similar applications of KOH in nonhydroxylic solvents will be found. By using dimethyl sulfoxide as the solvent, we have similarly prepared the potassium salt of triphenylmethane (p$K \approx 32$). The discrepancy between this latter result and the above thermodynamic calculation is probably attributable to a particularly high solvation energy in dimethyl sulfoxide.[9,12]

Reaction with Alkali Metals.—In the second method the weak acid is treated with an alkali metal, usually suspended in a finely divided state in a polar solvent. For example, the sodium salt of indene may be prepared by the reaction of indene with a dispersion of sodium in tetrahydrofuran[18]

$$C_9H_8 + Na \longrightarrow Na^+ + C_9H_7^- + 0.5H_2$$
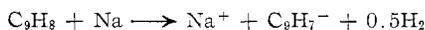
Reactions of this type may be broken into two parts
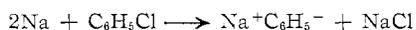
$$HA = H^+ + A^-$$
$$M + H^+ = 0.5H_2 + M^+$$
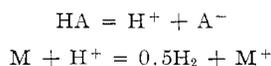
If we make the approximation that the free energy of formation of the dissolved salt is the same as that for the salt dissolved in water,[9] then we may readily calculate the pK value of the weakest acids which can react in this way by using the free energy of formation of the appropriate alkali metal ion.[14] Thus we calculate limiting pK values of 51, 46, and 49 for lithium, sodium, and potassium, respectively.

Metal–ammonia solutions are often used to deprotonate acids

$$e_{am}^- + HA_{am} \longrightarrow 0.5H_2 + A_{am}^-$$
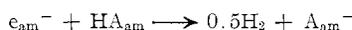
By applying the rule that the pK values of normal acids are 10 units higher in water than in ammonia[8] and by using available thermodynamic data,[19] we calculate that acids with aqueous pK values less than 44 should be capable of being deprotonated by metal–ammonia solutions. However, in practice, the limiting pK value is around 37, because anions of acids with aqueous pK values greater than 37 are ammonolyzed in liquid ammonia.

Cleavage by Alkali Metals.—In the third method, the salt of a weak acid is formed by the reaction of an alkali metal with a halo derivative of the weak acid. This method is useful for preparing the salts of extremely weak acids (*e.g.*, benzene) for which the above two methods are inapplicable.[20] For example, sodium phenyl is readily formed by the reaction of finely divided sodium with chlorobenzene[21]
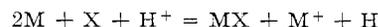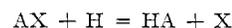
$$2Na + C_6H_5Cl \longrightarrow Na^+C_6H_5^- + NaCl$$

Reactions of this general category (in which a metal M reacts with a halide AX) may be broken into three parts

$$HA = H^+ + A^-$$
$$AX + H = HA + X$$
$$2M + X + H^+ = MX + M^+ + H$$

Obviously, for a given alkali metal and a given halogen, the over-all driving force depends not only on the pK of the acid, but also on the difference in the dissociation energies of the H–A and X–A bonds. Now, almost all of the acids for which this third method is practical are hydrocarbons. Thus we are principally concerned with the differences in the dissociation energies of C–H bonds and the corresponding C–X bonds. To the precision with which we may assume that the latter differences are constant on going from one weak carbon acid to another,[22,23] we may estimate the highest pK for which this type of reaction is thermodynamically possible. By considering the alkali metals lithium, sodium, and potassium and the halogens chlorine, bromine, and iodine, we find that the theoretical limiting pK value varies from 119 (for the cleavage of a chloro compound by potassium) to 102 (for the cleavage of an iodo compound by sodium).[14,15] Obviously it is unlikely that any hydrocarbon will be found whose alkali metal salts cannot be made by this method because of *thermodynamic* limitations.[24]

(22) The data in Table II of the paper by Benson[23] show that the difference between C–H and C–X bond energies is generally constant to about ±3 kcal/mole for a wide variety of organic radicals. For example $D(CH_3–H) = 104$, $D(C_6H_5CH_2–H) = 85$, $D(CH_3–I) = 56$, and $(C_6H_5CH_2–I) = 40$ kcal/mole.

(23) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(24) This research was supported by the U. S. Atomic Energy Commission.

