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A Molecular Orbital Treatment of the Spectrum of the Hexafluorotitanium(III) Anion

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Electronic energy levels for the d^1-complex $[TiF_6]^{3-}$ have been calculated using a molecular orbital scheme, assuming ideal octahedral coordination, taking into account π-bonding, but not considering ligand–ligand interactions. The inclusion of π-bonding is shown to be most important when the calculated energy levels are compared with the observed spectra of compounds containing the complex. The observed spectra of $(NH_4)_3TiF_6$, Na_2KTiF_6, and NaK_2TiF_6 show two bands at 15,000–16,000 and at 18,900 cm.$^{-1}$. The value of 17,500 cm.$^{-1}$ for $10Dq$ obtained from the calculated energy levels compares very favorably with the observed spectra, the splitting being attributed primarily to Jahn–Teller distortion of the excited state.

Introduction

The d^1 configuration of the Ti^{3+} ion makes an ideal case for the calculation of one-electron molecular orbital energy levels. A recent calculation of this nature for the tetragonal vanadyl ion has been carried out by Ballhausen and Gray,[1] using some of the approximations employed in an earlier work by Wolfsberg and Helmholz.[2] In the present work, an ion with six equivalent ligands was selected, so that O_h symmetry could be assumed. A system of such simplicity permits the straightforward inclusion of all π-bonding involving the F^- ligands in the molecular orbital calculations. It will be observed that the results of the calculations are in good agreement with the observed spectra of TiF_6^{3-} ions. All calculations were performed on a desk-type calculator.

Molecular Orbital Calculations

The TiF_6^{3-} ion was assumed to have O_h symmetry. The regular octahedron of six F^- ions around one Ti^{3+} ion is shown in Fig. 1, with the Ti–F distance assumed to be the sum of the ionic radii.[3] Table I shows the orbital transformation scheme in O_h symmetry.

The one-electron molecular orbitals may be approximated as

$$\Phi^b(\text{m.o.}) = \sum_{n=1}^{n} c_n\psi_n$$

$$\Phi^*(\text{m.o.}) = \sum_{n=1}^{n} c_n^*\psi_n$$

where ψ_n is either a Ti atomic orbital or the appropriate molecular orbital combination of ligand orbitals. The c_n values are subject to the usual orthogonality and normalization restrictions. In all but the t_{1u} case, $n = 2$, and it is assumed that each Ti atomic orbital interacts with one ligand molecular orbital of appropriate symmetry, yielding only a 2 × 2 determinant to be solved. In the t_{1u} case, two sets of ligand molecular orbitals interact with the Ti 4p-orbitals, giving a 3 × 3 determinant and three energy levels.

TABLE I

ORBITAL SCHEME IN O_h SYMMETRY

Representation	Ti oribitals	Ligand orbitals
a_{1g}	4s	$\sqrt{1/6}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$
e_g	$3d_{(x^2-y^2)}$	$\sqrt{1/4}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
	$3d_{z^2}$	$\sqrt{1/3}(\sigma_5 + \sigma_6) - \sqrt{1/12}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
t_{1u}	$4p_x$	$\sqrt{1/2}(\sigma_1 - \sigma_3)$
		$\sqrt{1/4}(\pi_{y5} + \pi_{x2} + \pi_{y6} - \pi_{x4})$
	$4p_y$	$\sqrt{1/2}(\sigma_2 - \sigma_4)$
		$\sqrt{1/4}(\pi_{y1} + \pi_{x5} + \pi_{y3} - \pi_{x6})$
	$4p_z$	$\sqrt{1/2}(\sigma_5 - \sigma_6)$
		$\sqrt{1/4}(\pi_{x1} + \pi_{y2} - \pi_{x3} + \pi_{y4})$
t_{2g}	$3d_{xy}$	$\sqrt{1/4}(\pi_{y1} + \pi_{x2} - \pi_{y3} + \pi_{x4})$
	$3d_{xz}$	$\sqrt{1/4}(\pi_{x1} + \pi_{y5} + \pi_{x3} - \pi_{y6})$
	$3d_{yz}$	$\sqrt{1/4}(\pi_{x5} + \pi_{y2} + \pi_{x6} - \pi_{y4})$
t_{1g}	...	$\sqrt{1/4}(\pi_{y1} - \pi_{x2} - \pi_{y3} - \pi_{x4})$
	...	$\sqrt{1/4}(\pi_{x1} - \pi_{y5} + \pi_{x3} + \pi_{y6})$
	...	$\sqrt{1/4}(\pi_{x5} - \pi_{y2} + \pi_{x6} + \pi_{y4})$
t_{2u}	...	$\sqrt{1/4}(\pi_{y5} - \pi_{x2} + \pi_{y6} + \pi_{x4})$
	...	$\sqrt{1/4}(\pi_{y1} - \pi_{x5} + \pi_{y3} + \pi_{x6})$
	...	$\sqrt{1/4}(\pi_{x1} - \pi_{y2} - \pi_{x3} - \pi_{y4})$

The energies may be obtained by solving the secular determinants

$$|H_{ij} - G_{ij}E| = 0$$

It is obvious that, in order to solve for E, three quantities must be evaluated: H_{ii}, H_{ij}, and G_{ij}.

Overlap Integrals.—The G_{ij} terms represent group overlap integrals, that is, the overlap of the ligand molecular orbital with the Ti atomic orbital of appropriate symmetry. The G_{ij} terms are functions of the atomic overlap intergrals, S_{ij}, the functions being simple numerical factors. These functions are listed in the Appendix, with an example of the derivation of G_{ij} from S_{ij}.

The S_{ij} values were obtained using the expression

$$S_{ij} \equiv \int\psi_i\psi_j d\tau$$

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[1] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962); also see J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).

[2] M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952); also see corrections to this reference by L. L. Lohr and W. N. Lipscomb, *ibid.*, **38**, 1607 (1963).

[3] S. Y. Tyree and K. Knox, "Textbook of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1961, p. 19.

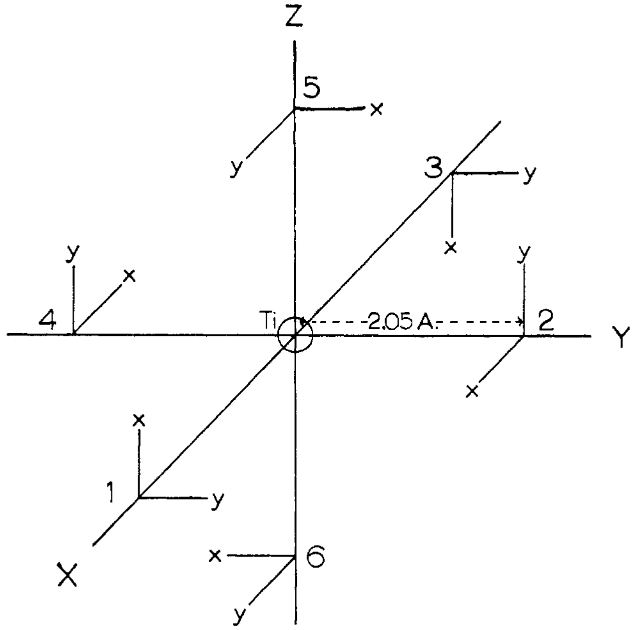

Fig. 1.—Model of TiF_6^{3-}, O_h symmetry.

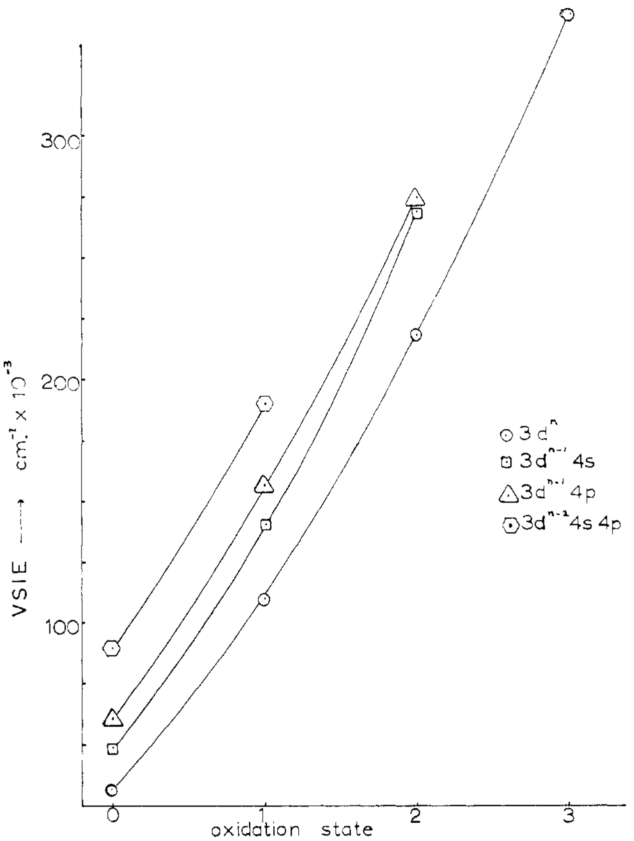

Fig. 2.—VSIE for Ti 3d level.

The wave functions used were in the form of combinations of normalized Slater orbitals, so that overlap integral tables[4-6] could be used to evaluate the individual terms. In some cases the tables were insufficient, and it was necessary to calculate values from master equations,[4,5] using Kotani's tables.[7] The atomic wave functions used are listed in the Appendix, together with an outline of the actual calculation of S_{ij}.

