mu_{eff}^2 = \frac{g^2\Sigma S^T(S^T + 1)(2S^T + 1)\exp(-E_{spin}(S^T, S^*, S^+)/kT)}{\Sigma(2S^T + 1)\exp(-E_{spin}(S^T, S^*, S^+)/kT)}$$

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

### TABLE I
### Allowed Quantum Numbers

| $S^*$ | $S^+$ | $S^T$ |
|---|---|---|
| 3 | 3 | 6, 5, 4, 3, 2, 1, 0 |
| 3 | 2 | 5, 4, 3, 2, 1 |
| 2 | 3 | 5, 4, 3, 2, 1 |
| 3 | 1 | 4, 3, 2 |
| 1 | 3 | 4, 3, 2 |
| 3 | 0 | 3 |
| 0 | 3 | 3 |
| 2 | 2 | 4, 3, 2, 1, 0 |
| 2 | 1 | 3, 2, 1 |
| 1 | 2 | 3, 2, 1 |
| 2 | 0 | 2 |
| 0 | 2 | 2 |
| 1 | 1 | 2, 1, 0 |
| 1 | 0 | 1 |
| 0 | 1 | 1 |
| 0 | 0 | 0 |

### TABLE II
### Magnetic Susceptibility Data for
### $[Cr_4(OH)_6(en)_6](N_3)_6\cdot 4H_2O$

| Temp, °K | $\chi_M$ (cor for diamagnetism), cm³/mol | $\mu_{eff}^2$, BM |
|---|---|---|
| 296.3 | 0.0202 | 47.8 |
| 292.9 | 0.0204 | 47.7 |
| 285.8 | 0.0210 | 47.6 |
| 273.8 | 0.0213 | 46.6 |
| 268.3 | 0.0216 | 46.3 |
| 265.7 | 0.0217 | 46.2 |
| 254.6 | 0.0224 | 45.5 |
| 244.4 | 0.0230 | 44.9 |
| 236.9 | 0.0234 | 44.4 |
| 228.5 | 0.0240 | 43.8 |
| 224.4 | 0.0241 | 43.3 |
| 204.2 | 0.0257 | 42.0 |
| 187.3 | 0.0274 | 41.0 |
| 173.5 | 0.0287 | 39.8 |
| 167.3 | 0.0293 | 39.2 |
| 154.5 | 0.0307 | 38.0 |
| 134.8 | 0.0333 | 35.9 |
| 120.6 | 0.0352 | 33.9 |
| 109.3 | 0.0366 | 32.0 |
| 97.0 | 0.0398 | 30.9 |
| 84.2 | 0.0430 | 29.0 |
| 80.0 | 0.0442 | 28.3 |
| 78.2 | 0.0446 | 27.9 |
| 77.5 | 0.0450 | 27.9 |
| 77.4 | 0.0459 | 28.4 |
| 71.4 | 0.0471 | 26.9 |
| 49.0 | 0.0602 | 23.6 |
| 39.3 | 0.0693 | 21.8 |
| 38.2 | 0.0709 | 21.7 |
| 37.2 | 0.0726 | 21.6 |
| 34.5 | 0.0773 | 21.3 |
| 33.9 | 0.0798 | 21.6 |
| 32.3 | 0.0823 | 21.4 |
| 31.4 | 0.0847 | 21.2 |
| 29.9 | 0.0884 | 21.1 |
| 4.2 | 0.407 | 13.6 |

