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Magnetism and Spectroscopy of a Series of Hexafluorotitanates(III)

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The infrared and electronic spectral data for the series of compounds K_2NaTiF_6, Na_3TiF_6, K_3TiF_6, and $(NH_4)_3TiF_6$ suggest a distortion of the hexafluorotitanate ion which is dependent on the cation and increases with the size of the cation. The magnetic moments of the compounds show a steady decrease from approximately 1.8 to 1.5 BM in the temperature range 300–77°K.

Introduction

In their early paper dealing with the molecular orbital theory of the hexafluorotitanate(III) ion, Bedon, Horner, and Tyree[1] noted that the visible absorption band of the TiF_6^{3-} ion in some of its salts showed distinct splittings in the spectra which were greater than 3000 cm^{-1} and that the splitting and the positions of the band components were dependent upon the cation. Since Bedon, *et al.*, also reported that the room-temperature magnetic moments varied from compound to compound, we felt that additional studies of the spectroscopy and magnetism of a series of hexafluorotitanate salts were in order. The results of our studies are reported herein.

Experimental Section

Preparation of the Compounds. (1) **Ammonium Hexafluorotitanate(III).**—Two methods were used for the preparation of $(NH_4)_3TiF_6$. In the method, a, described by Negoiu,[2] 30 ml of a 20% titanium(III) chloride solution was added dropwise to a stirred solution of 40 g of NH_4F in 50 ml of distilled water. The solution was contained in a 200-ml round-bottom flask equipped with a side arm so that a nitrogen stream could be maintained during the addition. The purple precipitate which formed was transferred to a plastic bottle and washed with several portions of distilled water. The precipitate was collected on a Büchner funnel and dried overnight under vacuum over P_2O_5.

In the second method, b, approximately 50 ml of 48% hydrofluoric acid was poured into a 1-qt plastic bottle and frozen in a Dry Ice–2-propanol bath. After flushing the system with nitrogen, 2 g of powdered titanium metal was added. The system was capped and allowed to warm slowly to room temperature. In a glove bag the bright purple solution was filtered through no. 40 Whatman paper into a plastic bottle containing 50 g of NH_4F which had been flushed with nitrogen. Distilled water was added in portions until all excess NH_4F was dissolved. The final wash water acquired a definite purplish tinge. The precipitate was filtered, washed, and dried as in method a. *Anal.* Calcd for $(NH_4)_3TiF_6$: N, 19.45; H, 5.60; Ti, 22.18. Found for method a: N, 19.61; H, 5.56; Ti, 22.86. Found for method b: N, 19.21; H, 5.72; Ti, 22.36.

(2) **Sodium Hexafluorotitanate(III).**—This compound was prepared similarly to procedure b used for $(NH_4)_3TiF_6$ except 50 g of NaF was used. Many washings were necessary since sodium fluoride is sparingly soluble in distilled water. The solution was allowed to leach 6–8 hr before the water was changed. The total time of the preparation was approximately 1 week. *Anal.* Calcd for Na_3TiF_6: Na, 29.88; Ti, 20.75. Found: Na, 30.35; Ti, 21.18.

(3) **Potassium Hexafluorotitanate(III).**—Ten grams of KHF_2 and 0.75 g of titanium metal were mixed in a platinum crucible. While nitrogen was passed over the crucible, the mixture was heated with a Meeker burner. After melting, the mixture was kept hot until bubbling ceased. It was allowed to cool under nitrogen, broken up, and placed in a plastic bottle. This was leached with water. After swirling the solid with several portions of water, it was collected on a Büchner funnel. The solid was placed in a vacuum desiccator and dried under vacuum over P_2O_5. *Anal.* Calcd for K_3TiF_6: K, 42.01; Ti, 17.16. Found: K, 42.28; Ti, 17.33.

(4) **Dipotassium Sodium Hexafluorotitanate(III).**—For this preparation 7.8 g (0.1 mol) of KHF_2 and 3.1 g (0.05 mol) of $NaHF_2$ were crushed and mixed together with 0.75 g of titanium metal. *Anal.* Calcd for K_2NaTiF_6: Na, 8.74; K, 29.72; Ti, 18.20. Found: Na, 9.37; K, 29.85; Ti, 18.40.

