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# Synthesis and Ligand Field Spectrum of Potassium Heptafluoroniobate(IV)[1]

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The cubic compound $K_3NbF_7$ has been synthesized by reduction of a molten KF–$NbF_5$ mixture at 850° with Nb metal. It is isostructural with other disordered cubic compounds $(NH_4)_3ZrF_7$ and $K_3NbOF_6$ of space group $O_h^5(Fm3m)$ where the transition metal atom is coordinated to seven anions in a distorted pentagonal bipyramid having approximate $D_{5h}$ symmetry. The ligand field spectrum has been found to consist of four bands which are assigned on the basis of a $d^1$ ion in a $D_{5h}$ field to the split component of the $e_1''$ ground state at 2150 $cm^{-1}$, the split $e_2'$ excited state at 16,556 and 19,762 $cm^{-1}$, and the $a_1'$ excited state at 28,570 $cm^{-1}$. The observed splitting of the degenerate states increases as the temperature is raised through, presumably, vibrational disordering.

## Introduction

The most common inorganic compounds of Nb(IV) are the halides, $NbX_4$. These have complex physical and chemical properties which often make them difficult to use either as reagents or reference materials. Their complexity is realized when considering electronic spectra where at least one band arising from the $d^1$ electron of Nb(IV) is expected and yet has not been measured or assigned. Furthermore, in spite of the attention which has been recently focused on the synthesis and characterization of other Nb(IV) compounds, especially those with organic ligands, little progress has been made in interpreting their electronic spectra.

To begin a study of the ligand field spectrum of the Nb(IV) ion, the inorganic ligands, especially the fluoride ions, provide an advantage over the organic ligands because the weak forbidden transitions should be well removed from the lowermost electronically allowed bands. We have sought the synthesis of a simple niobium(IV) fluoride compound in order to interpret its electronic spectrum as a function of coordination behavior. It was also anticipated that such a compound would have physical properties which would enable it to be handled more conveniently than $NbF_4$. A description of the Nb(IV) absorption spectrum in crystalline compounds is intended to aid in explaining its absorption spectrum in solution but this subject will be deferred until later reports. Because so few inorganic compounds of Nb(IV) are known, the synthesis and characterization of $K_3NbF_7$ are presented here.

## Experimental Section

**Synthesis.** Two procedures can be used to make $K_3NbF_7$: either direct fusion of 3 mol of KF with 1 mol of $NbF_4$ or reduction of $NbF_5$ with Nb in the presence of KF at 850° according to the reaction

$$15KF + 4NbF_5 + Nb \rightarrow 5K_3NbF_7$$

The direct-combination method is less satisfactory because it requires an additional step, the prior synthesis of $NbF_4$, and it produces a product of lower purity. Consequently the reduction synthesis was used extensively in this study and is described in the following paragraphs.

The reagent salts were purified as follows. Optical quality KF crystal scrap (Harshaw Chemical Co.) was sparged with HF gas while molten in a graphite crucible to remove oxide impurities. The HF was displaced from the melt by next sparging with dry helium.

The $NbF_5$ was prepared by direct combination of the elements in a closed nickel container at 200° and was purified by sublimation in a sealed quartz tube. The oxide content of the resulting $NbF_5$ crystals was less than 100 ppm as determined by the $BrF_3$ method.

The synthesis of $K_3NbF_7$ was performed in a glove box containing a helium atmosphere maintained at less than 1 ppm of $H_2O$ and $O_2$. Stoichiometric amounts of KF and $NbF_5$ were ground together to produce a 2-g batch. The intimate grinding of these components prevented the evaporation of $NbF_5$ when the mixture was melted in an open 3-ml platinum crucible (as shown by the negligible weight loss at the end of the preparation). The mixture was heated with a simple resistance furnace located in the glove box and was monitored by a thermocouple placed between the furnace and crucible walls. The mixture melted at approximately 800° to produce a transparent, colorless liquid which could then be stirred with a platinum rod.

The Nb(V) melt was reduced with a stoichiometric amount of Nb wire (10-mil diameter) coiled on the end of the platinum stirrer. The melt was observed to turn dark immediately after it came in contact with the Nb coil. As the reduction proceeded to completion over a 30-min interval, the temperature had to be increased steadily in order to maintain a molten mixture. The final melt temperature reached was approximately 850°.