The sum is over the allowed values of $S^T$, $S^*$, and $S^+$ as given in Table I. The equation for $S = 3/2$, as well as equations for the trigonal-planar and tetrahedral models, is listed in the Appendix.
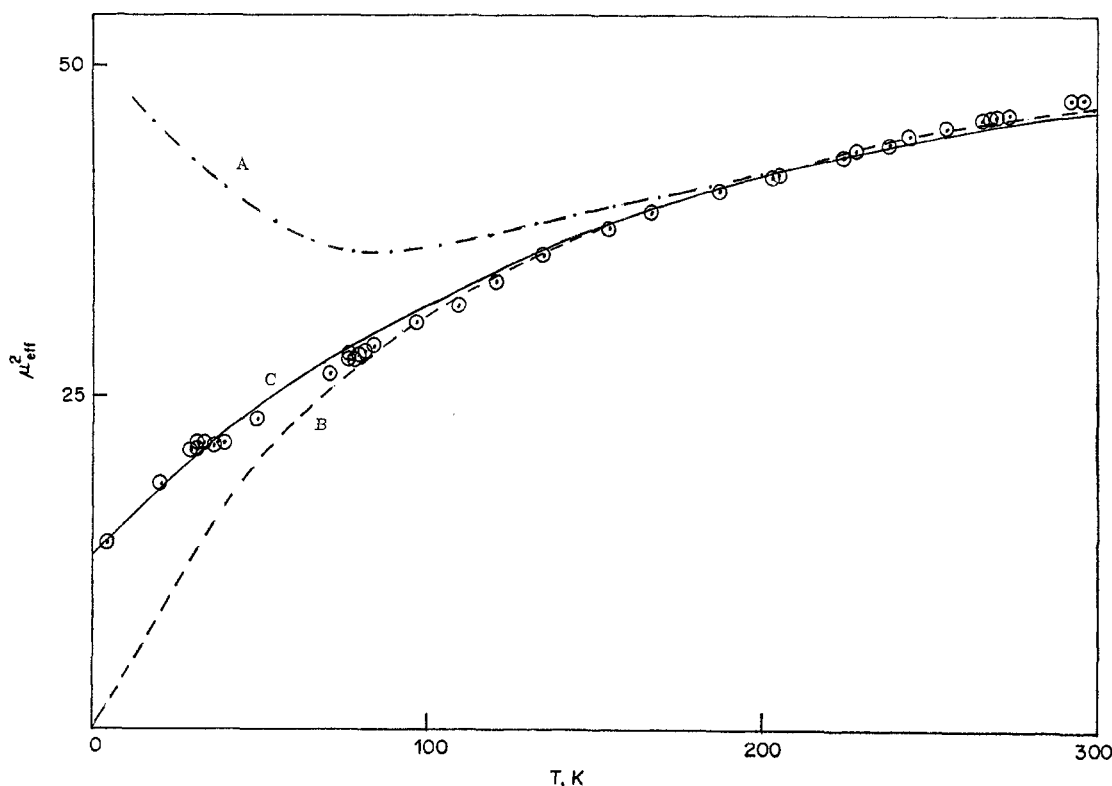
Figure 1.—Effective magnetic moment squared (calculated per tetranuclear ion) *vs.* temperature calculated for a trigonal-planar model (curve A, $J = -20k$), tetrahedral model (curve B, $J = -10k$), and planar-rhomboid model (curve C, $J = -10.5k$, $J_{12} = -20k$). Experimental data are indicated by the dotted circles.

## Results and Discussion

The experimental values of the magnetic susceptibility over the temperature range 4.2–300°K are given in Table II. Figure 1 shows a comparison of the experimental results with the theoretical equation for the rhomboid model assuming $J = -10.5k$, $J_{12} = -20k$, and $g = 2.00$. The agreement between theory and experiment is seen to be quite satisfactory. It should be noted, however, that the suggested fit of the magnetic data is not unique, and a small variation in the $J$ values results on changing the assumed $g$ value. For example, for $g = 1.98$, a fit essentially as satisfactory as curve C may be constructed with $J = -10k$ and $J_{12} = 19k$.

The theoretical curves for reasonable parameter choices in the tetrahedral and trigonal models[3] are also given in Figure 1, clearly showing that neither of these models is correct. We emphasize that the parameters chosen for these two models are of course not unique, but in order to force agreement with experiment between 100 and 300°K, they are restricted to a narrow range. Within this range, as illustrated, we have the conditions $\mu_{eff}^2$(tetrahedral) → 0 as $T$ → 0, and $\mu_{eff}^2$(trigonal) must show a minimum below 100°K. Therefore both of these models are eliminated on the basis of our susceptibility measurements between 4.2 and 100°K. The point of giving the theoretical curves for all three models is more to show the danger of naive fitting of data in a limited temperature range rather than to prove the rhomboid model.

It is interesting to note that experimental results very similar to those shown in Figure 1 have recently been obtained for $[Cr_4(OH)_6(en)_6](SO_4)_3 \cdot 10H_2O$.[8] In this work the authors assumed a trigonal model and found it necessary to introduce an extra interaction of the form $(\hat{S}_i \cdot \hat{S}_j)^2$ to obtain agreement between experiment and theory. Now that the structure of the cation is known[4] not to be trigonal, there is no need to postulate this more elaborate form of interaction.

As so frequently occurs with antiferromagnetic interactions, there seems no way of deciding whether the interaction is due to direct overlap of the metal orbitals or superexchange through the bridging groups. However, the fact that $J$ only falls to half of $J_{12}$ while the Cr–Cr distance goes from 2.93 to 3.61 Å suggests that superexchange must be the major mode of interaction. The values of the interaction constants are very similar to those found for the basic chromium acetate derivatives, where the paramagnetic unit is $Cr_3O(CH_3COO)_6$-$(H_2O)_3^+$.[9] In one case the bridging group is an oxide ion, and in the other it is a hydroxide ion, but they appear to give very similar effects.

