This equation compares well to Gearhart's eq 6 if we take into account their different sign convention as expressed in eq 7, 8, and 9 and equate $K = e^2$. The only difference is that eq 24 replaces $(\partial M_\delta/\partial\delta)$ by $(\partial M_{\text{elec}}/\partial a)$. However, we can show that:

$$(\partial M_{\text{elec}}/\partial a) = (\partial M_\delta/\partial\delta) \qquad (25)$$

and hence the equations are identical.

Registry No. $Na(AlCl_4)$, 7784-16-9; $Cs(AlCl_4)$, 17992-03-9; $Cs(GaCl_4)$, 21646-31-1; $Ga(GaCl_4)$, 24597-12-4; $AlCl_4^-$, 17611-22-2; $GaCl_4^-$, 15201-06-6.

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The Ligand-Field Spectrum of Niobium(IV) in Fluoride Melts[1]

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Ligand-field spectra of the second-row transition-metal ions have not received as much attention as those of the first row, and consequently, rather little is known about the coordination behavior of these ions when they occur in dilute solutions. A continuing study at this laboratory is concerned with the characterization of niobium redox chemistry in fluoride melts by absorption spectroscopy. A prerequisite to this study is that the species involved in the redox equilibria and their absorption spectra be identified. High coordination numbers about the metal ions are favored in fluoride systems due to the size of the ligand and, as a result, some interesting spectra have been observed. An earlier paper[2] described the coordination behavior of Nb(IV) in the compound K_3NbF_7 and in this report its spectrum and behavior in fluoride melts are described.

Experimental Section

The spectrum of Nb(IV) in fluoride melts was obtained by dissolving either NbF_4 or K_3NbF_7 in a $LiF-BeF_2$ solvent. The preparation and characterization of these salts have been described before in detail.[2] Briefly, the experimental procedure[3] was as follows. A background spectrum of the molten $LiF-BeF_2$ (66–34 mol % or 48–52 mol %) was measured in a diamond-windowed graphite spectrophotometric cell at 550°C. The solvent and cell assembly were then cooled to room temperature and transported to a helium glove box of less than 1 ppm H_2O and O_2 content. There a weighed amount of solute was added to the top of the frozen salt. The cell was returned to the spectrophotometric furnace and reheated to 550°C. After the solvent melted, the solution was stirred with a platinum rod to ensure complete dissolution of the solute.

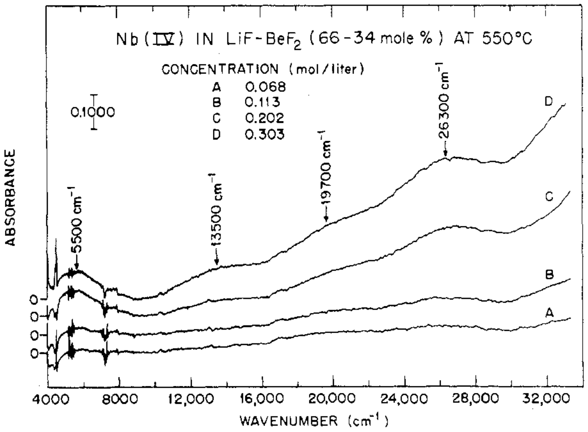

Figure 1. Nb(IV) in $LiF-BeF_2$ (66–34 mol %) at 550°C.

Absorption spectra were measured on a Cary 14H recording spectrometer equipped with a digital output accessory. The solvent background spectrum was subtracted from the solution spectrum using standard computing techniques.

Results

Spectra of Nb(IV), which were recorded using the K_3NbF_7 in $LiF-BeF_2$ (66–34 mol %) solution, are shown in Figure 1. Other spectra, not shown here, were measured using NbF_4 solutions and were found to be identical with those in Figure 1. Because the binary salt was easier to handle and dissolved more readily in the melt, most of the work reported here was performed using it as a solute. No change in the Nb(IV) spectrum was observed in going to the $LiF-BeF_2$ (48–52 mol %) melt.