(5) **Attempted Preparation of Disodium Potassium Hexafluorotitanate(III).**—The compound Na_2KTiF_6 reported by Bedon, Horner, and Tyree[1] could not be prepared. When stoichiometric amounts of $NaHF_2$ and KHF_2 were mixed together and permitted to react with titanium metal or $TiCl_3$, the melt produced a purple compound which always had the same X-ray powder pattern as K_2NaTiF_6. Furthermore, as shown in Table I, alkali metal elemental analysis proved that both compounds were K_2NaTiF_6.

TABLE I

PREPARATIVE DETAILS AND ANALYTICAL DATA FOR $K_xNa_yTiF_6$

	Wt, g			
Prepn	KHF_2	$NaHF_2$	% K	% Na
K_2NaTiF_6				
From Ti metal	7.8	3.1	29.85	9.37
Calcd alkali metal content			29.72	8.74
KNa_2TiF_6				
From Ti metal	3.9	6.2	30.12	9.71
From $TiCl_3$	3.9	6.2	29.67	9.15
Calcd alkali metal content			15.82	18.62

Methods of Analysis. (1) **Titanium Analysis.**—The method reported by Negoiu[2] and Bedon, *et al.*,[1] was used. A weighed sample of hexafluorotitanate(III) was oxidized to Ti(IV) with approximately 2 ml of concentrated nitric acid. The acid solution was neutralized with excess 3 *M* ammonium hydroxide (as noted by a white precipitate and a strong ammoniacal odor) and diluted to 200 ml with distilled water. After the mixture was warmed on a hot plate for several hours to coagulate the precipitate, the precipitare was collected on high-quality analytical filter paper and then washed with ammonium hydroxide solution when necessary to remove all traces of the alkali metal.

The filter paper and precipitate were placed in a weighed porcelain crucible and ignited over a Meeker burner until constant weight was obtained. The product was weighed as TiO_2.

(2) **Sodium Analysis.**—Sodium analysis was done by flame

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[1] H. D. Bedon, S. M. Horner, and S. Y. Tyree, *Inorg. Chem.*, **3**, 647 (1964).

[2] D. Negoiu, *Stud. Cercet. Chim.*, **11**, 61 (1963); *Chem. Abstr.*, **60**, 125*h* (1964).

emission at 5890 Å on a Beckman Model B flame photometer with a hydrogen–oxygen flame. The direct-intensity method described by Willard, Merritt, and Dean[3] was used.

(3) **Potassium Analysis.**—The method described for sodium was used except that the potassium emission line at 7665 Å was used and potassium chloride was used as the standard.

(4) **Nitrogen and Hydrogen Analyses.**—Nitrogen and hydrogen were analyzed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Magnetic and Spectroscopic Measurements. Magnetic Susceptibility.—Magnetic susceptibilities of powdered samples were measured in the temperature range 77–300°K using apparatus which has been described previously.[4] The balance was calibrated[5] with $HgCo(NCS)_4$, and diamagnetic corrections were estimated from Pascal's constants.[6]

Vibrational Spectra.—All spectra were obtained in the region 4000–200 cm^{-1} using both KBr and polyethylene pressings. The instrument was purged with dry air in order to remove interfering bands from atmospheric water and carbon dioxide. With both the KBr and polyethylene pressings identical values for the ν_3 vibration of the $TiF_6{}^{3-}$ salts were obtained.

The method used for the preparation of powdered polyethylene has been described by May and Schwing.[7] Fifty grams of polyethylene pellets was dissolved in 500 ml of hot xylene. After cooling the solution, 100% pure ethanol was added slowly to precipitate the polymer. The solution was decanted and the precipitate was washed with two 0.5-pt portions of ethanol. The white mass was filtered by suction and dried under vacuum for several days. The powdered polyethylene was checked by infrared spectroscopy from 200 to 700 cm^{-1}, and no spurious bands were found.

Polyethylene disks were made using a mold, press, and heater manufactured by Buehler, Ltd. A 1% sample of polyethylene mixture was gently ground in an agate mortar and pestle, and the pellet was pressed at 1000 psi and 100°. The clear pellets were mounted on a KBr pellet sample holder.

Electronic Spectra.—Spectra of powdered samples of the series of hexafluorotitanates(III) were obtained on a Cary Model 14 spectrophotometer in the range 10,000–3000 Å. After trying KCl or KBr pellet pressings and Nujol mulls, it was found that the best procedure involved sealing the sample between the two thin polyethylene pellets whose preparation is described above.