Although it was hoped that a low-temperature spectrum of the polynuclear ion would show chromium atoms in two different environments, this proved not to be the case. The spectrum of $[Cr_4(OH)_6(en)_6][B-(C_6H_5)_4]_6$ in a frozen solution of 2-$CH_3THF$–$CH_3OH$ at 77°K shows bands at 15,320 cm$^{-1}$ ($\epsilon$ 28), 15,670 cm$^{-1}$

(8) H. Kobayashi, I. Tsujikawa, and I. Kimura, *J. Phys. Soc. Japan*, **24**, 1169 (1968).

(9) A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc., A*, 1656 (1966).

($\epsilon$ 26), 19,500 cm$^{-1}$ ($\epsilon$ 308), and 25,580 cm$^{-1}$ ($\epsilon$ 319). The two more intense peaks in the visible spectrum may be assigned to the $^1A_{2g} \to {}^4T_{2g}$ and $^4A_{2g} \to {}^4T_{1g}$ transitions in octahedral symmetry; the fact that no splitting can be resolved in these bands indicates that the ligand field environments of the two types of Cr(III) ions are very similar and shows the danger of using ligand field

spectra to deduce subtle coordination structural differences. The two peaks of low intensity observed at lower energies are undoubtedly due to spin-forbidden transitions.

## Appendix

A.   The equation for the square of the magnetic moment of a rhomboid $S = {}^3/_2$ array, if $-J_{12}/2kT = x$, $J_{34} = 0$ and $-J/kT = y$, can be written

$$
\mu^2 = g^2 \left\{
\frac{546\exp(-9x-18y) + 510\exp(-9x-6y) + 180\exp(-9x+4y)}{13\exp(-9x-18y) + 20\exp(-9x-6y) + 9\exp(-9x+4y)}
\right.
$$

$$
\frac{+114\exp(-9x+12y) + 30\exp(-9x+18y) + 6\exp(-9x+22y)}{+12\exp(-9x+12y) + 5\exp(-9x+18y) + 3\exp(-9x+22y)}
$$

$$
\frac{+330\exp(-9x-12y) + 180\exp(-9x-2y)}{+\exp(-9x+24y) + 11\exp(-9x-12y) + 9\exp(-9x-2y)}
$$

$$
\frac{+84\exp(-9x+6y) + 6\exp(-9x+16y) + 84\exp(-9x+2y)}{+7\exp(-9x+6y) + 3\exp(-9x+16y) + 7\exp(-9x+2y)}
$$

$$
\frac{+30\exp(-9x+8y) + 84\exp(-9x) + 330\exp(3x-12y) + 180\exp(3x-2y)}{+5\exp(-9x+8y) + 7\exp(-9x) + 11\exp(3x-12y) + 9\exp(3x-2y)}
$$

$$
\frac{+120\exp(3x+6y) + 30\exp(3x+12y) + 6\exp(3x+16y)}{+15\exp(3x+6y) + 6\exp(3x+12y) + 3\exp(3x+16y)}
$$

$$
\frac{+180\exp(3x-8y) + 84\exp(3x) + 6\exp(3x+10y) + 84\exp(3x-4y)}{+9\exp(3x-8y) + 7\exp(3x) + 3\exp(3x+10y) + 7\exp(3x-4y)}
$$

$$
\frac{+30\exp(3x+2y) + 30\exp(3x) + 180\exp(11x-6y) + 120\exp(11x+2y)}{+5\exp(3x+2y) + 5\exp(3x) + 9\exp(11x-6y) + 15\exp(11x+2y)}
$$

$$
\frac{+30\exp(11x+8y) + 84\exp(11x-4y) + 6\exp(11x+6y)}{+5\exp(11x+8y) + 7\exp(11x-4y) + 3\exp(11x+6y)}
$$

$$
\left.
\frac{+30\exp(11x-2y) + 6\exp(11x) + 120\exp(15x)}{+5\exp(11x-2y) + 3\exp(11x) + 16\exp(15x) + \exp(11x+4y)}
\right\}
$$

B.   The equation for the square of the magnetic moment of a trigonal planar $A(A)_3$ array (with $S = {}^3/_2$)
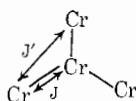


if $x = -J/2kT$ and $J' = 0$, can be written

$$
\mu_{\mathrm{eff}}^2 = g^2 \left\{
\frac{546\exp(-27x) + 330\exp(-3x) + 180\exp(17x) + 84\exp(33x)}{13\exp(-27x) + 11\exp(-3x) + 9\exp(17x) + 7\exp(33x)}
\right.
$$

$$
\frac{+660\exp(-21x) + 360\exp(-x) + 168\exp(15x) + 60\exp(27x)}{+22\exp(-21x) + 18\exp(-x) + 14\exp(15x) + 10\exp(27x)}
$$

$$
\frac{+540\exp(-15x) + 252\exp(x) + 90\exp(13x) + 18\exp(21x)}{+27\exp(-15x) + 21\exp(x) + 15\exp(13x) + 9\exp(21x)}
$$