DEPARTMENT OF CHEMISTRY   WILLIAM L. JOLLY
UNIVERSITY OF CALIFORNIA AND
INORGANIC MATERIALS RESEARCH DIVISION
LAWRENCE RADIATION LABORATORY
BERKELEY, CALIFORNIA 94720

The Paramagnetism of [Cr$_4$(OH)$_6$(en)$_6$]I$_6$·4H$_2$O

Sir:

In this laboratory, the paramagnetism of a number of polynuclear ions is being studied, including Pheiffer's [Cr$_4$(OH)$_6$(en)$_6$]$^{6+}$ ion.[1] With [Cr$_4$(OH)$_6$(en)$_6$]I$_6$·4H$_2$O,[2] the effective magnetic moment per metal ion is 3.53 BM at room temperature, a value somewhat less than those previously reported for dimeric hydoxo-bridged chromium(III) complexes.[3] The variation of the effective moment with temperature is shown in Figure 1 along with that of the reciprocal susceptibility. The experimental results can be described by the Curie-Weiss expression

$$\chi_A = \frac{1.93}{T + 76}$$

(1) P. Pheiffer, *Z. Anorg. Chem.*, **58**, 286 (1908).

(2) Prepared as red-violet crystals by the addition of solid NaI to a hot solution of the chloride. *Anal.* Calcd for Cr$_4$C$_{12}$H$_{62}$N$_{12}$O$_{10}$I$_6$: C, 9.58; H, 4.15; N, 11.18. Found: C, 9.55; H, 4.19; N, 11.48.

(3) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 395 (1961).

(18) R. B. King, "Organometallic Syntheses," Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press Inc., New York, N. Y., 1965, p 74.

(19) W. L. Jolly, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, Chapter 3, p 27.

(20) The pK of benzene is about 42 (private communication from A. Streitwieser, Jr.), and thus benzene should be thermodynamically capable of reacting with the alkali metals. However, no reaction takes place. Probably the deprotonation reaction has a high activation energy.

(21) G. E. Coates, "Organo-Metallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 23.
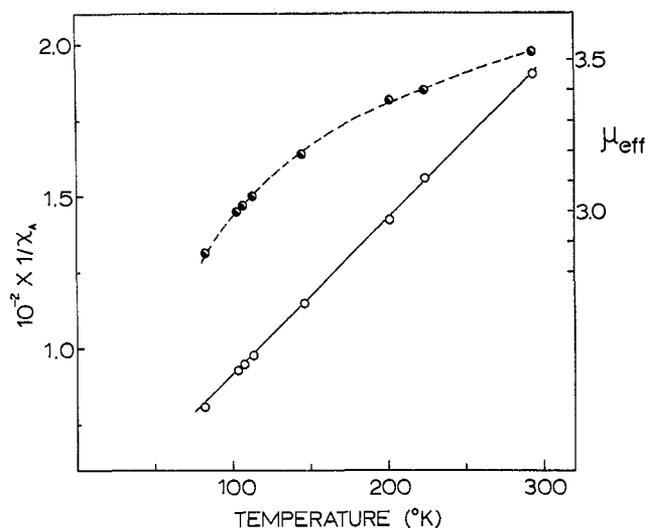
Figure 1.—Experimental magnetic moments are given by the half-filled circles while the reciprocal susceptibilities are indicated by the open circles. The lines represent calculated values.

where the large Weiss temperature is considered to be due to intramolecular spin coupling.[4]

The Hamiltonian for a system of equivalent neighboring spins[5] is given by

$$\mathcal{H} = -2J \sum \hat{S}_i \cdot \hat{S}_j$$

where the summation extends only over nearest neighbors. The eigenvalues of this Hamiltonian are then functions of a new spin quantum number S' and are of the form

$$E(S') = -\frac{z}{n-1} J[S'(S'+1) - nS(S+1)]$$

where z is the average number of nearest neighbors, n is the number of spins within the system, and the maximum value of S' is nS. For the ion in question, $n = 4$ and S' can assume values of 6, 5, ..., 0. The value used for z will depend upon the molecular arrangement.

The structure of this ion is not known with certainty, but it is assumed that I is the basic skeletal arrangement which permits eight possible isomers. In all of these, however, the spin system can be characterized by a central atom with $S = {}^3/_2$ which is surrounded by and coplanar with an equilateral triangle of similar atoms. The helical sense of the central octahedron will have no bearing on the paramagnetism. Furthermore, if coupling between the atoms at the apices of the triangle is negligible, then the helical senses of the peripheral octahedra should also have no magnetic effect. Each apical atom has then but one effective nearest neighbor,

(4) Intermolecular spin coupling or lattice antiferromagnetism is, of course, a possible explanation. This phenomenon can usually be detected by comparing magnetic data from crystalline materials to that obtained from those materials in solution. Our present experimental apparatus (Faraday) does not lend itself to the study of aqueous solutions. However, the good agreement between the experimental data and that obtained from theory, as well as the favorable agreement of the magnetic parameters with those obtained for dimeric hydroxo-bridged complexes of Cr(III), points to intramolecular coupling.