Results

Magnetic Properties.—Magnetic susceptibilities and magnetic moments for the series of hexafluorotitanates(III) are given in Table II. Inspection of the data listed there reveals two important trends. First, there is a steady decrease of the magnetic moment with temperature for each of the compounds, and, second, the magnitude of the room-temperature moment decreases in the order $K_2NaTiF_6 > Na_3TiF_6 > K_3TiF_6 > (NH_4)_3TiF_6$. As will be noted later, this trend in physical properties shows up in each of the sets of experimental data collected in this study.

TABLE II

MAGNETIC PROPERTIES OF THE HEXAFLUOROTITANATE(III) SALTS

Temp, °K	$10^6\chi_M$, cgsu	μ_{eff}, BM	Temp, °K	$10^6\chi_M$, cgsu	μ_{eff}, BM
K_2NaTiF_6 with $\chi_{dia} = -106 \times 10^{-6}$ and Mol Wt 263.1					
294	1427.4	1.84	152	2266.9	1.67
270	1505.8	1.81	134	2385.3	1.61
255	1568.3	1.80	121	2672.1	1.62
240	1639.2	1.78	105	2997.2	1.59
224	1717.4	1.76	98	3081.5	1.56
207	1824.2	1.75	91	3268.2	1.55
190	1932.6	1.72	85	3356.6	1.52
171	2086.9	1.70	78	3628.4	1.51
Na_3TiF_6 with $\chi_{dia} = -90 \times 10^{-6}$ and Mol Wt 230.9					
304	1338.7	1.80	128	2469.6	1.58
279	1396.4	1.76	119	2610.0	1.57
259	1493.9	1.75	101	2948.5	1.54
240	1581.2	1.74	96	3072.1	1.53
216	1683.0	1.70	90	3197.7	1.51
195	1824.3	1.68	84	3352.8	1.50
173	1978.3	1.65	78	3527.8	1.48
147	2242.2	1.62			
K_3TiF_6 with $\chi_{dia} = -114 \times 10^{-6}$ and Mol Wt 279.2					
293.5	1316.5	1.77	153	2078.7	1.60
272	1380.2	1.74	128	2382.5	1.57
251	1455.3	1.72	107	2785.4	1.55
227	1576.7	1.70	97	2971.3	1.52
211	1657.4	1.68	90	3145.6	1.51
190	1782.2	1.65	83	3305.8	1.49
173	1903.4	1.63	78	3473.3	1.48
$(NH_4)_3TiF_6$ with $\chi_{dia} = -109.5 \times 10^{-6}$ and Mol Wt 215.9					
304	1197.0	1.71	128	2372.1	1.55
269	1307.1	1.68	108	2724.9	1.53
241	1449.4	1.67	100	2981.4	1.54
220	1531.6	1.64	92	3171.2	1.52
200	1659.9	1.62	87	3288.2	1.51
178	1810.4	1.60	78	3579.7	1.49
153	2046.1	1.58			

The room-temperature magnetic moments obtained here agree well with the room-temperature data for $(NH_4)_3TiF_6$ reported by Bedon, *et al.*, but the high moments reported by these workers for K_2NaTiF_6 were not found. Our room-temperature magnetic moment for K_2NaTiF_6 of 1.84 BM is in excellent agreement with the magnetic moment that they reported for the substance identified as Na_2KTiF_6.

The results obtained here for the potassium compound are slightly higher than those reported by Ehrlich,[8] and we were unable to find a previous report of the magnetic properties of Na_3TiF_6 for comparison.

Electronic Spectra.—The visible spectral data for the hexafluorotitanate(III) salts are given in Table III.

TABLE III

VISIBLE SPECTRAL DATA OF VARIOUS $TiF_6{}^{3-}$ SALTS

Compd	Exptl bands, cm^{-1}		Dq, cm^{-1}	Δ', cm^{-1}
K_2NaTiF_6	16,210	19,310	1775	3100
Na_3TiF_6	15,570	18,940	1726	3370
K_3TiF_6	15,630	19,230	1743	3600
$(NH_4)_3TiF_6$	14,980	19,340	1716	4360

Each of the spectra consisted of a broad band with a rather well-defined shoulder on the low-energy side. The splitting of the octahedral ^2E_g state, called Δ', has been attributed by Liehr and Ballhausen[9] to an in-

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[3] H. H. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis," 4th ed, Van Nostrand, Princeton, N. J., 1965, pp 351–352.

