venient means for handling diborane for chemical applications and can be used to prepare high-purity borane adducts.

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Magnetic Properties of Hexaamminechromium(III) Pentachlorocadmate(II)

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Recent structural investigations[2,3] have revealed interesting variances in the equatorial *vs.* axial metal–ligand bond distances in the trigonal-bipyramidal anions $CuCl_5{}^{3-}$ and $CdCl_5{}^{3-}$. In the copper compound the axial and equatorial bond distances are 2.295 and 2.392 Å, respectively, while in the cadmium compound $(Cd-Cl)_{ax} = 2.527$ Å and $(Cd-Cl)_{eq} = 2.564$ Å. These unique five-coordinate complexes may be stabilized in the solid state by hexaammine cations of cobalt(III), chromium(III), and rhodium(III). It has been suggested that the electronic structure of the copper ion is responsible for the inequivalences of the bond distances. This question remains as an interesting problem to be considered elsewhere. Recently, it was shown that the pentachlorocuprate ions in $[Co(NH_3)_6][CuCl_5]$ are antiferromagnetically coupled with a transition near 8°K.[4] It was of interest to determine whether comparable interactions occurred between hexaamminechromium(III) cations in the analogous compound $[Cr(NH_3)_6][CdCl_5]$. The results of our studies are reported in this note.

Experimental Section

Preparation of Hexaamminechromium(III) Pentachlorocadmate(II).—Hexaamminechromium(III) chloride (0.8 g, 4.6 mmol) and cadmium chloride dihydrate (2.0 g, 91 mmol) were dissolved in water (60 ml), and the resulting solution was filtered and heated to 60°. Concentrated hydrochloric acid (20 ml) was added to the warm solution and the resulting mixture was cooled in an ice bath for 30 min. The bright yellow crystals which precipitated were collected on a Büchner funnel, washed with ethanol (95%, 10 ml) and then with diethyl ether (10 ml), and were allowed to air dry on the filter frit for 20 minutes. The large well-formed crystals (0.35 g) were stored in the absence of light. *Anal.* Calcd for $[Cr(NH_3)_6][CdCl_5]$: N, 18.94; H, 4.09; Cl, 39.93. Found: N, 18.73; H, 4.05; Cl, 39.81.

Characterization.—The X-ray powder photograph obtained using a Philips X-ray generator and a Debye–Scherrer (114.6 mm) camera was substantially identical with the powder photographs of $[Cr(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuCl_5]$. This similarity is considered to be good evidence that the $CdCl_5{}^{3-}$ ion has the trigonal-bipyramidal structure in $[Cr(NH_3)_6][CdCl_5]$. However, we must call attention to the difference in solubilities of the compound prepared here and the cobalt analog reported previously by Long, *et al.*[3] In the latter case it was necessary to use diffusion techniques in order to grow even the microcrystals necessary for X-ray diffraction studies.

Magnetic Measurements.—Magnetic susceptibilities of a powdered sample of the complex were determined at 294 and 77°K using a Faraday balance.[5] At several temperatures below 25°K, measurements were made with a Foner-type vibrating sample magnetometer,[6] with temperatures being measured with a calibrated germanium resistance thermometer. Both systems were calibrated using the magnetic susceptibility standard HgCo-$(NCS)_4$.[7] Corrections were made for the diamagnetism of the constituent atoms using Pascal's constants[8] and for that of the sample holder assemblies.

Epr Measurements.—A sample of $[Cr(NH_3)_6][CdCl_5]$ diluted in the diamagnetic host $[Co(NH_3)_6][CdCl_5]$ was prepared by the method described above for the chromium compound except a 1:10 mole ratio of $[Cr(NH_3)_6]Cl_3$ to $[Co(NH_3)_6]Cl_3$ was used. The epr spectrum of a powdered sample of the diluted material was obtained at room temperature using a Varian Model 4502 X-band spectrometer with 100-kHz modulation at a frequency of 9.480 GHz. Magnetic field strengths were calibrated with an nmr probe. Cylindrical quartz sample tubes were used with the standard Varian E-4531 cavity.