After reduction was completed, the melt was cooled at 0.8°/min to enhance crystal growth. No reaction with the platinum was evident when the deep violet button of salt was removed from the crucible. The analyses performed on $K_3NbF_7$ gave the following results. *Anal.* Calcd: K, 34.18; Nb, 27.07; F, 38.75. Found: K (by flame emission), 34.5; Nb (by gravimetry), 27.02; F (by pyrohydrolysis), 37.89. The amount of oxygen was 0.16 wt%. Spectrographic analysis (of impurities 10 ppm or greater): Ag, 30; Al, 80; Li, 100; Na, 500, Rb, 100; Sb, 100; Si, 15; Ti, 10.

**X-Ray Measurements.** Samples for X-ray powder patterns were loaded into thin-walled quartz capillaries in a glove box and sealed off with black sealing wax. Debye–Scherrer powder patterns were recorded using filtered Cu K$\alpha$ radiation according to standard procedures.

**Microscopic Measurements.** The compound was examined under a standard polarizing-light microscope to determine its optical properties. Indices of refraction were measured by the oil immersion method.

**Differential Thermal Analysis (Dta) and Thermogravimetric Analysis (Tga).** A 60-mg sample of $K_3NbF_7$ was examined simultaneously by dta and tga in an atmosphere of flowing argon. Two heating and cooling cycles were recorded through the melting point region at a rate of 6°/min.

**Spectral Measurements.** Absorption spectra in the 4000–50,000-$cm^{-1}$ region were measured with a Cary 14-H recording spectrometer equipped with a Datex digital output accessary. A 1.5 mm thick polished disk of $K_3NbF_7$ which measured approximately 1 cm in diameter was used to record the transmission spectra. This sample provided the quantitative determination of the absorption coefficients for the bands in the visible region. An estimate of the other band intensities (*i.e.*, those in the infrared and the ultraviolet regions) was made by comparison with the visible region.

The sample was enclosed in an inert-atmosphere furnace[2] for both the ambient- and the high-temperature spectra. Absorption spectra of $K_3NbF_7$ in Kel-F mulls were measured according to the method of Ryan and Jorgensen[3] in a variable path length cell set at approximately 1 mm. Diffuse reflectance spectra were measured with a Cary Model 1411 diffuse reflectance accessary (ring collection system) on the Cary spectrometer against a LiF reference.

Infrared transmission spectra of a 1 mm thick polished disk measuring 1 cm in diameter were recorded from 500 to 4000 $cm^{-1}$ on

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) Details of the furnace are given by L. M. Toth and L. O. Gilpatrick, *J. Phys. Chem.*, 77, 2799 (1973).

(3) J. L. Ryan and C. K. Jorgensen, *J. Phys. Chem.*, 70, 2845 (1966).

a Perkin-Elmer Model 621 spectrometer. The sample was enclosed in an O-ring sealed cell fitted with KBr windows and filled with dry helium. Spectra were recorded in the absorbance mode to be consistent with the visible-uv spectra. The same infrared spectrum was also scanned on a Digilab FTS-20 spectrometer in an effort to obtain better results but is not presented here because no substantial improvement over the one obtained on the Perkin-Elmer instrument was achieved. High-temperature (up to 600°) infrared transmission spectra were attempted in a small sealed furnace fitted with AgBr windows but emission from the hot sample obscured the absorption spectrum. It was not possible to measure an emission spectrum from the hot crystalline sample on the FTS-20 because the small furnace used to heat the $K_3NbF_7$ was not adaptable to the design of the interferometer spectrometer.