(5) J. H. Van Vleck, "Electric and Magnetic Suceptibilities," Oxford University Press, London, 1932.

I
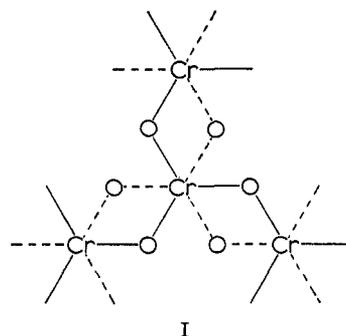
and since the central atom has three neighbors, $z = {}^3/_2$. The resulting energy levels and degeneracies are given in Table I.

TABLE I
ENERGY LEVELS AND DEGENERACIES

S'	Energy (J)	Degeneracy/($2S' + 1$)
6	-21	1
5	-15	3
4	-10	6
3	-6	10
2	-3	11
1	-1	9
0	0	4

The average susceptibility per chromium atom is then readily obtained from the Van Vleck expression[5] as

$$\chi_A = \frac{N\beta^2}{3kT} \frac{3g^2}{4} \times$$

$$\frac{18x^{20} + 110x^{18} + 280x^{15} + 360x^{11} + 330x^6 + 182}{4x^{21} + 27x^{20} + 55x^{18} + 70x^{15} + 54x^{11} + 33x^6 + 13}$$

with $x = \exp(-J/kT)$. A reasonable fit can be had at temperatures greater than $120°K$ with $J/k = -16°$ and $g = 2.00$. However, a pronounced curvature in the reciprocal susceptibility occurs at lower temperatures and is not in agreement with the experimental results. This deviation can be removed by including a small contribution of temperature-independent paramagnetism. Excellent agreement can be obtained with $J/k = -16°$, $g = 1.99$, and $N(\alpha) = 50 \times 10^{-6}$ cgs unit, as shown in Figure 1. These values compare favorably to those found by Earnshaw and Lewis[3] for a series of dimeric dihydroxo-bridged complexes (Table II).

TABLE II
MAGNETIC PARAMETERS FOR SOME
HYDROXO-BRIDGED POLYNUCLEAR COMPLEXES

Compound[a]	J/k, $°K$	g	$10^6 N \cdot$ (α), cgs units
[(o-phen)Cr(OH)$_2$Cr(o-phen)]I$_4 \cdot$4H$_2$O[b]	-10	1.99	58
[(gly)Cr(OH)$_2$Cr(gly)] $\cdot$H$_2$O[b]	-6	2.01	52
[(phal)Cr(OH)$_2$Cr(phal)][b]	-7	2.03	44
[Cr$_4$(OH)$_6$(en)$_6$]I$_6 \cdot$4H$_2$O	-16	1.99	50

[a] o-phen = o-phenanthroline; gly = glycine; phal = phenylalanine. [b] See ref 3.

The coincidence of the experimental data to that predicted for I cannot be considered as structural proof.

If the correct structure consisted of a chain of four chromium atoms, then $z = \frac{3}{2}$ and J/k would remain the same. For a tetrahedral arrangement, $z = 3$ and $J/k = -8°$; while for a square arrangement, $z = 2$ and $J/k = -12°$. However, unless the structure is stereochemically unusual, either I or the chain arrangement is the correct structure.

Interestingly, the similar polynuclear complex of Co(III) crystallizes as the anhydrous iodide whose powder diffraction pattern is unlike that of the Cr(III) compound. It was previously shown[6] that only two geometric isomers of the Co(III) polynuclear ion were

formed in its synthesis. The absorption spectra appeared to be due to a composite of those of the CoN_4O_2 and CoO_6 groups, in agreement with I. In the case of the Cr(III) ion, the spectrum affords little definitive evidence since no splitting is observed. However, the methods of synthesis of the Co(III) and Cr(III) compounds differ vastly, and it may be that different isomers of I are produced in each case.

(6) R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1018 (1967).

DEPARTMENT OF CHEMISTRY   R. A. D. WENTWORTH
INDIANA UNIVERSITY   R. SAILLANT
BLOOMINGTON, INDIANA 47401