[4] W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

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

[6] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

[7] L. May and K. J. Schwing, "Spectroscopic Tricks," L. May, Ed., Plenum Press, New York, N. Y., 1967, pp 153–156.

[8] P. Ehrlich, *Angew. Chem.*, **64**, 617 (1952).

[9] A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, **3**, 304 (1958).

herent instability of the state according to the Jahn–Teller theorem. The low-symmetry component of the crystal field must be tetragonal or rhombic since a trigonal distortion will not split the ${}^2E_g$ state, and the observed splittings are much too large to be due to spin–orbit coupling. An alternate explanation for the origin of the distortion would involve ionic packing forces. Although the following treatment is presented in terms of the Jahn–Teller theorem, the results and discussion do not depend on the origin of the distortional forces.

If we make the assumption that the distortional mode adopted by the hexafluorotitanate(III) ion is one of the highest symmetry which will still remove the degeneracy, then simple crystal field theory predicts an axial compression resulting in four long and two short titanium–fluorine bonds. Broad-line nmr experiments for K_2NaTiF_6[10] and Na_3TiF_6[11] support the axial compression mode for distortion Unfortunately, detailed structural information for the hexafluorotitanate(III) salts is not available, and the powder patterns do not reveal any information concerning the distortional mode. All of the compounds crystallize in lattices which are very close to cubic.[12] The magnitude of the splitting of the ${}^2E_g$ level increases in the order $K_2NaTiF_6 < Na_3TiF_6 < K_3TiF_6 < (NH_4)_3TiF_6$.

Vibrational Spectra.—An octahedral molecule has the following normal modes of vibration:[13] infrared active, $2T_{1u}(\nu_3, \nu_4)$; Raman active, $A_{1g}(\nu_1)$, $E_g(\nu_2)$, $T_{2g}(\nu_5)$; inactive, $T_{2u}(\nu_6)$. The two infrared-active normal modes of vibration may involve both angle deformation and bond stretching, but the absorption at the higher frequency, ν_3, corresponds largely to the asymmetric bond vibration while that at the lower frequency, ν_4, arises largely from angle deformations.

If, according to the dictates of the Jahn–Teller effect, the symmetry is lowered to D_{4h} or to D_{2h}, the degeneracies of some of the normal modes of vibration are lifted according to the following scheme

O_h		D_{4h}	D_{2h}
A_{1g}	→	A_{1g}	A_g
E_g	→	$A_{1g} + B_{1g}$	$2A_g$
T_{2g}	→	$B_{2g} + E_g$	$B_{1g} + B_{2g} + B_{3g}$
T_{1u}	→	$A_{2u} + E_u$	$B_{1u} + B_{2u} + B_{3u}$
T_{2u}	→	$B_{2u} + E_u$	$B_{1u} + B_{2u} + B_{3u}$

In D_{4h} the A_{2u} and E_u modes are infrared active, while B_{1u}, B_{2u}, and B_{3u} are infrared active in D_{2h}.

Consequently, ν_3 and ν_4 are expected to be split or at least broadened by a distortion from an octahedral structure and a new band arising from the E_u component of the T_{2u} normal mode should appear.

Upon examination of the infrared spectra displayed in Figure 1 a clear trend is seen in the half-width of the high-energy ν_3 band. The most symmetrical band occurs in the spectrum of K_2NaTiF_6. A noticeable broadening occurs in the band for Na_3TiF_6, and a suggestion of band splitting is seen in the spectrum of K_3TiF_6. Finally, in the spectrum of $(NH_4)_3TiF_6$, the splitting of ν_3 is reasonably well resolved. The widths of ν_3 at half-height for the series of compounds are as follows (cm^{-1}): K_2NaTiF_6, 105; Na_3TiF_6, 140; K_3TiF_6, 190; $(NH_4)_3TiF_6$, 210.