Results

The magnetic susceptibility data for $[Cr(NH_3)_6]$-$[CdCl_5]$ are presented in Table I. The data obey the

TABLE I
MAGNETIC SUSCEPTIBILITY DATA FOR HEXAAMMINECHROMIUM(III) PENTACHLOROCADMATE(II)

Temp, °K	$10^{-6}\chi_m{}^{cor}$, cgsu	Temp, °K	$10^{-6}\chi_m{}^{cor}$, cgsu	Temp, °K	$10^{-6}\chi_m{}^{cor}$, cgsu
4.2	307,800	6.2	238,900	14.0	119,500
4.9	288,300	7.0	219,400	22.0	73,690
5.2	276,800	8.3	193,000	77.0	24,200
5.7	255,400	10.4	158,000	293.8	6,080

Curie–Weiss law over the entire temperature range with an intercept on the temperature axis at $\chi^{-1} = 0$ of $-1.4°$; thus $\theta = 1.4°K$. From the relationship $\mu_{eff} = 2.828C^{1/2}$, with $C = 1.813$, we calculate a magnetic moment of 3.81 BM.

The epr spectrum of a powdered sample of $[Cr(NH_3)_6]$-$[CdCl_5]$ diluted in the corresponding cobalt matrix is shown in Figure 1. The spectrum was analyzed by the method described recently by Mohrman, Garrett, and Lewis[9] using the axial spin Hamiltonian

$$\mathcal{H} = \beta \vec{H} \cdot g \cdot \vec{S} + D(S_z{}^2 - {}^5/_4) \qquad (1)$$

The energies of the components of the $^4A_2$ ground state manifold are given by[10]

$$H = H_z$$

$$E({}^3/_2, -{}^1/_2) = g_{||}\beta H/2 \pm (D + g_{||}\beta H) \qquad (2)$$

$$E(-{}^3/_2, +{}^1/_2) = -g_{||}\beta H/2 \pm (D - g_{||}\beta H)$$

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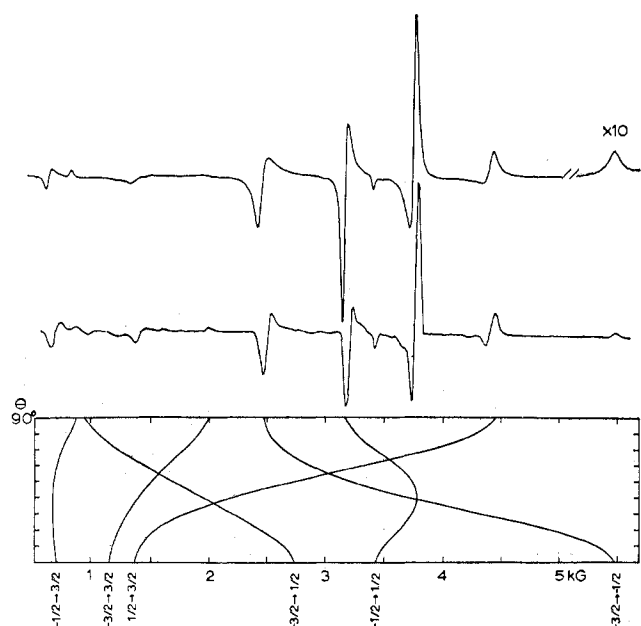(10) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1967).

Figure 1.—A comparison of the experimental and simulated epr spectra of [Co(Cr)(NH₃)₆][CdCl₅]. Top: experimental X-band powder spectrum. Bottom: computer-simulated spectrum ($g_\perp$ = 1.974, $g_{||}$ = 1.984 E = 0.0, D = 0.0949 cm⁻¹) with graph showing the angular dependence of the resonance fields. At θ = 0° the magnetic field is parallel with the z symmetry axis, and at θ = 90° the magnetic field is in the xy plane.

$$H = H_y = H_z$$

$$E(^3/_2, -^1/_2) = g_\perp\beta H/2 \pm (g_\perp{}^2\beta^2H^2 + D^2 - g_\perp\beta HD)^{1/2} \quad (3)$$

$$E(^1/_2, -^3/_2) = -g_\perp\beta H/2 \pm (g_\perp{}^2\beta^2H^2 + D^2 + g_\perp\beta HD)^{1/2}$$

Zero-field and magnetic parameters were calculated from these equations using resonance fields assigned from easily recognizable spectral features.[11] Assignments for the [Cr(NH₃)₆][CdCl₅] spectrum are given in Table II. As shown in Table III, the spin Hamilto-

TABLE II

Transition	$H_x = H_y$, G	H_z, G
$-^3/_2 \rightarrow -^1/_2$	2470.8	5462.1
$-^1/_2 \rightarrow ^1/_2$	3178.9	3410.8
$^1/_2 \rightarrow ^3/_2$	4389.3	1362.1