In the case of π-molecular orbitals, the fluorine wave functions were the atomic 2p radial functions, but for σ-orbitals, the fluorine wave functions are assumed to be hybrids of the form

$$\psi_\sigma = (\sin \theta)\Phi_{2s} \pm (\cos \theta)\Phi_{2p\sigma}$$

The degree of hybridization was estimated after the manner of Ballhausen and Gray,[1] by minimizing the quantity VSIE(θ)/S(θ). S(θ) is the overlap integral of the $Ti_{3d\sigma}$ orbital with F hybrid orbitals of varying values of θ, while VSIE(θ) is the valence state ionization energy of the same F hybrid orbital. The minimum occurred at $\theta = 0.36$ radian, corresponding to approximately 13% s- and 87% p-character in the hybrid. It should be noted that this method of estimating hybridization, which worked well for Ballhausen and Gray,[1] is in good agreement with the experimental results of Knox and Shulman[8] for $KNiF_3$. Their nuclear magnetic resonance measurements on this octahedral nickel complex indicate a fluorine hybridization between 8.1 and 12.7% s-character.

Valence State Ionization Energies.—For Ti orbitals, the H_{ii} term is estimated as the VSIE for the Ti ion of appropriate charge. Curves of ionization energy as a function of charge on Ti for various electronic configurations were interpolated for fractional charge on Ti. The ionization potentials for various valence states of integral charge were obtained from Moore's[9] tables of atomic spectra. A typical set of curves for 3d VSIE values is shown in Fig. 2. An example of how VSIE values were obtained for a selected charge and electronic configuration is given in the Appendix.

Since the fluorine atoms will have some net negative charge, satisfactory VSIE's cannot be obtained from Moore's tables.[9] Using the electron affinity of fluorine as the ground state ionization potential for F^- and interpolating for a fractional negative charge on F gives unreasonably high values for the energy levels. Therefore, the ionization energy for fluorine in TiF_6^{3-} was estimated from the experimental ionization potentials for HF.[10,11] The ionization potential for the 2pπ level is 15.77 e.v., or −127,200 cm.$^{-1}$, and for the 2pσ level, 16.97 e.v., or −136,900 cm.$^{-1}$.

In order to obtain an energy for the 2s level in HF (and therefore TiF_6^{3-}), it was assumed that the energy difference between 2s and 2pπ was the same in HF as in fluorine, as given in Moore's tables.[9] A fractional charge of −0.6 was assumed, since this is very close to the final calculated charge on F in TiF_6^{3-}. According to Moore's tables, the 2s level in $F^{0.6-}$ is at −210,000 cm.$^{-1}$, and the 2p at −65,000 cm.$^{-1}$. These data infer a 2s level in TiF_6^{-3} 145,000 cm.$^{-1}$ below the 2pπ level,

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(4) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(5) H. H. Jaffé, *ibid.*, **21**, 258 (1953).

(6) H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953).

(7) M. Kotani, A. Amemiya, and Simose, *Proc. Phys. Math. Soc. Japan*, **20**, 1 (1938); **22**, 1 (1940).

(8) R. G. Shulman and K. Knox, *Phys. Rev. Letters*, **4**, 603 (1960).

(9) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, 1949 and 1952.

(10) J. W. C. Johns and R. F. Barrow, *Nature*, **179**, 374 (1957).

(11) J. A. R. Coope, D. C. Frost, and C. A. McDowell, *ibid.*, **179**, 1186 (1957).

or at $-272{,}200$ cm.$^{-1}$. The energy level of fluorine σ-hybrid orbitals was then obtained by combining 13% of the 2s ionization energy and 87% of the 2pσ ionization energy. The value obtained for the σ-hybrid level was $-154{,}500$ cm.$^{-1}$.

Evaluation of H_{ij}.—The diagonal terms were approximated in the manner used by Ballhausen and Gray.[1]

$$H_{ij} = -2G_{ij}\sqrt{H_{ii}H_{jj}}$$

This is a modification of the approximation used by Wolfsberg and Helmholz.[2]

Calculation of Energy Levels.—The values of H_{ii}, H_{ij}, and G_{ij} were substituted into the secular determinants, which were solved for E. The H_{ii} values used for Ti depended on both the charge and the electronic distribution selected.

Substitution of the molecular orbital energies into the secular equations

$$c_1(H_{11} - E) + c_2(H_{12} - G_{12}E) = 0$$
$$c_1(H_{12} - G_{12}E) + c_2(H_{22} - E) = 0$$

along with the use of normalization conditions, allowed the calculation of the weighting coefficients.

Using the normalization condition

$$\Sigma c_i^2 + 2\Sigma c_i c_j G_{ij} = 1$$

for one-electron molecular orbitals, and Mulliken's plan[12] of dividing the overlap population equally between Ti and F, the electronic population in each Ti atomic level was calculated. The net charge on Ti was calculated from the population. The calculated charge and population did not agree with the initially assumed one, so a new charge and population were assumed. New Coulomb energies (H_{11} values) for Ti atomic orbitals were calculated, then new molecular orbitals, c values, and, finally, a new charge and population were calculated. This iteration was repeated until the calculated charge and population agreed with the assumed one.

The final electron population on Ti was $3d^{2.75}4s^{0.37}4p^{0.34}$, giving an effective charge of $+0.54$ on Ti and -0.59 on F. A sample calculation of c values and electron population is given in the Appendix.