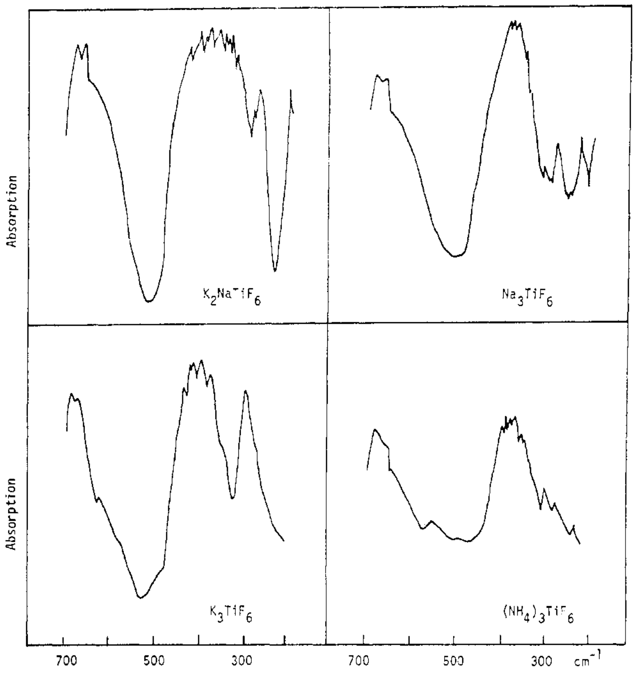

Figure 1.—Infrared spectra for the series of hexafluorotitanates.

The analysis of the low-energy part of the spectrum is much more difficult since the limit of the spectrometer available to us was 200 cm^{-1}, and it is apparent that some of the absorption bands continue below that limit. In addition, inspection of spectral data for some representative octahedral metal fluorides[14] reveals that ν_6, the out-of-plane bend, which becomes infrared active in D_{4h}, usually occurs at lower energies than ν_4. However, in the spectrum of K_2NaTiF_6, an intense band is found at 235 cm^{-1} and a considerably less intense band occurs at 287 cm^{-1}. On the basis of intensity arguments, the more intense band would be expected to be the ν_4 (in O_h) band, with the less intense one arising from the E_u out-of-plane motion. This assignment has been given earlier by Fritz and coworkers.[10]

Discussion

The infrared, electronic, and broad-line nmr spectral data can all be interpreted in terms of a distorted octahedral structure for the hexafluorotitanate(III) ion, where the distortion is dependent on the nature of the cation and appears to increase in the order $K_2NaTiF_6 < Na_3TiF_6 < K_3TiF_6 < (NH_4)_3TiF_6$. Except for the first compound in the series the order parallels the increase in the size of the cation. The structural

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[10] P. Burkert, H. P. Fritz, and G. Stefaniak, *Z. Naturforsch. B*, **23**, 872 (1968).

[11] H. M. MacIntyre, private communication.

[12] J. G. Gurm, L. Gravel, and R. J. A. Potvin, *J. Electrochem. Soc.*, **104**, 301 (1957); N. F. H. Bright and J. G. Wurm, *Can. J. Chem.*, **36**, 615 (1958).

[13] F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963, Chapter 9.

[14] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 119.

variations can be understood in terms of the variations observed in the corresponding aluminum compounds as discussed by Steward and Rooksby.[15] In the ideal cubic lattice there are two kinds of sites for the alkali metal (or ammonium) ions and these occur in the ratio of 2:1. When two alkali metal ions of different radii are present, these ions occupy the sites preferentially and Steward and Rooksby concluded that as a consequence of this ordering, a symmetrical orientation of the octahedral framework is more readily maintained than in those cases where only one kind of alkali metal ion is present. Potentially, the magnetic susceptibility data should yield information about the splitting in the $^2T_{2g}$ ground state which should support the conclusions pertaining to the order of the distortion. We have carried out a complete analysis of the magnetic data and, in view of the nature of our results, as contrasted with the large numbers of seemingly successful analyses, present here a detailed discussion of the treatment.

Crystal Field Potential and Spin–Orbit Coupling.—In an octahedral complex in which the metal ion has a d^1 electronic configuration the effect of the crystal field, spin–orbit coupling, and the magnetic field on the ^2D Russell–Saunders term may be represented by the Hamiltonian $\mathcal{H} = \mathcal{H}^0 + V_{\text{cubic}} + V' + \lambda L_i \cdot S_i + \beta H \cdot (kL_i + 2S_i)$, where $\mathcal{H}^0$ is the Hamiltonian for the free ion, $V_{\text{cubic}} + V'$ is the electrostatic energy of the field of neighboring ligands, λ is the spin–orbit coupling constant, β is the Bohr magneton, and H is the magnetic field. It is assumed that the low-symmetry component of the crystal field and spin–orbit coupling are comparable in magnitude, while the magnetic energy term is regarded as a small perturbation.

The ten free-ion wave functions, taken as a basis set for diagonalization, as designated by the m_l quantum numbers are

$$\phi_1 = |0\rangle$$

$$\phi_2 = (1/\sqrt{2})(|2\rangle + |\bar{2}\rangle)$$

$$\phi_3 = |1\rangle$$

$$\phi_4 = |\bar{1}\rangle$$

$$\phi_5 = (1/\sqrt{2})(|2\rangle - |\bar{2}\rangle)$$

where ϕ_i may have a spin of α $(+{}^1/_2)$ or β $(-{}^1/_2)$. Application of the Hamiltonian to this basis set of functions yields the secular determinant[16] shown in Chart I. When Δ and Δ', the splittings in the T_{2g} and E_g states, respectively, are positive, the $^2B_{2g}$ state lies lowest, but for negative values for these parameters, corresponding to axial elongation, the ^2E_g state is the ground state. Spin–orbit coupling splits the ^2E_g state, giving Γ_6 and Γ_7 of the double group D_4' and the magnetic field removes the degeneracy of the Kramer's doublets Γ_7, while Γ_6 is nonmagnetic. The octahedral

CHART I

$$\begin{array}{cccccccccc}
\phi_1\alpha & \phi_1\beta & \phi_2\alpha & \phi_2\beta & \phi_3\alpha & \phi_3\beta & \phi_4\alpha & \phi_4\beta & \phi_5\alpha & \phi_5\beta
\end{array}$$

$$\left|\begin{array}{cccccccccc}
6Dq + \Delta'/2 & & & & & \sqrt{6}\lambda/2 & & & & \\
& 6Dq + \Delta'/2 & & & & & \sqrt{6}\lambda/2 & & & \\
& & 6Dq - \Delta'/2 & & & & & \lambda/\sqrt{2} & \lambda & \\
& & & 6Dq - \Delta'/2 & \lambda/\sqrt{2} & & & & & -\lambda \\
& & & \lambda/\sqrt{2} & \begin{array}{c}-4Dq + \Delta/3\\ + \lambda/2\end{array} & & & & & \lambda/\sqrt{2} \\
\sqrt{6}\lambda/2 & & & & & \begin{array}{c}-4Dq + \Delta/3\\ - \lambda/2\end{array} & & & & \\
& \sqrt{6}\lambda/2 & & & & & \begin{array}{c}-4Dq + \Delta/3\\ - \lambda/2\end{array} & & & \\
& & \lambda/\sqrt{2} & & & & & \begin{array}{c}-4Dq + \Delta/3\\ + \lambda/2\end{array} & -\lambda/\sqrt{2} & \\
& & \lambda & & & & & \lambda/\sqrt{2} & -4Dq - 2\Delta/3 & \\
& & & \lambda & \lambda/\sqrt{2} & & & & & -4Dq - 2\Delta/3
\end{array}\right| = 0$$

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[15] E. G. Steward and H. P. Rooksby, *Acta Crystallogr.*, **6**, 49 (1953).

[16] M. Gerloch, *J. Chem. Soc. A*, 2023 (1968). The matrix element $\langle\phi_2\beta|\text{Op}|\phi_3\alpha\rangle = \lambda/\sqrt{2}$, not zero as given by Gerloch: P. J. Nassiff, Ph.D. Dissertation, University of North Carolina, 1969.

^2E_g and $^2T_{2g}$ states are mixed by spin-orbit coupling, and although this mixing has little effect on bulk susceptibility values, it was retained in this treatment. There is no reason to expect the spin-orbit coupling constant and the orbital reduction factor, k, to be isotropic, but we have made this simplifying assumption since the problem is already heavily overparameterized. It is unfortunate that the compounds crystallize in cubic systems since anisotropic magnetic data may have yielded valuable information.

The Zeeman Effect.—The Zeeman coefficients were calculated using the corrected wave functions obtained from the diagonalization of the crystal field plus spin-orbit coupling matrix and the magnetic moment operators $\mu_\parallel$ (eq 1) and $\mu_\perp$ (eq 2) for the axial field. Ex-

$$\hat{\mu}_\parallel = \hat{\mu}_z = (k\hat{L}_z + 2\hat{S}_z)\cdot\beta\hat{H} \qquad (1)$$

$$\hat{\mu}_\perp = \hat{\mu}_x = \hat{\mu}_y = (k\hat{L}_x + 2\hat{S}_x)\cdot\beta H \qquad (2)$$

amination of the wave functions and the operators reveals that there will be first-order Zeeman effects in both directions. In the z direction, the off-diagonal elements of the five 2×2 determinants vanish, while the opposite is true for the x (or y) direction. There are second-order Zeeman effects in both the perpendicular and parallel directions. The general forms of the various matrix elements were determined, and the first- and second-order Zeeman coefficients calculated for a choice of the crystal field, orbital reduction, and spin-orbit coupling parameters were substituted into the Van Vleck equation[17] for magnetic susceptibility

$$\chi_M = \frac{N\sum\limits_{njm}[(W_{njm}^{(1)})^2/kT - 2W_{njm}^{(2)}]\exp(-W_{njm}^{(0)}/kT)}{\sum\limits_{njm}\exp(-W_{njm}^{(0)}/kT)} \qquad (3)$$

A nonlinear least-squares-fitting program was written in Fortran IV, and the sets of parameters which would fit the experimentally measured magnetic data to theory were determined. The 10×10 matrix was diagonalized each time one of the input parameters Dq, Δ, Δ', k, or λ was changed, and the Zeeman coefficients were calculated from the returned corrected wave functions using degenerate perturbation theory. Several sets of the parameters were found to give a good fit for the temperature variation of the magnetic moment. Before attempting a discussion of the significance of the parameters which were obtained from the fitting process, it is instructive to examine the effect of the various parameters on the magnetism.

Inspection of the crystal field corrected wave functions for selected values of the parameters expected to obtain for Ti(III) showed that the E_g functions were not mixed into the low-lying states to a significant extent. Consequently, the magnetic moment is not affected by a variation in Δ' from 0 to 5000 cm^{-1}. Neither is the magnetic moment affected by a change in Dq, from 1500 to 2000 cm^{-1}. However, as expected, the magnetic moment is markedly dependent on k, λ, and Δ. Thus, the experimentally determined values for Dq and Δ' were used in all subsequent calculations.

In order to determine the effect of the values of k, λ, and Δ on the calculated magnetism, a three-dimensional lattice was constructed within the expected ranges of the parameters from the sum of the squares of the deviations of the experimental data and the calculated magnetic moments. Inspection of the lattices revealed irregular volumes within the parameter space which gave good fits to the magnetic data. The mutual dependencies suggested that it would have been possible to arrive at a unique solution if one of the parameters could have been fixed. Not having that additional information, we assumed that the order of the splitting of the $^2T_{2g}$ level, Δ, in the series of compounds ran parallel to the order of the splitting in the ^2E_g level, Δ', as determined in the electronic spectra. This is a reasonable assumption in view of previous ionic model calculations for tetragonally distorted octahedral molecules.[18] With this constraint the best values for the parameters Δ, λ, and k were found to be those below.

	K_2NaTiF_6	Na_3TiF_6	K_3TiF_6	$(NH_4)_3TiF_6$
Δ, cm^{-1}	280	320	364	459
λ, cm^{-1}	105	122	134	150
k	0.795	0.772	0.776	0.770

While the constancy of k and the magnitude of Δ appear to be reasonable, this variation in λ of 50% cannot be explained away. On the basis of the data for the series of compounds we conclude that it is not possible to obtain supporting evidence for the order of the distortion from the magnetic data without making perhaps unwarranted assumptions concerning the relationship between Δ and Δ' and between k and λ.

An additional factor which may affect the variation of the magnetic moment with temperature and which was not included in the treatment concerns intermolecular magnetic interactions. Preliminary investigations[19] of the magnetism at 4.2°K indicate that the magnetic moments for the compounds are comparable (±0.2 BM) to those calculated at that temperature for the parameters derived from the high-temperature (77–300°K) data.

Conclusions and Comments

While it has not been possible to determine the magnitude, the spectral evidence strongly supports a distorted structure for the hexafluorotitanate ion in the compounds K_2NaTiF_6, Na_3TiF_6, K_3TiF_6, and $(NH_4)_3TiF_6$. The magnitude of the distortion must await X-ray crystal structure determinations. Also, it has not been possible to determine the nature of the splitting of the $^2T_{2g}$ energy level from the magnetic

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(17) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(18) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 1295 (1964).

(19) E. R. Jones, private communication.

data. Gladney and Swalen[20] have suggested electronic Raman and fluorescence experiments for this measurement. Magnetic resonance determinations of spin–lattice relaxation times should also provide information concerning the low-lying electronic states. These experiments will probably have to be carried out near 4.2°K. However, this work has shown that unusually high magnetic moments do not obtain in this series of hexafluorotitanates, and the results also demonstrate that unique sets of parameters Δ, λ, and k cannot be derived from the variation of magnetic susceptibilities in the range 300–77°K.

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CONTRIBUTION FROM HERCULES INC.,
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Palladium(II) Chloride–Lithium Chloride Equilibria in Acetic Acid[1]

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NaCl causes $PdCl_2$ to dissolve in acetic acid to give solutions with the composition $(NaPdCl_3)_n$. Molecular weight measurements indicate this material is a dimer, $Na_2Pd_2Cl_6$. Spectral measurements suggest that at low LiCl concentration the dimer $Li_2Pd_2Cl_6$ is also the main species. The extent of association of lithium chloride into dimers was also determined by molecular weight measurements. The value of K_D for the equilibrium

$$2LiCl \xrightleftharpoons{K_D} Li_2Cl_2$$

was found to be 2.4 M^{-1} at 37.5°, close to the value previously reported at 16°. From an ultraviolet spectral study it was found that $Li_2Pd_2Cl_6$ reacts with lithium chloride according to the following equilibrium where K has a value of 0.1 M^{-1} at 25°

$$Li_2Pd_2Cl_6 + 2LiCl \xrightleftharpoons{K} 2Li_2PdCl_4$$

Introduction

Recently the field of Pd(II) catalysis has received considerable attention as witnessed by the discovery of many new Pd(II)-catalyzed reactions.[2] The solvent used for a number of these new reactions is acetic acid. In spite of the importance of solvent acetic acid in Pd(II) catalysis, little is known about the state of Pd(II) salts in this solvent. This paper will describe equilibrium studies of the interaction of palladium(II) chloride with lithium chloride in acetic acid.

Experimental Section

Materials.—Palladium chloride (Engelhard Industries) was used without further purification. The acetic acid was dried by refluxing over $B(OOCCH_3)_3$.[3] The water content was less than 0.01% as determined by Karl Fischer. The lithium and sodium chlorides were of reagent grade.

Preparation and Analysis of Solutions.—The Pd(II) stock solutions were prepared by heating solid $PdCl_2$ in the presence of a solution of LiCl in acetic acid or, as in the case of the sodium system, with a mixture of solid NaCl and acetic acid. They were analyzed for Pd(II), chloride, and H_2O by standard procedures. LiCl stock solutions were prepared under carefully anhydrous conditions and analyzed for chloride and H_2O. They were used only if the water content was below 0.02%.

Pd(II) determinations were carried out by polarographic[4a] or by gravimetric[4b] analysis using dimethylglyoxime. Chloride analyses were usually carried out by the Volhard titration. With Pd(II)-containing solutions it was necessary to precipitate the Pd(II) with zinc to obtain accurate results.[4b] However, some were made using the Aminco-Cotlove coulometric chloride titrator made by the American Instrument Co.

Solutions for molecular weight measurements and ultraviolet spectral measurements were prepared by diluting stock solutions with anhydrous acetic acid.

Molecular Weights.—Originally molecular weights were measured by the Signer method[5] at 25°. However, this method did not prove sufficiently reproducible or accurate for our purposes. For the molecular weights reported in this paper the Mechrolab vapor pressure osmometer, Model 301A, was used. The preset temperature of the instrument for molecular weight measurement was 37.5°. The instrument was calibrated using urea solutions of known concentration in acetic acid.

Ultraviolet Spectral Study.—The spectra were run on a Cary Model 11 spectrometer at 25°. In order to obtain reproducible spectra, it was found necessary to ensure that the solutions were

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[1] Hercules Research Center Contribution No. 1521.

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