CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MAINE, ORONO, MAINE 04473

Optical Spectrum of the Hexachloromolybdate(V) Ion in Single Crystals of Cesium Hexachlorozirconate(IV) at 4°K

BY HOWARD H. PATTERSON* AND JOHN L. NIMS

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The optical spectrum of $CsMoCl_6$ in single cubic crystals of Cs_2ZrCl_6 has been measured between 10,000 and 50,000 cm^{-1} at 4°K. One electronic absorption with sharp vibrational structure has been observed between 23,830 and 25,697 cm^{-1} for this $4d^1$ system and has been assigned as a transition from the $\Gamma_8(^2T_{2g})$ ground state to the excited electronic state $\Gamma_8(^2E_g)$. From the vibronic detail of the spectrum and from hot-band studies, vibrational mode energies for the $\Gamma_8(^2E_g)$ state have been determined. No evidence of a static Jahn–Teller distortion for the $MoCl_6^-$ ion in the cubic host Cs_2ZrCl_6 has been found.

Introduction

Dorain and coworkers have measured the optical spectra at 4°K of the hexachloride complexes of the d^3 system Re^{4+} [1] and the d^4 systems Os^{4+} [2] and Ru^{4+}.[3] The broad absorptions observed at room temperature are resolved into many series of sharp absorption lines at 4°K from which detailed information can be obtained to make assignments for the observed transitions. In this paper we report the optical spectrum of the hexachloromolybdate(V) ion in the cubic host of Cs_2ZrCl_6 at 4°K. This system is of particular interest because it provides an opportunity to study a d^1 ion in undistorted cubic site symmetry and to observe any static or dynamic Jahn–Teller effects that may be present.

Horner and Tyree[4] have observed at room temperature the optical spectrum of $KMoCl_6$. A single asymmetric band was observed at 24,100 cm^{-1} and was assigned to the transition $^2T_{2g} \rightarrow {}^2E_g$ in $MoCl_6^-$. Stronger higher energy transitions were assigned as charge transfer. Brisdon and Walton[5,6] have investigated the room temperature solid-state spectrum of tetraethylammonium hexachloromolybdate(V) and have reported peaks at 15,400, 21,700, and 26,700 cm^{-1}. The broad intense transition at 26,700 cm^{-1} was assigned as charge transfer and the lower energy peaks were assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition split either by a Jahn–Teller distortion or by spin–orbit coupling.

Experimental Section

Cesium hexachlorozirconate(IV) was prepared from zirconium tetrachloride (Matheson Coleman and Bell) and cesium chloride (A. D. Mackay Inc.) using the method of Axe, Stapleton, and Jeffries.[7]

Seven grams of zirconium tetrachloride was dissolved in 250 ml of hydrogen chloride saturated methanol solution in a 500-ml round-bottom flask and 17 g of cesium chloride was placed in a Soxhlet extractor attached to the flask. The solution was heated at 50° for 6–12 hr until all the CsCl had dissolved. The white precipitate of Cs_2ZrCl_6 which formed was then washed with hydrogen chloride saturated methanol solution and dried under vacuum for 24 hr. It was then purified by sublimation in alumina boats at 800° in a chlorine atmosphere with the formation of a polycrystalline mass. The Cs_2ZrCl_6 was placed in an evacuated Vycor tube and fused into a single crystal at 800° by the Bridgeman technique. The tube was opened in a drybox under nitrogen and any black areas present were removed with a razor blade. The colorless Cs_2ZrCl_6 which remained was used as a host for $CsMoCl_6$. From previous studies[1,2] it is known that Cs_2ZrCl_6 is optically clear up to 45,000 cm^{-1}.

Cesium hexachloromolybdate(V) was prepared from cesium hexachloromolybdate(IV) and this compound was made using the method of Edwards, Peacock, and Said.[8] Since molybdenum in the 4+ or 5+ oxidation state is extremely sensitive to air and moisture, the handling of molybdenum compounds was done in a drybox under an atmosphere of nitrogen. Two grams of molybdenum pentachloride (D. F. Goldsmith Inc.), 2 g of cesium chloride, and 10 g of iodine monochloride (Matheson Coleman and Bell) were heated in a sealed Carius tube to 130° for 3 days. After the tube was opened, the iodine monochloride and other volatile components were removed under a high vacuum. The Cs_2MoCl_6 was then placed with Cs_2ZrCl_6 under 0.5 atm of chlorine gas in a sealed Vycor tube and heated to 800° for about 8 hr. Approximately 1 mol % of the molybdenum compound was present. After the tube was cooled to room temperature in about 3 hr, it was opened and the resulting single green crystals of $CsMoCl_6$ in Cs_2ZrCl_6 were sliced into thin sections with a razor blade. An infrared spectrum (250–4000 cm^{-1}) of the mixed crystals revealed that only trace amounts of Cs_2MoOCl_5 were present from the intensity of the Mo–O stretching mode at 952 cm^{-1}.[9] Further, in related experiments on the corresponding tungsten(V) salt to be reported at a later date,[10] it was found that when the purple Cs_2WCl_6 was heated with Cs_2ZrCl_6 and Cl_2, the resulting crystals had a blue-green color corresponding to $CsWCl_6$. Thus, we concluded that our mixed crystals correspond to molybdenum in the 5+ oxidation state.