TABLE II

COULOMB ENERGIES FOR ATOMIC ORBITALS CORRESPONDING TO $Ti^{+0.54}$, ELECTRONIC CONFIGURATION $3d^{2.75}4s^{0.37}4p^{0.34}$

Ti		F	
Orbital	H_{11}, cm.$^{-1}$	Orbital	H_{22}, cm.$^{-1}$
3d	$-95{,}540$	2pπ	$-127{,}200$
4s	$-83{,}340$	2pσ	$-136{,}900$
4p	$-51{,}450$	2s	$-272{,}200$
		hyb. σ	$-154{,}500$

Table II lists the final values of the Coulomb energies used for the Ti and F orbitals. Table III shows the energy levels of the molecular orbitals, the coefficients, and the group overlap integrals used. The molecular orbital energy level diagram, drawn to scale, is shown in Fig. 3.

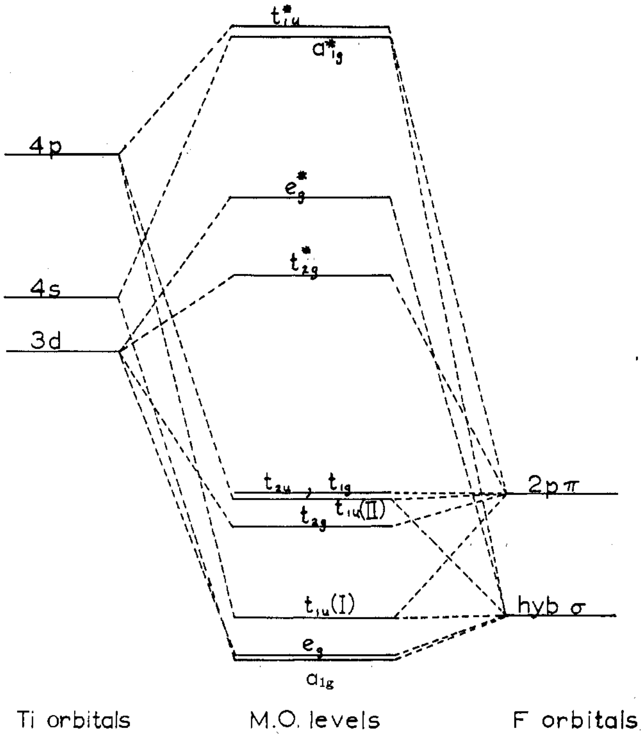

Fig. 3.—Molecular orbital diagram for TiF_6^{3-}.

Results and Discussion

The absorption spectra of NaK_2TiF_6, Na_2KTiF_6, and $(NH_4)_3TiF_6$ solids were observed in KCl and KBr pellets. We have been informed that the Ti atom occupies an O_h site symmetry in NaK_2TiF_6.[13] To our knowledge, no crystallographic information is available for the other two compounds.

The positions of absorption bands in the electronic spectra of the three compounds are shown in Table IV. It should be noted that the bands are separated by 3900 cm.$^{-1}$ in $(NH_4)_3TiF_6$, and by only 2800 cm.$^{-1}$ in NaK_2TiF_6. Presumably the splitting is due primarily to Jahn–Teller distortion of the excited ^2E_g state in the latter case. The amount of splitting is comparable to that observed for octahedral Cu^{2+} compounds,[14] which exhibit splitting of the ^2E_g ground state. The 3900 cm.$^{-1}$ separation of bands in $(NH_4)_3TiF_6$ could well be due to some crystallographic ground-state distortion, imposing approximately 1000 cm.$^{-1}$ further splitting on that observed for the excited state.

If the two bands are due to Jahn–Teller excited state splitting, the mean of the two transitions should be $10Dq$ for a pure octahedral field. (Prior interpretations of the $[Ti(H_2O)_6]^{3+}$ spectrum have assumed that the higher energy band is equated with $10Dq$.)[15] Values of $10Dq$ for hypothetical octahedral symmetry are listed for the compounds in Table IV. They compare remarkably well with the calculated 17,510 cm.$^{-1}$ separation of the t_{2g}^* and e_g^* levels in the molecular orbital scheme.

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(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(13) K. Knox, private communication.

(14) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 286.

(15) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 227.

TABLE III

GROUP OVERLAP INTEGRALS AND MOLECULAR ORBITAL ENERGIES FOR TiF_6^{3-}

M.O. symmetry	G_{12}	G_{13}	Bonding levels $-E$, cm.$^{-1}$	c_1	c_2	c_3	Antibonding levels $-E$, cm.$^{-1}$	c_1^*	c_2^*	c_3^*
t_{2g}	0.201		134,770	0.375	0.855		78,790	0.949	−0.558	
e_g	0.311		163,490	0.312	0.858		61,280	1.005	−0.609	
a_{1g}	0.429		163,670	0.285	0.844		25,440	1.070	−0.716	
t_{1u}^a (I)	0.279	0.270	154,910	0.0620	0.981	0.00416	23,810	0.976	−0.322	−0.352
t_{1u} (II)	0.279	0.270	128,180	0.104	−0.0554	0.967				

[a] In the t_{1u} case, subscript 1 refers to Ti_{4p}, 2 to F_σ, and 3 to $F_{2p\pi}$.

TABLE IV

Compound	Position of absorption bands, cm.$^{-1}$		10*Dq* for pure octahedral field, cm.$^{-1}$
$(NH_4)_3TiF_6$	19,010	15,110	17,060
Na_2KTiF_6	18,900	16,000	17,450
NaK_2TiF_6	18,900	16,100	17,500
Calcd. for octahedral TiF_6^{3-}	17,510		17,510

No charge-transfer bands were observed at lower energies than approximately 50,000 cm.$^{-1}$. In one or two preparations, a weak band was observed at about 30,000 cm.$^{-1}$. This band became intense in pellets which had been exposed to moist air for a week or so, indicating that it was probably due to an impurity of some hydrolyzed titanyl species. The absence of charge-transfer bands within the range of the instrument is not surprising considering the large electronegativity of F^- and the relatively small electronegativity of Ti^{3+}. The molecular orbital calculations show a separation of approximately 48,400 cm.$^{-1}$ between the degenerate t_{1g}, t_{2u} nonbonding levels and the t_{2g}^* level. Such a transition should correspond to the first charge-transfer band, if repulsion energies were considered also, showing good agreement with the observed spectra.

An examination of the molecular orbital energy level diagram indicates the necessity for considering π-bonding. If π-bonding were ignored, the t_{2g}^* level would be a nonbonding 3d level at −95,500 cm.$^{-1}$, giving a calculated 10*Dq* of 34,200 cm.$^{-1}$ and the first charge-transfer band at 31,700 cm.$^{-1}$, ignoring repulsion effects. These values obviously do not correspond to experimental observations, while the values obtained by including π-bonding are most satisfactory.

Experimental

Preparation of Compounds.—$(NH_4)_3TiF_6$ was prepared as described in Gmelin,[16] by adding a water solution of $TiCl_3$ (obtained from Columbia Organic Chemicals) to a saturated, slightly acidic NH_4F solution. The purple precipitate was washed sparingly with H_2O and dried under nitrogen. The product was analyzed for Ti by reduction through a Jones reductor followed by titration with standard Ce(IV) solution. *Anal.* Calcd. for $(NH_4)_3TiF_6$: Ti, 22.18. Found on different preparations: Ti, 22.26, 22.15, 21.86.

Na_2KTiF_6 and NaK_2TiF_6 were prepared according to directions furnished by Knox.[13] Powdered Ti metal was added to a fused melt of $NaHF_2$ and KHF_2, in the appropriate ratio. Alternatively, NaK_2TiF_6 was prepared by dissolving solid $TiCl_3$ in a fused melt of KHF_2 and $NaHF_2$, in a 2:1 mole ratio. The resulting melts, in each case, were leached thoroughly with water, and the insoluble purple products were filtered and dried. The oxidation states were determined by direct titration with Ce(IV) solution; total Ti by reduction in a Jones reductor and subsequent titration. *Anal.* Calcd. for Na_2KTiF_6: Ti, 19.39. Found: Ti, 19.03; oxidation state, 2.98. Calcd. for NaK_2TiF_6: Ti, 18.21. Found: on preparation using Ti metal as a starting material: Ti, 18.06; oxidation state, 3.05. Found on preparation using $TiCl_3$ as a starting material: Ti, 18.37; oxidation state, 3.01.

Determination of Magnetic Moments.—Magnetic susceptibilities were measured by the Gouy method as described elsewhere.[17] Values of μ_{eff} were calculated assuming a Weiss constant of 0°K. The values obtained were: $(NH_4)_3TiF_6$, $\mu_{eff} = 1.70, 1.77$ (on different preparations); Na_2KTiF_6, $\mu_{eff} = 1.86$; NaK_2TiF_6 (prepared from Ti metal), $\mu_{eff} = 2.09$; NaK_2TiF_6 (prepared from $TiCl_3$), $\mu_{eff} = 2.06$. The μ_{eff} values for the latter two salts were unaccountably high. Oxidation state determinations indicate that essentially all the Ti was present as Ti(III). Also, the $TiCl_3$ used in the NaK_2TiF_6 preparation was the same as was used in preparing $(NH_4)_3TiF_6$, which has a moment close to the expected spin-only value. No explanation is offered for the unusually high moments; the data are simply reported here as a matter of interest.

Absorption Spectra.—Reagent grade KCl was fused and cooled to a solid in a 110° oven. It was ground to a powder just before use in making pellets. A small amount of the appropriate Ti compound was ground with the KCl powder in an agate mortar and the mixture pressed into a translucent pellet. Absorption spectra of such pellets were run on a Cary Model 14 recording spectrophotometer, using a pellet holder described previously.[18] A few pellets were prepared using infrared quality KBr, to ensure that there was no effect due to the matrix material of the pellet. The spectra of KBr pellets did not differ appreciably from those of corresponding KCl pellets.

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Appendix

Group Overlap Integrals.—The method of converting atomic overlap integrals to group overlap integrals is outlined in detail by Ballhausen.[19] An example of the method, retaining Cartesian coordinates, is given below.

Consider the calculation of G_{e_g} for the d_{z^2}-orbital interacting with the appropriate set of F-orbitals.

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(16) Gmelin's Handbuch der Anorganischen Chemie, 8 Auflage, System No. 41, "Titan," Verlag Chemie, Weinheim, 1951, p. 406.

(17) S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 122, 1962.

(18) S. M. Horner and S. Y. Tyree, *ibid.*, **2**, 568 (1963).

(19) C. J. Ballhausen, ref. 15, pp. 174–175.

Convert the Ti coordinates, in turn, to each of the six F-coordinates. Assume the z axis of each F lies along the σ-bond direction.

$$\sigma_1:\ x^2 \rightarrow z^2,\ y^2 \rightarrow y^2,\ z^2 \rightarrow x^2$$
$$\sigma_2:\ x^2 \rightarrow x^2,\ y^2 \rightarrow z^2,\ z^2 \rightarrow y^2$$
$$\sigma_3:\ x^2 \rightarrow z^2,\ y^2 \rightarrow y^2,\ z^2 \rightarrow x^2$$
$$\sigma_4:\ x^2 \rightarrow x^2,\ y^2 \rightarrow z^2,\ z^2 \rightarrow y^2$$
$$\sigma_5:\ x^2 \rightarrow y^2,\ y^2 \rightarrow x^2,\ z^2 \rightarrow z^2$$
$$\sigma_6:\ x^2 \rightarrow y^2,\ y^2 \rightarrow x^2,\ z^2 \rightarrow z^2$$
$$G_{e_g} = \int \psi_{d_{z^2}} \psi_{F_{MO}}\, d\tau$$
$$G_{e_g} = \int [\sqrt{1/3}(3z^2 - r^2)][\sqrt{1/3}(\sigma_5 + \sigma_6) - \sqrt{1/12}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)]\, d\tau$$

The d_{z^2} wave function is converted to the appropriate coordinates, in turn, for each σ-orbital, as indicated above.

$$G_{e_g} = \int {}^1/_3[3z^2 - y^2 - x^2 - z^2]\sigma_5 + \int {}^1/_3[3z^2 - y^2 - x^2 - z^2]\sigma_6 - \int {}^1/_6[3x^2 - z^2 - y^2 - x^2]\sigma_1 - \int {}^1/_6[3y^2 - x^2 - z^2 - y^2]\sigma_2 - \int {}^1/_6[3x^2 - z^2 - y^2 - x^2]\sigma_3 - \int {}^1/_6[3y^2 - x^2 - z^2 - y^2]\sigma_4$$

After such conversion, all σ's are alike, and subscripts may be dropped. Then

$$G_{e_g} = \int [2z^2 - y^2 - x^2]\sigma\, d\tau = \int [3z^2 - r^2]\sigma\, d\tau$$
$$G_{e_g} = \sqrt{3} \int \sqrt{1/3}(3z^2 - r^2)\sigma\, d\tau = \sqrt{3} \int \psi_{d_{z^2}} \psi_{F_\sigma}\, d\tau$$
$$G_{e_g} = \sqrt{3} S_{3d\sigma,\mathrm{hyb}\,\sigma}$$

In a similar manner, all G_{ij} values were determined as a function of S_{ij}.

Representation	$G_{ij} = f(S_{ij})$
e_g	$\sqrt{3}S_{\mathrm{hyb}\sigma,3d\sigma}$
a_{1g}	$\sqrt{6}S_{\mathrm{hyb}\sigma,4s\sigma}$
t_{1u} (σ)	$\sqrt{2}S_{\mathrm{hyb}\sigma,4p\sigma}$
t_{1u} (π)	$\sqrt{4}S_{2p\pi,4p\pi}$
t_{2g} (π)	$\sqrt{4}S_{2p\pi,3d\pi}$

Wave Functions and Atomic Overlap Integrals.—The Ti atomic wave functions used were those published by Richardson[20,21] using Watson's SCF functions. The fluorine wave functions were obtained from from Allen and Lohr.[22,23] The functions used were for Ti^+, and, in the case of the 4p function, for the d^2p configuration.

$$R(3d) = 0.4391\Phi_3(4.55) + 0.7397\Phi_3(1.60)$$
$$R(4s) = -0.02231\Phi_1(21.40) + 0.07751\Phi_2(8.05) - 0.1985\Phi_3(3.64) + 1.0164\Phi_4(1.20)$$
$$R(4p) = 0.04642\Phi_2(8.8) - 0.17729\Phi_3(3.31) + 1.01438\Phi_4(1.08)$$
$$R(2p) = 0.16774\Phi_2(5.954) + 0.06352\Phi_2(3.068) + 0.58026\Phi_2(1.752) + 0.03579\Phi_2(0.7863) + 0.27530\Phi_3(4.17)$$
$$R(2s) = 0.05531\Phi_1(12.187) - 0.35720\Phi_1(8.189) + 0.01767\Phi_2(14.296) + 0.13038\Phi_2(4.096) + 0.67725\Phi_2(2.767) + 0.23491\Phi_2(1.716) + 0.04834\Phi_3(3.75)$$

where $\Phi_n(\mu) = N_\mu r^{n-1} e^{-\mu r}$.

To calculate the atomic overlap integral of Ti $3d\sigma$ with F $2p\sigma$

$$S_{3d\sigma,2p\sigma} = \int \psi_{(3d)}\psi_{(2p)}\, d\tau$$

The first of the ten terms in the product of the wave functions is $(0.4391)(0.16774)\Phi_3(4.55)\Phi_2(5.954)$. The overlap integral tables[4-6] are given as functions of parameters p and t, defined as

$$p \equiv \frac{R(\mu_A + \mu_B)}{2(0.529)}$$
$$t \equiv \frac{\mu_A - \mu_B}{\mu_A + \mu_B}$$

where μ_A refers to a Slater-type orbital exponent in the fluorine function, μ_B to such an exponent in the titanium function, and R is the interatomic distance in Ångstrom units. For the first term of the product indicated above

$$p = \frac{2.05(5.95 + 4.55)}{2(0.529)} = 20.34$$
$$t = \frac{5.95 - 4.55}{5.95 + 4.55} = +0.133$$

The value of S_{ij} for these values of p and t is obtained from the overlap integral table for $2p\sigma$,$3d\sigma$ and multiplied by the product of the weighting factors. S_{ij} is determined for each of the ten terms, and the sum of the values is $S_{3d\sigma,2p\sigma}$. The atomic overlap integrals obtained were: $S_{3d\sigma,2p\sigma} = 0.130$; $S_{3d\sigma,2s\sigma} = 0.161$; $S_{4s\sigma,2p\sigma} = 0.103$; $S_{4s\sigma,2s\sigma} = 0.219$; $S_{4p\sigma,2p\sigma} = 0.0765$; $S_{4p\sigma,2s\sigma} = 0.350$; $S_{3d\pi,2p\pi} = 0.101$; $S_{4p\pi,2p\pi} = 0.135$.

The overlap of Ti atomic orbitals with F σ-hybrid orbitals was obtained using the relation

$$S_{3d\sigma,\mathrm{hyb}\,\sigma} = \sqrt{0.13}S_{3d\sigma,2s\sigma} + \sqrt{0.87}S_{3d\sigma,2p\sigma}$$

Overlap integrals involving the σ-hybrid bonds are: $S_{3d\sigma,\mathrm{hyb}\sigma} = 0.180$; $S_{4s\sigma,\mathrm{hyb}\sigma} = 0.175$; $S_{4p\sigma,\mathrm{hyb}\sigma} = 0.174$.

Valence State Ionization Energies.—The ionization energy of $Ti^0 \rightarrow Ti^+ \rightarrow Ti^{2+}$ depends on the electronic configuration and on the type of electron being removed. If a curve of ionization potential *vs.* charge for the 3d level is desired, one considers the removal of a 3d-electron from various electronic configurations. Several such configurations are

$$\begin{array}{llll} Ti^0 & \rightarrow Ti^{1+} & \rightarrow Ti^{2+} & \rightarrow Ti^{3+} \\ 3d^4 & \rightarrow 3d^3 & \rightarrow 3d^2 & \rightarrow 3d^1 \\ 3d^34s & \rightarrow 3d^24s & \rightarrow 3d^14s & \rightarrow 4s \\ 3d^24s4p & \rightarrow 3d4s4p & \rightarrow 4s4p & \end{array}$$

Let us estimate the 3d VSIE for the $3d^n4s$ configuration of Ti^0. For the $3d^34s$ configuration one selects the lowest energy state for which a state of identical L value exists in the $3d^24s$ configuration of Ti^+. The difference in energy between these states is an approximation of the energy required to remove a 3d-electron from Ti^0, having an electron distribution $3d^34s$.

For example, the following data are taken from Moore's tables.[9]

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(20) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(21) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

(22) L. C. Allen, *ibid.*, **34**, 1156 (1961).

(23) Corrections to previous paper by L. L. Lohr and L. C. Allen, to be published.

State (configuration)	$^5F(3d^34s)$ →	$^4F(3d^24s)$
Promotion energy (P.E.) above ground state, cm.$^{-1}$	6557	0

I.P. of Ti^0 in the ground state = 55,138 cm.$^{-1}$

$$VSIE = I.P._{Ti^0} + P.E._{Ti^+} - P.E._{Ti^0} = 55{,}138 + 0 - 6557$$

$$VSIE = 48{,}581 \text{ cm.}^{-1}$$

Similar points are obtained for the $3d^n4s$ configuration of Ti^+ and Ti^{2+}, establishing the $3d^n4s$ curve. In the same manner, 3d curves are obtained for each possible configuration. For a 4s VSIE curve, all possible configurations are again used, this time removing a 4s-electron from each configuration. Curves are interpolated to obtain VSIE values for fractional charges and combinations of configurations.