$$
\frac{+336\exp(-9x) + 60\exp(3x) + 24\exp(11x)}{+28\exp(-9x) + 20\exp(3x) + 12\exp(11x) + 4\exp(15x)}
$$

$$
\left.
\frac{+60\exp(-3x) + 12\exp(5x)}{+10\exp(-3x) + 6\exp(5x)}
\right\}
$$

C.   The equation for the square of the magnetic moment of a tetrahedral $A_4$ array (with $S = ^3/_2$), if $x = J/kT$, can be written

$$\mu_{\text{eff}}^2 = g^2 \left[ \frac{546 \exp(42x) + 990 \exp(30x) + 1080 \exp(20x) + 840 \exp(12x)}{13 \exp(42x) + 33 \exp(30x) + 54 \exp(20x) + 70 \exp(12x)} \frac{+330 \exp(6x) + 54 \exp(2x)}{+55 \exp(6x) + 27 \exp(2x) + 4} \right]$$

# Seven-Coordination in Some Mononuclear and Binuclear Iron(III) Complexes Containing a Pentadentate Macrocyclic Ring

BY S. MARTIN NELSON AND DARYLE H. BUSCH

The preparations and properties of two novel series of seven-coordinate iron(III) complexes are reported.  In both series, the stereochemistry involves pentagonal-bipyramidal coordination about the iron atom with the five donor atoms of a pentadentate macrocycle occupying a single plane and monodentate groups above and below that plane.  The macrocycle is 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (ligand B).  Monomeric $FeBX_2Y$ compounds are formed for X = Cl, Br, I, or NCS and Y = $ClO_4$, $BF_4$, or NCS.  The species are high spin and act as uni-univalent electrolytes in nitromethane.  Dimeric $[XBFe-O-FeBX]Y_2$ (X = $ClO_4$ or NCS;  Y = $ClO_4$) involves spin–spin coupling across the Fe–O–Fe linkage.

## Introduction

Considerable interest attaches to the synthesis of transition metal compounds in which the metal atom exhibits high coordination numbers, *i.e.*, greater than 6.[1]   Until recently, known examples of seven-coordination were limited mostly to elements of the second and third transition series and to elements of the lanthanides and actinides, in combination with fluorine or oxygen.  In such compounds, the metal–ligand bond is relatively polar and the cation:anion size ratio is generally large; high coordination numbers are therefore to be expected.

The past few years have seen the synthesis of a number of seven-coordinate transition metal complexes containing ligands which favor the formation of covalent bonds.  Typical ligands in compounds of this class are carbon monoxide, cyanide, and chelating tertiary arsines.  For the first transition metal series seven-coordination is now known for titanium[2] (in $TiCl_4$(TAS)), vanadium[2,3] (in $VCl_4$(TAS) and $(C_6H_5)_3$-PAuV(CO)$_6$), and chromium[4] (in [Cr(DAS)$_2$(CO)$_2$I]I).  (DAS and TAS are bidentate and tridentate tertiary arsines.)   It seems probable that in this class of compound the coordination number of 7 is related to the availability of at least three d orbitals for $d^3sp^3$ hybridization and also to the $\pi$-acceptor capacity of some of

the ligands, which permits the withdrawal of excess charge away from the metal.

The manganese(II) and iron(III) complexes with ethylenediaminetetraacetic acid and *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, studied by Hoard and coworkers,[5] are conveniently considered as constituting a third class of seven-coordinate compounds.  With these metal ions the hexadentate ligands are not well suited to coordinate in an octahedral fashion.  The distortion the ligands impose is such that an extra coordination site is made available for a molecule of water.  In these cases seven-coordination is a consequence of ligand geometry and metal ion size.  The compounds to be described in this paper also fall in this class.[6]   Here, a pentadentate macrocycle, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (ligand B, structure I),

I
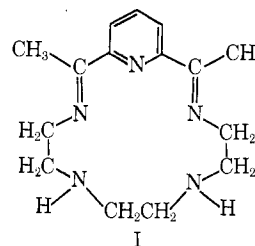
(1)  E. Muetterties, *Quart. Rev.* (London), **21**, 109 (1967).
(2)  R. J. H. Clark, M. L. Greenfield, and R. S. Nyholm, *J. Chem. Soc.,* A, 1254 (1966).
(3)  A. S. Kasenally, R. S. Nyholm, R. J. O'Brien, and M. H. B. Stiddard, *Nature,* **204**, 871 (1964).
(4)  J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.,* 3009 (1964).

(5)  S. N. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.,* **3**, 27 (1964);  M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.,* **3**, 34 (1964);  G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.,* **88**, 3228 (1966).
(6)  A preliminary account has appeared:  S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.,* 641 (1966).