The spectra fade after sitting for several days at 550°C presumably because of a reaction of the niobium species with the graphite spectrophotometric cell. At higher temperatures (600–700°C) the loss of Nb(IV) occurs within a few hours. No new bands appear as a result, suggesting that the products of the reaction are *not soluble* niobium species with valences less than five.[4]

The four bands were found to obey the Beer–Lambert law within the accuracy of the baseline determination for concentration changes up to 0.303 mol/l. However, the test should be qualified in the 5500-cm^{-1} region because of rapidly changing instrument parameters which occur at the ir limit and are evident in Figure 1 by the abrupt drop-off of the curves at 4000 cm^{-1}. As a result, the position of the band at 5500 cm^{-1} is not considered to be very accurate.

The Beer–Lambert behavior in the 4000–30000 cm^{-1} region indicates that either a single species is present in solution or, if there is more than one, their concentrations are in constant proportion at all the concentrations studied. As the temperature was increased up to 700°C, the spectra broadened slightly, but did not shift perceptibly in area. The spectra faded at these temperatures (as mentioned earlier) and did not return when the temperature was dropped. If there had been more than one species in solution, the change in temperature would be expected to produce a much larger change in the spectrum, and therefore, it is concluded that the spectrum in Figure 1 arises from a single Nb(IV) species.

The species giving rise to the spectrum in Figure 1 can be identified by the relationship of its spectrum to that of crystalline K_3NbF_7.[2] The spectrum of K_3NbF_7 consists of four bands which are assigned on the basis of a slightly distorted D_{5h} complex as indicated in Table I. Thermal disordering of the ligands with increasing temperature causes further distortions from D_{5h} symmetry and results in increased splittings for the degenerate e states of the Nb(IV) ion. In the limit defined by the melting point of the crystal, all bands should be completely separated. These would be assigned as arising from a seven-coordinated species with C_1 symmetry.

Table I. Comparison of the Nb(IV) Melt Spectrum with the K_3NbF_7 Spectrum[a,d]

Nb(IV) in LiF-BeF$_2$ (66-34 mol %)	K_3NbF_7 Position	K_3NbF_7 Assignment[b]
5500 (0.39)	2150	e_1'' $[(yz), (zx)]$[c]
13500 (0.44)	16556 (1.8)	e_2' $[(x^2-y^2), (xy)]$
19700 (1.1)	19762 (2.3)	
26300 (2.1)	28570	a_1' (z^2)

[a] K_3NbF_7 data taken from ref 2. [b] Assignment based on D_{5h} symmetry. [c] The e_1'' degenerate state is split to give a ground electronic state and the one indicated here. [d] All values are given in cm^{-1}. Molar extinction coefficients in l. mol^{-1} cm^{-1} are given in parentheses.

The melt spectrum of Figure 1, with bands similar in intensity to those of the crystal (cf. Table I), is consistent with this interpretation and represents the type of spectrum expected from a completely disordered seven-coordinated Nb(IV) ion.

Evidence in support of the implication that the coordination number remains seven on dissolution of K_3NbF_7 in the melt can be derived from the coordination behavior studies of similar tetravalent transition metal ions in fluoride melts. These studies[5] which include Zr(IV), Th(IV), and U(IV) ions, show that a variety of species ranging from eight to six coordination are possible in the melts. It was observed that the coordination number of the ion in the fluoride solvent is dependent on both the availability of "free fluoride"[6] ions with which to associate and the size of the metal ionic radius. Therefore, lower coordination numbers will occur for Nb(IV) and Zr(IV) in comparison with U(IV) and Th(IV). Because a seven–eight coordination equilibrium was observed for U(IV) in LiF–BeF_2 melts, any decrease in the size of the metal ion would tend to favor the lower coordination, i.e., seven.

In conclusion, the spectrum of Nb(IV) in fluoride melts is interpreted as arising from a NbF_7^{3-} species which has very low symmetry. The spectrum represents the very interesting case of a simple d^1 ion in which the degeneracy of the 4d subshell is completely removed.

Registry No. K_3NbF_7, 57049-46-4; NbF_4, 13842-88-1.

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Reduction of Trimethyl Phosphite–Borane. Formation of a New Type of Diphosphine Derivative

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The reactions of phosphine–boranes have not been widely investigated as compared, for example, to those of amine–boranes. We have recently studied some of the chemical characteristics of alkyl phosphite–boranes to compare these with amine–borane systems. In particular the reactions of phosphine–boranes and their derivatives with alkali metals were considered. We wish to report here on the reaction of trimethyl phosphite–borane with sodium naphthalide.