TABLE III
EPR PARAMETERS FOR Cr(NH₃)₆³⁺ IN TWO CRYSTAL MATRICES

	$g_\perp$	$g_{||}$	g^a	D, cm⁻¹	E, cm⁻¹
Powder[b]					
[Co(NH₃)₆][CdCl₅]	1.974	1.984	1.977	0.0949	0.0
Single crystal[12]					
[Co(NH₃)₆]Cl₃			1.986[c]	0.0313	0.0019
			1.984	0.0537	0.0119
			1.984	0.0688	0.0203

[a] The average g value. [b] Estimated uncertainty in these parameters is ±1% corresponding to an uncertainty of 10 G in the assignments of one or more resonance fields. [c] Parameters for three inequivalent crystal sites.

nian parameters obtained for this compound reflect a crystal environment of higher symmetry than do the

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parameters for [Cr(NH₃)₆]Cl₃, as deduced from single-crystal studies.[12]

A powder spectrum generated with the fitted epr parameters is compared with the experimental spectrum in Figure 1. The simulated spectrum was generated with a modification of the program of Lewis, Hempel, and Morgan.[13] A Gaussian line shape was used to represent individual resonances, assuming a constant half-width of 27 G for the $-^1/_2 \rightarrow ^1/_2$ transition and 45 G for all others. The excellent agreement of reproduced and experimental spectra substantiates the interpretation of the [Cr(NH₃)₆][CdCl₅] powder epr spectrum.

Discussion

In a cubic octahedral field the ground electronic state arising from the $(t_{2g})^3$ configuration of the chromium-(III) ion is a $^4A_{2g}$. Due to spin–orbit coupling, properties of excited states may be mixed into the ground state, and the magnetic moment is predicted to differ from the spin-only moment of 3.88 BM by the factor $1 - (4\lambda''/10Dq)$,[14] where, following Figgis, Lewis, and Mabbs, λ'' implies a spin–orbit coupling constant $(\zeta/3)$ reduced to account for covalent bonding. Thus, in a first approximation, the observed moment of 3.81 BM is in excellent agreement with the theoretical prediction if we take the free-ion value of 91 cm⁻¹ for the spin–orbit coupling constant and the experimental $10Dq$ of 22,000 cm⁻¹. Additional analyses are made possible by the structural information available for the compound.

In view of the finding that the hexaamminechromium(III) ion in [Cr(NH₃)₆][CuCl₅] and the hexa-amminecobalt(III) ion in [Co(NH₃)₆][CdCl₅] sit on sites with $\bar{3}$ symmetry,[2,3] it is likely that the Cr(NH₃)₆³⁺ ion in [Cr(NH₃)₆][CdCl₅] has the same structure since all three compounds appear to be isomorphous. The $\bar{3}$ site requires that all six ligands be identical, and in [Cr(NH₃)₆][CuCl₅] the N–Cr–N angle is 89.65°. This departure from O_h symmetry along with the expected intramolecular spin–spin interaction is sufficient to produce a zero-field splitting of the $^4A_{2g}$ state. From the epr spectrum the zero-field splitting parameter D was measured to be 0.0949 ± 0.009 cm⁻¹.

We will now consider the magnetic susceptibility in view of the zero-field splitting. By substitution of the energies of the parallel components of the $^4A_{2g}$ state given in eq 2 into the Van Vleck[15] equation

$$\chi_m = \frac{N\sum_{n,m}\{(E^I_{n,m})^2/kT - 2E^{II}_{n,m}\}\exp(-E^0_n/kT)}{\sum_{n,m}\exp(-E^0_n/kT)} \quad (4)$$

the magnetic susceptibility parallel to the z direction is[16]

$$\chi_{||} = \frac{Ng_{||}{}^2\beta^2[1 + 9\exp(-2D/kT)]}{4kT[1 + \exp(-2D/kT)]} \quad (5)$$

A somewhat more complicated expression for $\chi_\perp$ may be generated by substitution of the appropriately

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recast forms of the energy roots (3) into the Van Vleck equation (4) and the mean susceptibility calculated from $\chi = (\chi_{||} + 2\chi_{\perp})/3$. At temperatures where kT is greater than D, the expression for the parallel component of the susceptibility reduces to

$$\chi_{||} = N\beta^2 g_{||}^2(5 - 9D/kT)/4kT \tag{6}$$

At 4.2°K, where $kT = 2.9$ cm^{-1} and with the above value of D, $\chi_{||}$ is estimated from eq 6 to be reduced by a factor of only 0.06 from the susceptibility predicted from the spin-only formula. Thus, since the magnitude of the perpendicular component is comparable to that of the parallel component of the susceptibility, the departure of the experimental data from the calculated susceptibility of an isolated hexaamminechromium(III) ion, as is indicated by the Weiss constant, must arise from intermolecular magnetic interactions. Since θ is positive, these magnetic interactions are antiferromagnetic.

With the assumption that the structural details for hexaamminechromium(III)   pentachlorocadmate(II) are similar to those of the analogous copper compound, we may now consider the question of the magnetic interactions between ions in these cubic lattices. First we know that there is a weak antiferromagnetic interaction between the CuCl$_5^{3-}$ ions in [Co(NH$_3$)$_6$]-[CuCl$_5$], and it has been suggested[4] that these intermolecular interactions are transmitted through the orbitals of the axial ligands since the unpaired electron is located in the d$_{z^2}$ orbital. These chloride–chloride intermolecular distances are 4.11 Å. This is to be compared with the closest nitrogen–nitrogen intermolecular distance which is 4.057 Å in [Cr(NH$_3$)$_6$]-[CuCl$_5$]. However, in the chromium case, the unpaired electrons are in the t$_{2g}$ orbitals, and the molecular features which are necessary for the discussion of the magnetic interactions are available from the structural data. In the crystal structure, a given hexaaminechromium(III) ion has 12 nearest Cr(NH$_3$)$_6^{3+}$ ions (Cr–Cr internuclear separations of 7.9 Å) located at the end of vectors which have their origin at the chromium ion and which pass near the 12 edges of the trigonally distorted octahedron. Also, ammine ligands of neighboring complex cations are directed toward the points of closest contact. Due to this orientation the magnetic wave functions, which are not expected to have an appreciable amplitude at such distances from the chromium(III) ion, may not overlap effectively, and consequently the resulting interaction is rather weak. Presumably, interactions between hexaamminechromium(III) ions which may be transmitted through intervening pentachlorocadmate anions are negligible in comparison to the interactions between nearest neighbors since there are no known precedents for such transmissions.

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The Enthalpy of Ilmenite–Perovskite Transformation in Cadmium Titanate

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The compounds CdTiO$_3$[1] and CdSnO$_3$[2] are unusual among solids of the stoichiometry ABO$_3$ in that each exists in both ilmenite and perovskite forms at atmospheric pressure. Liebertz and Rooymans[3] have shown that the transformation is reversible, with the ilmenite occurring at low temperature and pressure and the perovskite at high temperature and pressure. A knowledge of the thermodynamic parameters for this transition would offer quantitative insight into the energy relations, at least in one specific case, among two very important and widespread structure types. Since some difficulty was encountered in reversing the transformation under hydrothermal conditions at lower temperatures[3] and since thermodynamic properties calculated by the application of the Clausius–Clapeyron relation to the phase boundary are often subject to rather large uncertainties, a direct determination of the enthalpy of this transformation is desirable. This communication reports the results of a study of the enthalpy of the ilmenite–perovskite transformation in CdTiO$_3$ and of the enthalpy of formation of CdTiO$_3$ from the oxides, by high-temperature solution calorimetry at 692 ± 2°, using molten 3Na$_2$O·4MoO$_3$ as solvent.

Experimental Section

Sample Preparation.—The starting materials were Baker Analyzed reagent CdO and TiO$_2$ (anatase) dried to constant weight at 200°. A mixture of the appropriate stoichiometry was weighed, ground under acetone, and annealed in a platinum crucible at about 850° for a total of 24 hr, with three intermediate grindings. The X-ray pattern of this product, a white powder, showed it to be single-phase α-CdTiO$_3$, the ilmenite form. Complete conversion of a portion of this sample to the perovskite form was achieved by heating at about 1150° for a total of 36 hr, with four intermediate grindings. This material was initially pale yellow but slowly turned a very light brown upon standing in air. It was shown not to invert back to the α form upon heating overnight near 700°, thus ensuring the possibility of making meaningful solution calorimetric experiments at that temperature.

Calorimetry.—The calorimeter, sample assembly, and technique have already been described.[4,5] The molten oxide mixture 3Na$_2$O·4MoO$_3$ has been shown to be a satisfactory calorimetric solvent for both CdO and TiO$_2$, as well as for a number of Cd^{2+}- and Ti^{4+}-containing spinels.[5] Accordingly, this solvent, prepared as before,[5] was used in the present work. Samples of 40–150 mg of solute were dissolved in 10–12 g of melt. No difficulty was observed in the solution of the low-temperature α form, but samples of the β form initially tended to leave an undissolved residue detectable at the end of the calorimetric experiment. This problem was overcome by the use of quite small (40–50 mg)

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