## Results and Discussion

The compound $K_3NbF_7$ is most conveniently prepared from the melt since it is stable at temperatures up to its melting point and melts to form a liquid that does not disproportionate into other oxidation states of niobium. It is stable in air at 25° for several weeks and can be sparingly washed with dry methanol. By comparing Debye-Scherrer powder patterns, $K_3NbF_7$ was found to be isostructural with $K_3NbOF_6$[4a] and $(NH_4)_3ZrF_7$[4b] which have the cubic structure $O_h{}^5(Fm3m)$. The Miller indices are given for $K_3NbF_7$ in Table I along with their relative intensities. The occurrence of the two niobium compounds with identical crystal structures and similar lattice constants [*cf.* $a(K_3NbF_7) = 8.93$ Å and $a(K_3NbOF_6) = 8.87$ Å][4a] is understandable realizing the similar ionic radii for $O^{2-}$ and $F^-$ and that the fluorine and Nb(IV) ions in $K_3NbF_7$ probably occupy equivalent oxygen and Nb(V) ion sites, respectively, in $K_3NbOF_6$.

The isostructural nature of $K_3NbF_7$ and $K_3NbOF_6$ made it difficult to distinguish between the two compounds by their X-ray powder patterns. Alternate methods of characterizing $K_3NbF_7$ were sought since it was remotely possible that the Nb(IV) compound had been oxidized to Nb(V) during the preparation and the "$K_3NbF_7$" was, in fact, only $K_3NbOF_6$. The oxide analysis of 0.16 wt % was one such means of demonstrating that this concern was unwarranted. Furthermore, when $K_3NbOF_6$ was separately prepared for further comparative examination, it was found to have no chemical or physical resemblance to $K_3NbF_7$ other than in crystal structure.

Optical microscopy using a petrographic microscope ultimately proved to be the most convenient method of assessing purity and differentiating between the above two niobium compounds. Optically, both were estimated to be better than 98% pure and were found to have readily distinguishable indices of refraction, $n(K_3NbF_7) = 1.431$ and $n(K_3NbOF_6) = 1.463$. An estimate of the change in $n$ was made in order to rationalize the measured values. It was assumed that the Lorentz-Lorenz molar refractivities were additive and that the major difference between the two measured indices of refraction lay in the difference between the molar refractivities of $F^-$ and $O^{2-}$.[5] Using Fajans' values for these molar refractivities, $n = 1.52$ was calculated for $K_3NbOF_6$ (*cf.* $n = 1.461$, measured) by starting with $n$ for $K_3NbF_7$ and substituting an oxide ion for a fluoride ion. The calculated value confirms that a higher index of refraction for $K_3NbOF_6$ is expected, in agreement with the measured value and the general observation that the oxides have higher $n$ values than do the fluorides.

**Table I.** Debye–Scherrer Diffraction Pattern for $K_3NbF_7$ ($a = 8.9327 \pm 0.0005$ Å; Cu K$\alpha$ ($\lambda$ 1.5418 Å))

| *hkl* | *d*, Å | $I/I_0$ | *hkl* | *d*, Å | $I/I_0$ |
|---|---|---|---|---|---|
| 111 | 5.155 | 40 | 800 | 1.116 | 3 |
| 200 | 4.450 | 25 | 644 | 1.083 | 3 |
| 220 | 3.153 | 100 | 660 | 1.053 | 5 |
| 311 | 2.687 | 9 | 840 | 0.999 | 5 |
| 400 | 2.227 | 40 | 753 | 0.981 | 4 |
| 331 | 2.045 | 5 | 842 | 0.975 | 3 |
| 420 | 1.993 | 13 | 664 | 0.952 | 3 |
| 422 | 1.822 | 50 | 931 | 0.937 | 3 |
| 333 | 1.714 | 13 | 844 | 0.912 | 3 |
| 440 | 1.576 | 15 | 862 | 0.876 | 5 |
| 531 | 1.509 | 7 | 862 | 0.874 | <1 |
| 600 | 1.487 | 5 | 951 | 0.864 | 2 |
| 620 | 1.413 | 13 | 953 | 0.834 | 2 |
| 533 | 1.361 | 3 | 1042 | 0.816 | 4 |
| 444 | 1.288 | 7 | 1042 | 0.814 | <1 |
| 711 | 1.250 | 5 | 775 | 0.806 | 1 |
| 642 | 1.193 | 13 | 955 | 0.781 | 3 |
| 553 | 1.163 | 5 | | | |

The dta analysis was performed to establish the melting point and the purity of the compound. Three different samples were examined, one at the stoichiometric $K_3NbF_7$ composition, one at the $K_3NbF_7$ composition plus 2 mol % of excess KF, and one at the 2:1 KF-$NbF_4$ composition. These melted at 840 (±5), 805 (±5), and 807 (±5)°, respectively. The second sample also showed a pronounced thermal effect at 720 (±5)° which was interpreted as being the eutectic point on the KF-rich side of $K_3NbF_7$. This 720° effect was barely perceptible in the nominal 3:1 composition and therefore indicated that the sample was not precisely of the indicated composition. The third sample melted at a lower temperature than the $K_3NbF_7$ and showed no 720° thermal effect. On the basis of these thermal data, it was concluded that $K_3NbF_7$ was a congruently melting compound which was stable from its melting point to room temperature.

**Spectral Measurements.** The purpose of the work with the crystalline niobium salts was to define a ligand field spectrum of Nb(IV) which would then serve as a guide in studying the absorption spectrum of this ion in solution. The visible-uv absorption spectrum of $K_3NbF_7$ from 4000 to 40,000 $cm^{-1}$ is shown in Figure 1. Curve A is the transmission spectrum of a 1.5 mm thick plate showing bands at 16,556 and 19,762 $cm^{-1}$ (both with molar absorption coefficients, $\epsilon \sim 1.5$ l. $mol^{-1}$ $cm^{-1}$ after base line correction). These lie beside a very steep shoulder which rises at approximately 25,000 $cm^{-1}$. Light scatter from the polycrystalline plate was responsible for a large amount of the tail which extends from the uv to the infrared region and precluded the measurement of absorption spectra in the near-ultraviolet region. Because it was impractical to cut and polish thinner plates for absorption measurements, a diffuse reflectance spectrum of the ultraviolet region was obtained (*cf.* curve B, Figure 1) and reveals a third band at 28,570 $cm^{-1}$. Also shown in this figure is a mull spectrum (curve C) which, by comparison with the bands in the visible region, enabled the molar absorption coefficient of the 28,570-$cm^{-1}$ band to be estimated as $\leqslant 10$ l. $mol^{-1}$ $cm^{-1}$. The spectrum shown in curve C was measured against a LiF mull reference which tended to overcompensate for the light scatter thus depressing this band relative to the two in the visible. The intensity of the three bands strongly suggests that they are due to ligand field d-d transitions.

The weak intensity of the two bands in the visible region simplified the experimental procedure since it was possible to use a relatively thick (1.5 mm) plate for the measurement of the absorption spectrum. A low-temperature absorption

(4) (a) M. B. Williams and J. L. Hoard, *J. Amer. Chem. Soc.*, 64, 1139 (1942); (b) H. J. Hurst and J. C. Taylor, *Acta Crystallogr., Sect. B*, 26, 417 (1970).

(5) (a) Although this is an oversimplification, a more detailed treatment is not warranted for the purposes sought here. (b) This must be assumed because refractivities for Nb(IV) and Nb(V) cannot be accurately estimated.

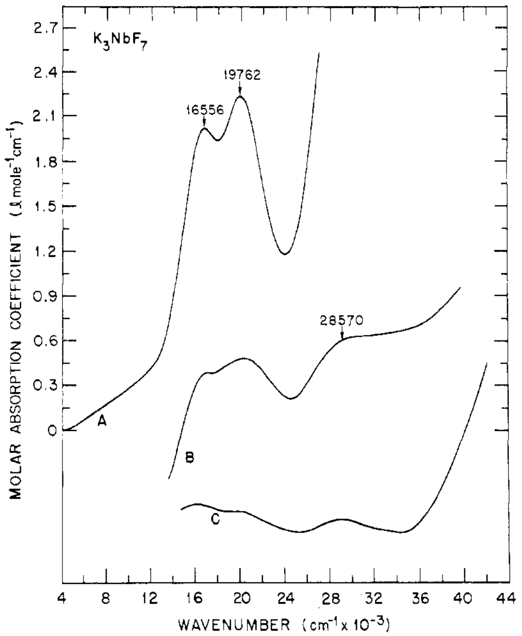

**Figure 1.** Electronic spectrum of $K_3NbF_7$ at 25°: curve A, absorption spectrum of a polycrystalline plate with 1.5-mm path length; curve B, diffuse reflectance spectrum of a powdered sample against a LiF reference; curve C, Kel-F mull spectrum against a LiF mull reference. The molar absorption coefficient scale applies only to curve A.

spectrum was not attempted after we had observed earlier that crystals shattered on cooling below 25°. However a high-temperature spectrum was measured to test a previous suggestion[6] that thermal effects lowered the local symmetry about the transition metal ion in this crystal system and removed the degeneracy of some transitions. The absorption spectra of $K_3NbF_7$ at 300, 450, and 600° are shown in Figure 2 with the two dashed vertical lines indicating the position of the bands at 25°. It is evident from this figure that the two bands separate in a continuous fashion as the temperature is increased. The apparent growth in the band intensity in going from curves A to C was actually due to light scatter arising from degradation of the polished crystalline surfaces at these temperatures. The surface damage was caused by reaction with either traces of embedded polishing compound or impurities in the furnace atmosphere. Although the ultraviolet region was obscured by the intense scatter background, the infrared portion of the spectrum was largely unaffected. A gradual rise in the base line at the extreme 4000-cm$^{-1}$ position is therefore evident and suggests the presence of an additional band which has shifted at higher temperatures from the infrared into the range of the Cary 14.

The assignment of the $K_3NbF_7$ spectrum is based on a geometry derived from the X-ray study of the isostructural compound $(NH_4)_3ZrF_7$[4b] where the Zr(IV) atom is coordinated to seven fluoride ions in a slightly distorted pentagonal bipyramid. Despite some inadequacies in this structure determination,[7] recent Raman and infrared spectra[8] support the pentagonal-bipyramidal coordination geometry of $D_{5h}$ symmetry.

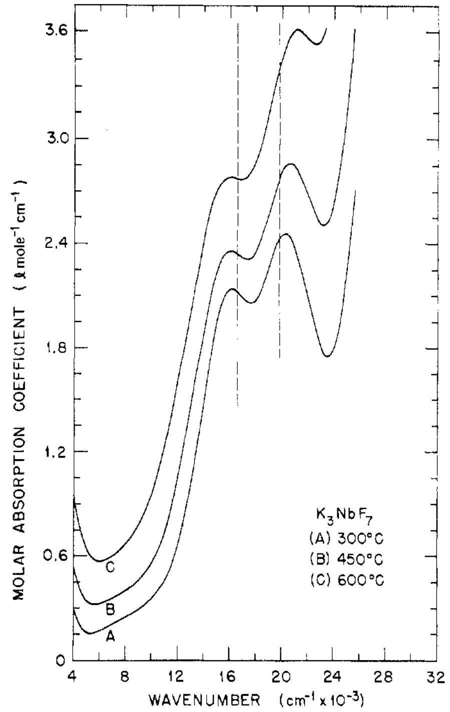

**Figure 2.** Absorption spectra of $K_3NbF_7$ *vs.* temperature for a 1.5-mm path length sample.

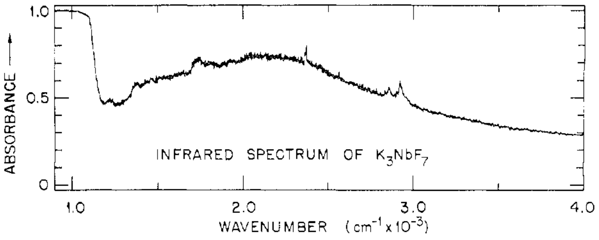

**Figure 3.** Infrared absorption spectrum of $K_3NbF_7$ measured from a 1 mm thick polished plate.

In a $D_{5h}$ field, the five degenerate d orbitals split into three groups, a degenerate $e_1''[(yz),(zx)]$ ground state, a degenerate $e_2'[(x^2-y^2),(xy)]$ excited state, and an $a_1'(z^2)$ excited state.[9] The band at 28,570 cm$^{-1}$ is assigned to the $a_1'$ state while the two bands at 16,556 and 19,762 cm$^{-1}$ are assigned to the degenerate $e_2'$ state which is split by the slight distortion of the $D_{5h}$ point group which was reported by Hurst and Taylor.[4b] If the $e_2'$ state is split by the distortion, then the $e_1''$ ground state is expected to be split also. However it should appear in the infrared region outside the range of the Cary. It has already been shown that the separation of the two bands assigned to the $e_2'$ state increases at higher temperatures, and it is expected that the splitting of the $e_1''$ state should behave in a similar fashion. Therefore the appearance of another band at 4000 cm$^{-1}$ for the high-temperature spectra should be attributed to a component of the $e_1''$ ground state.