A charge and electronic population are assumed, and corresponding VSIE values calculated. For example, assume a charge of 0.54 on Ti and a configuration of $3d^{2.75}4s^{0.37}4p^{0.34}$. In order to obtain the 3d VSIE for this population, a properly weighted combination of configurations must be used. One such combination is given below. The configurations refer to VSIE curves at Ti^0, where the population adds up to $3d^{3.29}4s^{0.37}4p^{0.34}$. The VSIE values for each configuration are read from the curves at the point of $Ti^{+0.54}$. For example, the VSIE for the 3d level, $Ti^{+0.54}$, d^nsp configuration is $-140{,}500$ cm.$^{-1}$, as read from Fig. 2. The 3d VSIE for the assumed population is estimated as

$$3d = 0.30(d^2sp) + 0.07(d^3s) + 0.04(d^3p) + 0.59(d^4)$$

$$3d = 0.30(-140{,}500) + 0.07(-94{,}000) + 0.04(-108{,}300) + 0.59(-72{,}000)$$

$$3d = -95{,}540 \text{ cm.}^{-1}$$

VSIE values for the 4s and 4p levels were obtained from the following combinations of configurations.

$$4s = 0.34(d^2sp) + 0.75(d^3s) - 0.09(d^2s^2)$$

$$4s = 0.34(-101{,}000) + 0.75(-75{,}350) - 0.09\,(-83{,}500)$$

$$4s = -83{,}340 \text{ cm.}^{-1}$$

$$4p = 0.37(d^2sp) + 0.75(d^3p) - 0.12(d^2p^2)$$

$$4p = 0.37(-58{,}900) + 0.75(-48{,}900) - 0.12(-58{,}450)$$

$$4p = -51{,}450 \text{ cm.}^{-1}$$

It should be noted that there are available curves for only three configurations in the 4s and 4p cases, and, with three population parameters to fit, only one weighting of configurations is possible. In the 3d case, there are four curves, so more than one combination of configurations will give the same over-all population. Varying the weighting coefficients between the widest possible extremes only caused a difference of about 2000 cm.$^{-1}$ in the 3d energy level, however.

Calculation of Coefficients and Electron Population.—An example of the calculation of coefficients for the e_g bonding level is given below.

$$E_{e_g} = -163{,}495 \text{ cm.}^{-1} \qquad H_{22}(\text{F hyb}) = -154{,}500 \text{ cm.}^{-1}$$

$$H_{11}(\text{Ti 3d}) = -95{,}540 \text{ cm.}^{-1} \qquad H_{12} = -75{,}567 \text{ cm.}^{-1}$$

$$(H_{11} - E)c_1 + (H_{12} - G_{12}E)c_2 = 0$$

$$(-95{,}540 + 163{,}495)c_1 + [-75{,}567 - 0.311(-163{,}495)]c_2 = 0$$

$$c_1 = 0.36377c_2$$

$$c_1^2 + c_2^2 + 2c_1c_2G_{12} = 1$$

$$c_2 = 0.8579$$

$$c_1 = 0.3121$$

Using the values of c_1 and c_2 the electron population was determined.

$$\Phi_{e_g}{}^b = c_1\psi_{3d} + c_2\psi_{hyb\sigma}$$

$$c_1^2 + 2c_1c_2G_{12} + c_2^2 = 1$$

for a one-electron orbital. The fraction of electrons in the $e_g{}^b$ level belonging to Ti = $c_1^2 + {}^1/_2(2c_1c_2G_{12})$ = 0.1807. The $e_g{}^b$ level holds four electrons, so Ti "owns" 0.7228 of a 3d electron in this level.

The population of Ti electrons in each level was determined in the above manner. The distribution in individual molecular orbitals is given in Table V.

TABLE V

Atomic level	Molecular orbital	Total electrons in m.o.	Ti electrons
3d	$e_g{}^b$	4	0.7228
	$t_{2g}{}^b$	6	1.2319
	$t_{2g}{}^*$	1	0.7947
	Total		2.7494
4s	$a_{1g}{}^b$	2	0.3691
4p	t_{1u} (I)	6	0.1252
	t_{1u} (II)		0.2189
	Total		0.3441

Total electrons = 3.463

Total charge on Ti = +4 − 3.463 = +0.537

The above populations were obtained using energies for an assumed population of $3d^{2.75}4s^{0.37}4p^{0.34}$.

It is interesting to note that the qualitative picture of the location of bonding and antibonding electrons is substantiated by the population distribution. In the $t_{2g}{}^b$ level, approximately 80% of the electrons are on the ligands, while 80% of the electrons in the $t_{2g}{}^*$ level are located on the central metal ion. It should also be noted that more than two of the total 3.46 electrons on Ti are in π-levels, once more emphasizing the importance of π-bonding.