Experimental Section

Equipment and Materials. Standard vacuum-line techniques were employed[1] with greaseless stopcocks on all parts and reaction equipment. A LabConCo glovebox equipped with a recirculating pump and drying train and flushed with dry nitrogen gas was used for intert-atmosphere manipulations.

Ir spectra were obtained on a Beckman Model 4250 IR spectrophotometer. A Cary 14 spectrophotometer was employed for the uv spectra. A Varian Model E-3 spectrometer was used to obtain EPR spectra. Conductivity measurements were made on a Yellow Springs Model 31 conductivity bridge. Proton NMR data were obtained on a Varian Model T-60 NMR spectrometer while ^{11}B spectra were obtained using a Varian Model HA-100 instrument at 32.1 MHz and a Bruker Scientific Model WH-90 spectrometer at 28.89 MHz (FT mode). The latter instrument was also used to obtain ^{31}P spectra at 36.4 MHz in the FT mode. A Varian Model CFT-20 spectrometer was employed for the ^{13}C spectra. A cryoscopy cell similar to that described by Shriver[1] was employed for molecular weight measurements.

Carbon and hydrogen analyses were carried out by Heterocyclic Chemical Corp. Boron and phosphorus determinations were made by literature methods.[2,3]

All starting materials were reagent grade except trimethyl phosphite which was practical grade. Naphthalene, sodium borohydride, and trimethyl phosphite were purchased from MCB and sodium metal was from J. T. Baker. Deuterium oxide (99.8%) was obtained from Diaprep. Alumina of activity "1" was purchased from EM Reagents.

All aprotic solvents were dried over sodium and distilled prior to use. Trimethyl phosphite–borane was prepared according to the method of Reetz.[4] Sodium naphthalide was formed by placing measured quantities of sodium and naphthalene (with an excess of sodium) in a dry vessel on the vacuum line and condensing in a quantity of dried 1,2-dimethoxyethane. In a typical preparation 62.8 mg-atoms of sodium and 47.8 mmol of naphthalene were placed in a 100-ml glass bulb and cooled to −196° whereupon about 25 ml of solvent was vapor-transferred into the vessel. Slow warming and stirring gave the dark green solution indicative of sodium naphthalide.

Preparation of $Na_2[(CH_3O)_3P{\cdot}BH_3]_2$. In the reaction of sodium naphthalide with trimethyl phosphite–borane, nitrogen was first admitted into the vessel containing the former, which was then removed from the vacuum line port and attached via an O-ring connector to a vacuum-line filtration apparatus. The bulb was cooled with liquid nitrogen and 8.7 g (63 mmol) of $(CH_3O)_3P{\cdot}BH_3$ was added. The entire apparatus was then evacuated and the reaction bulb was allowed to warm slowly to room temperature with stirring. Near 0°C the reaction mixture became red but after stirring overnight the mixture was light brown with some white precipitate. The product was precipitated by condensing in 25 ml of dry petroleum ether (bp 30–60°) and warming again to room temperature with stirring. The light brown solid was separated from the light yellow solution by filtration in vacuo followed by several washings with petroleum ether to help remove naphthalene. Solvents were removed by vapor transfer and the near-white solid was dried under dynamic vacuum for several hours. Dry nitrogen was admitted and the apparatus removed to a glovebox where the solid product was transferred to a preweighed vial. A crude yield of 8.00 g (79%) based on trimethyl phosphite–borane was obtained.

Further purification was accomplished by column chromatography using alumina and 1,2-dimethoxyethane. A glass column was filled with a slurry of alumina and allowed to stand overnight. The entire product (8.00 g) in 75 ml of 1,2-dimethoxyethane was added to the solvent reservoir and the solution was eluted under 10 psi of dry nitrogen. The separation was followed by ^1H NMR as fractions were collected. The first 100 ml contained naphthalene and was discarded. The next 150 ml was collected and the solvent was stripped off using a rotary evaporator yielding a light yellow solid. The solid was placed in 100 ml of dichloromethane and stirred for 2 hr. Filtration gave the white solid product (2.3 g) in about 23% yield.

An attempted melting point determination on the product showed color changes to yellow near 228° and to orange near 330° but no melting was observed up to 400°. Anal. Calcd for $C_3H_{12}BO_3NaP$: