metal–metal bond, but apparently it lies in a band available for conduction. Partial substitution of P for S in NbPS raises the valence of Nb toward +5, and the superconducting transition temperature is lowered. From the limited number of experiments, it appears that the T_c also decreases in direct proportion to the amount of Se or Ta substituted in NbPS.

The superconducting transition temperature of NbPS is the highest known for a compound of anion:cation ratio of 2. A fundamental physical study of these compounds should lead to a greater understanding of conditions permitting the occurrence of superconductivity.

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Contribution from the Reactor Chemistry Division, Oak Ridge
National Laboratory, Oak Ridge, Tennessee 37830

The Structure and Spectrum of Potassium Hexafluoromolybdate(III)[1]

By L. M. Toth, G. D. Brunton, and G. P. Smith

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The compound K_3MoF_6 (mp of 734 ± 10° and macroscopic ρ_{25} 3.23 ± 0.03 g/cm^3) was prepared in the form of pale yellow cubic crystals by fusing KF and MoF_3 in a sealed platinum tube at 800°. The crystals belong to the space group Fm3m with $a_0 = 8.7839 \pm 0.0009$ Å at 23° and contain octahedrally coordinated MoF_6^{3-} complex anions with an Mo–F bond length of 2.00 (2) Å. The diffuse reflectance spectrum shows three bands—one at 262 mμ, assigned to a charge-transfer transition, and the following ligand field bands: ${}^4T_{2g}(t_{2g}{}^2e_g) \leftarrow {}^4A_{2g}(t_{2g}{}^3)$ at 425 mμ and ${}^4T_{1g}(t_{2g}{}^2e_g) \leftarrow {}^4A_{2g}(t_{2g}{}^3)$ at 337 mμ with a *Dq* of 2350 cm^{-1} and a Racah *B* parameter of 570 cm^{-1}.

Introduction

The absorption spectrum of a 0.01–1.0 wt % solution of Mo(III) in molten $LiF-BeF_2$ (66–34 mol %[2]) contains ligand field bands that are reasonably attributed to octahedrally coordinated[3] MoF_6^{3-}. We wished to check this result by obtaining the spectrum of this complex ion in a crystalline system where the geometry had been determined by X-ray diffraction. In the compound MoF_3, Mo(III) is surrounded by a slightly irregular octahedral array of F^- ions[4] but we were unable to obtain a satisfactory ligand field spectrum of this material. Therefore, we allowed MoF_3 to react with KF to produce K_3MoF_6, used X-ray diffraction to demonstrate that Mo(III) in this compound is present as octahedrally coordinated MoF_6^{3-}, and measured the diffuse reflectance spectrum from 600 to 210 mμ. These results are reported here.

The synthesis of K_3MoF_6 has been reported previously by Peacock[5] and Aleonard.[6] Peacock described the reaction of K_3MoCl_6 with molten KHF_2 to produce brown cubic K_3MoF_6 while Aleonard describes the reduction–exchange reaction of MoO_3 with a solution of $KF-KBF_4$ (50:50 wt %) at 900° in a graphite crucible. However, no chemical analyses nor properties of the compound have ever been given to characterize it further. Aleonard was unable to isolate a pure K_3MoF_6 compound from the reaction mixture but a Debye–Scherrer powder pattern of the solid mixture revealed weak reflections, which were presumed to be cubic K_3MoF_6, in addition to the strong fluoroborate lines. Babel[7] has examined this cubic pattern and points out that it is identical with the pattern given for the oxide–fluoride compound $K_3MoO_3F_3$. Therefore, it is not clear that K_3MoF_6 has been prepared previously.

Experimental Section

Synthesis.—Stoichiometric quantities of KF and MoF_3 were weighed and mixed in an inert-atmosphere drybox of <1 ppm by volume water content. The KF had been crystallized from its melt and clear crystalline pieces were hand-picked. The MoF_3 was prepared by the reduction of MoF_6 with Mo in a Pyrex system. An oxide analysis on the KF revealed 240 ppm oxide. *Anal.* Calcd for MoF_3: Mo, 62.7; F, 37.3. Found: Mo, 62.7; F, 37.9. Major cation impurities were (in ppm): Al, ≤200; Ca, <100; Li, <500; Na, <300; Si, <300; W, ≤500. A Debye–Scherrer powder pattern of the MoF_3 starting material agreed with the previously reported pattern.[4]

Approximately 200 mg of the K_3MoF_6 stoichiometric mixture was loaded into a $^7/_8$-in. diameter × 1.5-in. long platinum tube which had been sealed on one end. The tube was collapsed around the sample and the open end was closed by folding tightly and crimping with pliers. The tube was removed from the drybox and immediately sealed with a small oxyacetylene torch. The platinum tube was then enclosed in a small heavy-walled silica tube filled with $^1/_3$ atm of dry nitrogen. The silica served to contain any reagents which might leak out of the platinum had the platinum not been properly sealed. Any leakage would be immediately apparent due to the rapid corrosion of quartz by most fluoride salts at temperatures of 600–900°.

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

[2] *I.e.*, a mixture of 66 mol % LiF and 34 mol % BeF_2.

[3] L. M. Toth, J. P. Young, and G. P. Smith, results to be submitted for publication.

[4] D. E. LaValle, R. M. Steele, M. K. Wilkinson, and H. L. Yakel, Jr., *J. Am. Chem. Soc.*, **82**, 2433 (1960).

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The materials were fused and held at 800° for 0.5 hr. During this time the collapsed platinum tube expanded fully and provided mixing space for the reagents. The container was then cooled to room temperature, removed to the drybox, and opened. The contents of the tube separated into two distinct regions—one consisting of small pale yellow cubic crystals (60–80% yield) which were subsequently shown to be K_3MoF_6 and the other, a dark blue heterogeneous mass, which could not be identified from its powder patterns. The yellow crystals were hand-picked under a 20× microscope and washed with acetone and/or ethanol to remove excess KF and other unidentified salts. Results of a spectrographic analysis on the pale yellow crystals (K_3MoF_6) in ppm are: Al, 40; B, 50; Ca, 7; Cr, 10; Fe, 70; K, major; Mg, 7; Mo, major; Si, 500. *Anal.* Calcd for K_3MoF_6: K, 35.8; Mo, 29.4; F, 34.9. Found: K, 35.2; Mo, 29.0; F (by difference), 35.8.

Melting Point Determination.—The melting points of several K_3MoF_6 crystals, approximately 150 μ in linear dimensions, were measured with a Zeiss hot-stage microscope in an inert-atmosphere drybox. The samples were placed on a thin sheet of platinum foil and illuminated from above by "top-lighting" (as opposed to "trans-illumination" from below the sample which requires that both the sample and the stage on which it rests be transparent). The significance of this method of lighting will be discussed later. The microscope was calibrated under identical conditions with CsCl, KCl, and NaCl (mp 640, 770, and 801°, respectively).

Density Measurements.—As an aid to the crystal structure determination, the density of several single K_3MoF_6 crystals was determined by mixing diiodomethane with tetrabromomethane until the crystals remained suspended in the solution. The density of the solution was then determined by conventional means.

Spectral Measurements.—Diffuse reflectance spectra were measured on a Cary Model 14 spectrometer fitted with a Model 1411 ring-collector diffuse reflectance accessory. The cell in which the K_3MoF_6 was contained consisted of a metal dish with an "O"-ring-sealed silica window over the top. Filter paper was used both as the background for the K_3MoF_6 crystals and as the reference spectrum. Crystals measuring approximately 150 μ were used for the spectrum.

A transmission spectrum of a small polycrystalline piece of K_3MoF_6 was measured by fitting it over a 0.20-in. diameter pinhole. The pinhole aperture fit in the sample compartment of the Cary 14 spectrometer and the air reference beam was attenuated with neutral-density screens.

X-Ray Data.—An approximately ellipsoidal crystal of K_3MoF_6, of dimensions 0.182 × 0.156 × 0.005 mm parallel to [001], [010], and [100], respectively, was sealed in a 0.2-mm glass capillary and mounted on a computer-controlled Picker four-circle goniostat. The intensities of reflections $h \geq k \geq l$ were measured to 70° in 2θ with a scintillation-counter detector (Tl-activated NaI crystal) using unfiltered Mo Kα radiation [λ(Mo Kα_1) 0.70926 Å and λ(Mo Kα_2) 0.713543 Å] and the 2θ-scan technique.[8] An angular range of 1.32° was step-scanned in increments of 0.02° with counts of 2 sec at each step and the background was counted for 120 sec at the beginning and end of each scan. The takeoff angle was 4°. A standard reflection (333) was used to check on intensity drift every 20 reflections. The (333) intensity varies less than 3%.

An absorption correction was made on each reflection using an unpublished program written by C. K. Johnson of the Chemistry Division, which calculates absorption corrections for crystals with ellipsoidal shape. The ellipsoid was subdivided into a 6 × 14 × 16 grid by gaussian quadrature.[9] The linear absorption coefficient μ is 37.341 cm^{-1} for Mo Kα radiation, and calculated transmission factors varied from 0.64 to 0.65. The lattice parameter, Table I, was refined by a least-squares fit of 16 Mo Kβ (0.63225 Å) reflections which were automatically centered[8] in a reduced-slit system with a takeoff angle of 1.2°.

TABLE I

LATTICE AND ATOMIC PARAMETERS FOR K_3MoF_6[a]

Atom	x	y	z	β_{11}[b]	β_{22}	Thermal displacement (rms), Å^2
Mo	0.0	0.0	0.0	0.0049 (0.3)	c	0.019
K(1)	0.5	0.5	0.5	0.049 (7)	c	0.192
K(2)	0.25	0.25	0.25	0.025 (2)	c	0.096
F	0.226 (3)	0.0	0.0	0.014 (3)	0.029 (3)[d]	0.054 and 0.115

[a] Space group Fm3m; $a_0 = 8.7839 \pm 0.009$ Å at 23°; X-ray density 3.2066 g/cm^3. The number in parentheses is $\sigma \times 10^3$. [b] Coefficients in the temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$. [c] $\beta_{33} = \beta_{22} = \beta_{11}$. [d] $\beta_{33} = \beta_{22}$.

Crystal Structure of K_3MoF_6

The structure was refined by iterative least squares using a modified Busing, Martin, and Levy[10] computer program. The starting parameters were taken from the atomic parameters of $(NH_4)_3FeF_6$:[11] Mo at 4(a), K(1) at 4(b), K(2) at 8(c), and F at 24(e) with $x = 0.22$; space group Fm3m. The scattering factors were taken from Cromer and Waber[12] and include the real and imaginary components of anomalous scattering. The quantity $\Sigma w|sF_o - F_c|^2$, where s is the scale factor, was minimized, with weights $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$. The variance, σ^2 was estimated by the empirical equation $\sigma^2(F_o^2) = [T + B + (0.05(T - B))^2]/[A(Lp)^2]$, where T is the total counts, B is the background counts, A is the absorption correction, and L and p are the Lorentz and polarization[13] corrections.

The atomic parameters are listed in Table I. The discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.103 for all data and 0.092 for reflections greater than $\sigma(F_o)$. Table II lists the calculated structure factors and the observed structure amplitudes all mutiplied by a factor of 10.

The standard deviation of an observation of unit weight, $[\Sigma(F_o - F_c)^2/(n_o - n_v)]^{1/2}$, is 3.00 where n_o = 142 reflections and n_v = 8 variables. The variables are one atomic parameter, five temperature factors, a scale factor, and an extinction correction (Table I).[14] The parameter r^*[14] was varied in the least-squares refinement as an independent parameter and the final result is $r^* = (-0.9 \pm 0.5) \times 10^{-4}$. The extinction correction was made on F_c for all reflections. The temperature factors for K(1) and K(2) appear to be abnormally large when compared to those of F, for instance (Table I), and a difference synthesis shows that both K(1) and K(2) should be slightly displaced from the special positions. Several models of the structure were tested in Fm3m and F$\bar{4}$3m but with no improvement in the final results. Perhaps the best model which describes the whole crystal is one in which K(1) and K(2) do not lie at $^1/_2$, $^1/_2$, $^1/_2$ or $^1/_4$, $^1/_4$, $^1/_4$ but are randomly displaced

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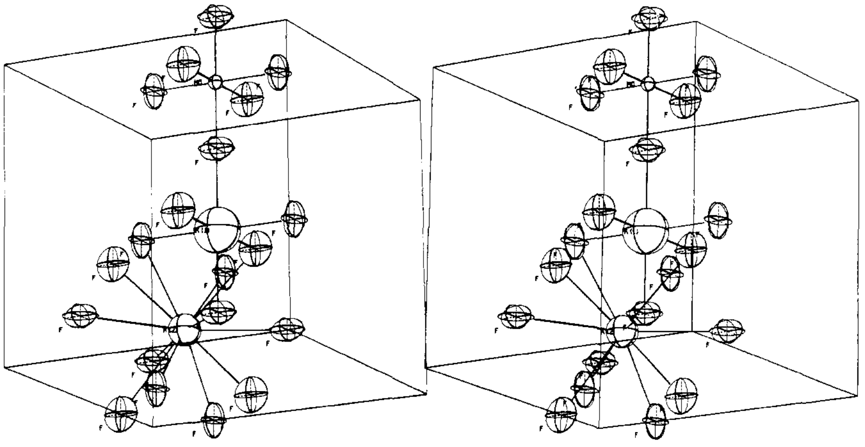

Figure 1.—Stereoview of the crystal K_3MoF_6. One asymmetrical unit with the unit cell outlined.

Table II

Observed and Calculated Structure Factors for K_3MoF_6 (×10)

L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL	L	FOBS	FCAL
	0 0	L	10	366	370	7	582	527		1 7	L	4	811	684	3	962	605	11	221	206		4 10	L	12	171	204
2	1385	1234	12	229	307	9	607	622	7	475	450	6	896	912	5	793	753		3 11	L	10	164	204		6 8	L
4	3008	3164	14	188	206	11	337	338	9	398	369	8	492	452	7	538	534	11	113	157		5 5	L	8	332	274
6	897	525		0 6	L	13	290	297	11	276	271	10	408	445	9	580	499		4 4	L	5	724	587	10	197	230
8	946	891	6	791	728	15	137	176	13	219	197	12	263	269	11	312	325	4	1371	1187	7	528	461	12	187	162
10	415	409	8	427	405		1 3	L		1 9	L	14	157	208	13	266	254	6	503	483	9	441	371		6 10	L
12	295	342	10	316	384	3	652	626	9	307	291		2 6	L	15	99	162	8	625	572	11	261	271	10	186	171
14	212	237	12	267	245	5	804	866	11	219	218	6	368	435		3 5	L	10	353	335	13	196	197		7 7	L
	0 2	L	14	154	183	7	507	539	13	148	157	8	473	519	5	708	680	12	241	273		5 7	L	7	345	324
2	2338	2376		0 8	L	9	570	551		1 11	L	10	290	318	7	536	510	14	185	183	7	428	385	9	275	259
4	804	878	8	362	413	11	332	334	11	119	165	12	220	258	9	477	425		4 6	L	9	319	308	11	192	195
6	1193	1126	10	291	274	13	274	273		2 2	L	14	195	173	11	305	299	6	578	609	11	226	230		7 9	L
8	478	510	12	191	216	15	155	169	2	0	-328		2 8	L	13	250	222	8	424	368	13	136	166	9	194	207
10	460	522		0 10	L		1 5	L	4	1837	1704	8	359	335		3 7	L	10	276	334		5 9	L	11	147	157
12	262	290	10	162	230	5	843	767	6	251	395	10	263	294	7	425	428	12	264	222	9	279	245		8 8	L
14	175	241	12	182	162	7	593	537	8	714	763	12	232	200	9	381	347	14	134	163	11	177	185	8	226	244
	0 4	L		1 1	L	9	516	460	10	325	386		2 10	L	11	250	257		4 8	L		6 6	L	10	209	180
4	1841	1773	1	1560	1142	11	321	313	12	268	324	10	226	211	13	186	186	8	353	358	6	420	380		9 9	L
6	560	520	3	623	734	13	266	237	14	178	220	12	153	162		3 9	L	10	290	247	8	338	383	9	241	166
8	734	699	5	1081	1068	15	141	154		2 4	L		3 3	L	9	313	275	12	160	192	10	276	260			

by small fixed increments from these positions for each unit cell, the observed structure being an average of these unit cells. In addition to the temperature factors representing thermal displacement in a temporal sense, they also represent averaged displacement in a spatial sense.

A stereoscopic view of the crystal structure of K_3MoF_6 is shown in Figure 1. The bond distances are as follows: six Mo–F distances, 2.00 (2) Å; six K(1)–F distances, 2.40 (2) Å; twelve K(2)–F distances, 3.112 (0.2) Å; and four F–F distances, 2.82 (3) Å where the number in parentheses following each value is $\sigma \times 10^2$ (σ = standard deviation). The K(1)–F octahedral bonds (2.40 (2) Å) are shorter than the sum of the usual ionic radii for K^+, F^- (2.66 Å).

Results and Discussion

Although there is some uncertainty in the exact location of the potassium atoms, the crystal structure demonstrates that the compound described here is K_3MoF_6 and particularly that the molybdenum(III) is octahedrally coordinated to fluoride ions. The measured macroscopic density of K_3MoF_6 is 3.23 ± 0.03 g/cm^3 at 26° and is consistent with the X-ray density of 3.2066 g/cm^3 given in Table I.

In an effort to avoid preparative procedures which would tend to introduce oxides, it was decided that a direct combination of KF and MoF_3 in a platinum tube was perhaps the simplest way to prepare K_3MoF_6 since previous experience with platinum had shown it to be unreactive toward these molybdenum fluoride compounds.

Because the object of our synthesis was to produce only enough K_3MoF_6 for a spectrum and crystal structure determination, an extensive study of the optimum reaction conditions was not made. We did notice, however, that long reaction times markedly reduced the amount of K_3MoF_6 recovered. In fact, reactions which lasted 16 hr under otherwise identical conditions yielded no K_3MoF_6. A maximum yield of 60–80% was obtained for reaction times of 15–30 min at 800°. On the assumption that K_3MoF_6 decomposes in the molten state one would expect a decrease in these variables to improve the yield. We were not able to confirm this assumption by identification of the dark blue material recovered from the reaction tube or by observation of the molten sample.

K_3MoF_6 has a melting point of 734 ± 10°. The melting point determination was undertaken not only for the purpose of characterizing the crystal but also, primarily, to investigate the behavior of K_3MoF_6 above its melting point. It was necessary to place the crystal on a small sheet of platinum foil because the K_3MoF_6 reacted rapidly with the ordinary siliceous supports of the microscope stage long before melting. It was then necessary to illuminate the sample with "top-lighting" (as described in the Experimental Section) because the opaque platinum foil blocked the transmitted light which is directed up from below. This method of illumination prevented the observation of the sample after it melted because it spread out on the foil and became impossible to see. For this reason, we could not observe any decomposition that would verify our speculations on improving the yield.

The K_3MoF_6 was first handled as a typical molybdenum fluoride compound, *i.e.*, in an inert atmosphere. Upon further examination, it was found to be quite unreactive to the room atmosphere. In contrast to MoF_3, the K_3MoF_6 crystals could be washed free of the excess reagents with acetone or ethanol and quickly dried with no reaction (confirmed by X-ray powder analysis before and after). Attempts to wash with water, however, produced reddish solutions which turned brown and then faded within seconds. Although the diffuse reflectance spectra were taken on material which had never been exposed to moisture, it was found that the transmission spectrum of the polycrystalline sample did not change on exposure to the open air. This evidence for the stability of K_3MoF_6 is consistent with that observed for other similar octahedrally coordinated d^3 ions such as chromium(III).[15]

The diffuse-reflectance spectrum of K_3MoF_6, shown in Figure 2, has three broad absorption bands with maxima at 262 mμ (*ca.* 38,200 cm^{-1}), 337 mμ (*ca.* 29,700 cm^{-1}), and 425 mμ (*ca.* 23,500 cm^{-1}). The transmission spectrum of the polycrystalline particle had absorption maxima at 337 and 425 mμ, but light scatter at 262 mμ was too severe to permit absorption measurements at this wavelength.

We assign the two lowest energy bands to the lowest energy spin-allowed ligand field transitions as follows: 23,500 cm^{-1} to ${}^4T_{2g}\ (t_{2g}{}^2e_g) \leftarrow {}^4A_{2g}\ (t_{2g}{}^3)$ and 29,700 cm^{-1} to ${}^4T_{1g}\ (t_{2g}{}^2e_g) \leftarrow {}^4A_{2g}\ (t_{2g}{}^3)$. The mean energy of the first of these transitions should approximate $10Dq$ so that Dq is on the order of 2350 cm^{-1}. By inserting this value of Dq and the energy of the second band into the appropriate Tanabe–Sugano[16] secular equation of a d^3 system, we obtain 570 cm^{-1} as an estimate of Racah's electronic repulsion parameter B. This value is 93% of a previous estimate of the free-ion value (610 cm^{-1}).[17]

These parameters can be compared with those previously reported[17,18] for $MoX_6{}^{3-}$ complexes where $X^- =$ Cl^- and Br^-. The Dq values for Cl^- and Br^- are 1910 and 1770 cm^{-1}, respectively, and their B values are 420 and 390 cm^{-1}. We find both the spectrochemical and the nephelauxetic series for Mo(III) to be $F^- > Cl^- > Br^-$, which is as expected.[17]

The assignment of the band at 38,200 cm^{-1} is less certain. The wave-number value is considerably lower than that predicted for the remaining spin-allowed transition, ${}^4T_{1g}\ (t_{2g}e_g{}^2) \leftarrow {}^4A_{2g}\ (t_{2g}{}^3)$, when the above values of Dq and B are substituted into the Tanabe–Sugano equation. (The predicted value is about 49,300 cm^{-1}.) Despite the deficiencies of the theory, this difference of about 10^4 cm^{-1} seems unreasonably large. Possibly this band is a spin-forbidden transition of the $t_{2g}{}^3 \rightarrow t_{2g}{}^2e_g$ type. Several of these should lie between the second and third spin-allowed transitions. The possibility of observing such a band would depend, of course, on the mixing of multiplicities as a consequence of the moderately large spin–orbit coupling constant for Mo(III). However, the band intensity appears to be much too large for such an assignment. The remaining possibility, and the one we regard as most plausible, is assignment as a charge-transfer absorption. Similar charge-transfer bands are known[16] for $MoCl_6{}^{3-}$.

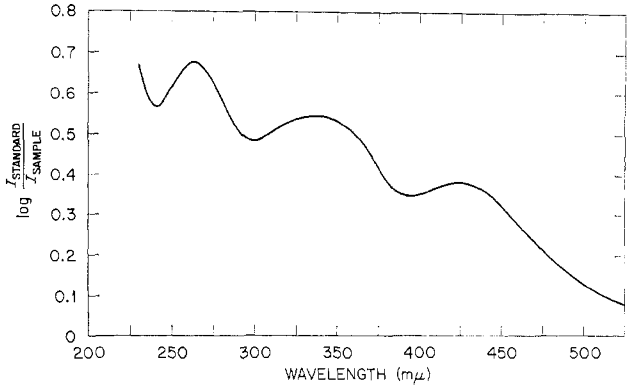

Figure 2.—Diffuse reflectance spectrum of K_3MoF_6.

The lowest energy spin-forbidden transitions give rise to two relatively sharp low-energy bands in $MoCl_6{}^{3-}$. The one at 9500 cm^{-1} is almost certainly due to the pair of transitions ${}^2T_{1g}(t_{2g}{}^3)$, ${}^2E_g(t_{2g}{}^3) \leftarrow {}^4A_{2g}(t_{2g}{}^3)$ which are theoretically predicted to lie close together. The positions of these transitions are not influenced significantly by Dq at the 2000-cm^{-1} level. Hence, if we assume that the ratio of Racah parameters B/C is not very different in $MoF_6{}^{3-}$ and $MoCl_6{}^{3-}$, these transitions should occur near the same positions in both complexes. Since 9500 cm^{-1} (1053 mμ) lies outside the range of our measurements, our failure to see this band is not surprising. The second spin-forbidden band in $MoCl_6{}^{3-}$ was found at 14,800 cm^{-1} (676 mμ). It should lie at a somewhat higher energy in $MoF_6{}^{3-}$ but because the longest accessible wavelength with our diffuse reflectance accuracy was 600 mμ, we did not observe this band either. In any event a careful search for these spin-forbidden bands by transmission spectroscopy at low temperatures on specimens of higher optical quality than we were able to prepare is clearly worthwhile and, if successful, would permit estimation of Racah's C parameter.

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