The spectrum shown in Figure 3 was measured to prove that there was indeed an electronic band in the infrared region. The sharp cutoff at 1100 cm$^{-1}$ is caused by the strong absorption of the $NbF_7^{3-}$ vibrational modes which would be measurable only at very reduced path lengths. The weak band centered at 2150 cm$^{-1}$ has a half-width (*ca.* 1000 cm$^{-1}$) and intensity comparable to the bands of Figure 1 which are assigned to ligand field transitions. At higher temperatures, it is presumed that this band shifts to higher fre-

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(6) L. M. Toth, *J. Phys. Chem.*, **75**, 631 (1971).

(7) R. A. Penneman, R. R. Ryan, and A. Rosenzweig, *Struct. Bonding (Berlin)*, 13, 15 (1973).

(8) L. M. Toth and J. B. Bates, unpublished results.

(9) S. T. Spees, Jr., and J. R. Perumareddi, *J. Phys. Chem.*, **72**, 1822 (1968).

**Table II.** Assignments of Measured Ligand Field Bands (in $cm^{-1}$) for $K_3NbF_7$ in Slightly Distorted $D_{5h}$ Symmetry[a]

| Measd freq | $D_{5h}$ assignment |
|---|---|
| 28,570 | $a_1'(z^2)$ |
| $\left.\begin{array}{r}19{,}762\\16{,}556\end{array}\right\}\Delta = 3206$ | $e_2'[(x^2-y^2), (xy)]$ |
| $\left.\begin{array}{r}2150\\0\end{array}\right\}\Delta = 2150$ | $e_1''[(yz), (zx)]$ |

[a] Splitting denoted by Δ.

quencies causing the appearance of its shoulder at 4000 $cm^{-1}$ in Figure 2. Attempts to demonstrate the temperature shift of this band failed because of instrument limitations. Nevertheless its appearance at 2150 $cm^{-1}$ is consistent with what would be predicted on comparison with the splitting observed for the $e_1'$ state. Table II summarizes the assignments which have been made for the electronic spectra.

The spectrum of $K_3NbF_7$ can be related to previously reported spectra of $D_{5h}$ complexes involving V(III)[10] and Ti(III).[11] Using the notation of Levenson and Dominguez,[10] $10\delta_1$ and $10\delta_1 + 10\delta_2$ for $NbF_7^{3-}$ are found to be 17,084 and 28,570 $cm^{-1}$, respectively, from average values for the $e_1''$ and $e_2'$ states shown in Table II. These values for Nb(IV) (when compared with those in Table III of ref 10) are equivalent to those measured for V(III) and considerably greater than those measured for Ti(III). In spite of the lower position of $F^-$ relative to $CN^-$ in the spectrochemical series, the second-row transition elements especially with a greater charge would be expected to compensate for the effect of the weaker ligand. Thus the energies measured for d-d electronic transitions in $NbF_7^{3-}$ are not viewed as unusual.

In conclusion, these assignments represent the complete ligand field spectrum of a seven-coordinated Nb(IV) ion in a field of slightly distorted $D_{5h}$ symmetry. The effect of higher temperatures causes further distortion of the $D_{5h}$ field as shown by the increase in the splitting of the originally degenerate states. In the limit, all four electronic bands should appear in the 4000–40,000-$cm^{-1}$ region. Such a spectrum would be anticipated for a seven-coordinated Nb(IV) ion in a solution containing a random arrangement of ligands about the cations.

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**Registry No.** KF, 7789-23-3; $NbF_5$, 7783-68-8; Nb, 7440-03-1; $K_3NbF_7$, 51773-97-8.

[10] R. A. Levenson and R. J. G. Dominguez, *Inorg. Chem.*, **12**, 2342 (1973).

[11] M. G. B. Drew, G. W. A. Fowles, and D. F. Lewis, *Chem. Commun.*, 876 (1969).

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# New Molybdenum(II) and Molybdenum(III) Species

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The preparations of $Mo(H_2O)_6{}^{3+}$, of a species with $NH_3$ coordinated to Mo(III) which we take to be $[Mo(NH_3)_4(H_2O)HCO_2]^{2+}$, of $K_4Mo_2(SO_4)_4$, of $Mo_2(en)_4Cl_4$, of $Mo_2{}^{4+}$(aq), and of miscellaneous related compounds are described. The continued investigation of $Mo(H_2O)_6{}^{3+}$ and of $Mo_2{}^{4+}$(aq) has led to a revision of the absorption spectra reported earlier. For $Mo(H_2O)_6{}^{3+}$, in place of the strong peaks in the uv region reported earlier, which we now believe were caused by Mo(V) present in trace amounts, we find $\lambda_{max}$ at 308 nm ($\epsilon$ 28 ± 1.4 $M^{-1}$ $cm^{-1}$) and at 370 nm ($\epsilon$ 16 ± 0.8 $M^{-1}$ $cm^{-1}$) and attribute these bands to spin-allowed d–d transitions. For $Mo_2{}^{4+}$(aq) we find $\lambda_{max}$ at 504 nm ($\epsilon$ 337 $M^{-1}$ $cm^{-1}$) and at 370 nm ($\epsilon$ 40 $M^{-1}$ $cm^{-1}$). For $Mo_2(en)_4{}^{4+}$, three bands are observed: 478 nm ($\epsilon$ 483), 360 nm ($\epsilon$ 36), and 235 nm ($\epsilon$ 966). Qualitative observations on some reactions of $Mo(H_2O)_6{}^{3+}$, $Mo_2(en)_4{}^{4+}$, and $Mo_2{}^{4+}$(aq) are reported.

As part of a program of research devoted to extending the chemistry of complexes of second and third row transition elements in low oxidation states, in combinations stressing saturated ligands, we have attempted to prepare aquo ions of Mo(III) and Mo(II) and of ammine or related complexes as well.

Hartmann and Schmidt[1] reported ligand field spectra of Mo(III) species prepared in 4 *M* hydrochloric, hydrobromic, or sulfuric acid, and from the fact that the spectra were found to be rather insensitive to the nature of the anion, they concluded that the green species they had in hand was the same in the different media and that it therefore was $Mo(H_2O)_6{}^{3+}$. This claim was disputed by Bowen and Taube[2] who outlined an alternative method for preparing what they believed to be $Mo(H_2O)_6{}^{3+}$, describing the species as being virtually colorless. Their conclusions as stated were supported by Kustin and Toppen,[3] who did, however, point out that the uv bands reported by Bowen and Taube[2] are not properties of $Mo(H_2O)_6{}^{3+}$.

In this paper, details of the preparation and characterizations of $Mo(H_2O)_6{}^{3+}$ are reported. We concede the correction to our earlier work on the matter of the uv spectrum of $Mo(H_2O)_6{}^{3+}$ and report values for the intrinsic spectrum more nearly in accord with expectations for absorption arising from d–d transitions. Work on the preparation of species containing $NH_3$ in the first coordination sphere of Mo(III) is also described. Little has been reported on the chemistry of the important class of saturated ligand complexes, namely the ammines. Rosenheim, *et al.*,[4] have claimed to have prepared the complexes $[MoCl_3(NH_3)_3]$, $[MoCl_2(NH_3)_4]Cl$, and [Mo-

[1] H. Hartmann and H. J. Schmidt, *Z. Phys. Chem. (Frankfurt am Main)*, **11**, 134 (1957).

[2] A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, **93**, 3287 (1971).

[3] K. Kustin and D. Toppen, *Inorg. Chem.*, **11**, 2851 (1972).

[4] A. Rosenheim, G. Abel, and R. Levy, *Z. Anorg. Allg. Chem.*, **197**, 189 (1931).