Spectroscopic Measurements.—The optical spectra taken at 4°K were recorded photographically with a Bausch and Lomb Research dual grating spectrograph and with a McPherson 1-m Model 2051 monochromator. A slit width of 10 μ was used and the gratings had a dispersion of about 8 Å/mm in first order. In the early experiments with the Bausch and Lomb Instrument the crystals were glued to a holder and immersed in liquid helium. However, in later experiments with the McPherson instrument the temperature of the crystals was varied between room temperature and 4°K by means of a Cryo-Tip manufactured by Air Products, Inc. The same spectrum was obtained at 4°K from both instruments.

Results and Discussion

One absorption with sharp vibronic detail was observed between 23,830 and 25,697 cm^{-1}. A microphotometer tracing of the spectrum observed at 4°K is given in Figure 1, and the energies of the various vibronic lines are listed in Table I. At higher energies several broad absorptions without structure were re-

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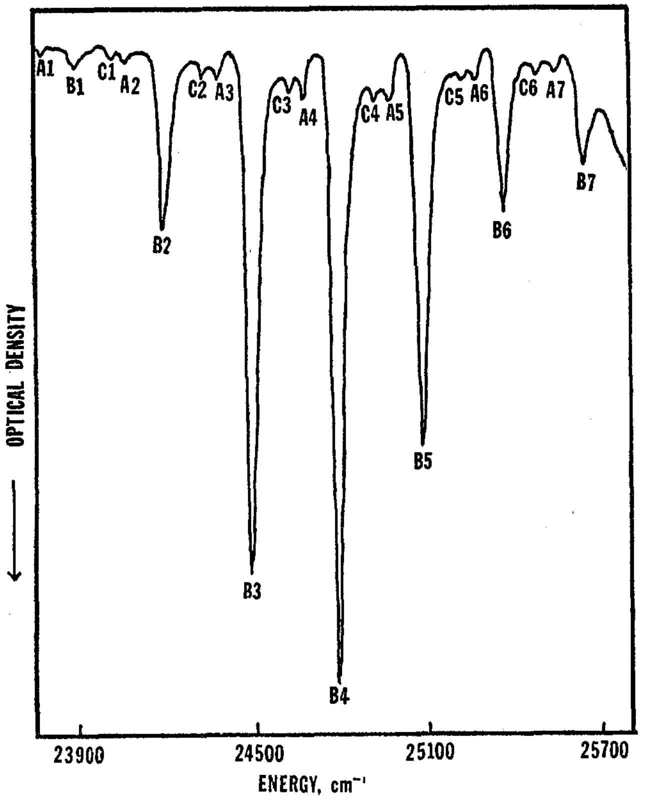

Figure 1.—Microphotometer tracing of the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2E_g)$ electronic transition at 4°K.

TABLE I

SPECTRAL DATA FOR $MoCl_6^-$ AT 4°K

Line no.	Energy, cm^{-1}	Assignment
A1	23,830	$\Gamma_8(^2E_g) + \nu_7$
B1	23,945	ν_4
C1	24,069	$5\ \nu_7$
A2	24,119	ν_3 and $\nu_7 + \nu_1$
B2	24,239	$\nu_4 + \nu_1$
C2	24,348	$5\ \nu_7 + \nu_1$
A3	24,418	$\nu_3 + \nu_1$ and $\nu_7 + 2\ \nu_1$
B3	24,533	$\nu_4 + 2\ \nu_1$
C3	24,648	$5\ \nu_7 + 2\ \nu_1$
A4	24,705	$\nu_3 + 2\ \nu_1$ and $\nu_7 + 3\ \nu_1$
B4	24,822	$\nu_4 + 3\ \nu_1$
C4	24,941	$5\ \nu_7 + 3\ \nu_1$
A5	24,991	$\nu_3 + 3\ \nu_1$ and $\nu_7 + 4\ \nu_1$
B5	25,111	$\nu_4 + 4\ \nu_1$
C5	25,231	$5\ \nu_7 + 4\ \nu_1$
A6	25,281	$\nu_3 + 4\ \nu_1$ and $\nu_7 + 5\ \nu_1$
B6	25,403	$\nu_4 + 5\ \nu_1$
C6	25,508	$5\ \nu_7 + 5\ \nu_1$
A7	25,564	$\nu_3 + 5\ \nu_1$ and $\nu_7 + 6\ \nu_1$
B7	25,697	$\nu_4 + 6\ \nu_1$

corded with essentially the same results as those of Horner and Tyree.[4]

Vibronic Assignments.—Molybdenum(5+) has a $4d^1$ configuration and in an octahedral field the following two terms arise: ^2E_g, $^2T_{2g}$. With spin–orbit interaction further splitting of states occurs, and the $^2T_{2g}$ level splits into a Γ_8 ground state and a Γ_7 excited state separated in first order from the ground state by three-halves the spin–orbit interaction. The ^2E_g level becomes a Γ_8 state. Here, we have used the Bethe notation to indicate the double-group representations of the octahedral group.

For d–d transitions in octahedral complexes both the initial and final states are *gerade* so that the intensity arises from vibronic coupling with *ungerade* electronic states. Thus, if resolution is sufficient, all vibronic structure should be *ungerade* at 4°K since at this temperature there is no thermal population of odd vibrational modes including the lattice mode.

The normal modes of vibration for the $MoCl_6^-$ complex[11] can be labeled $\nu_1(a_{1g})$, $\nu_2(e_g)$, $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, $\nu_5(t_{2g})$, and $\nu_6(t_{2u})$, where the irreducible representation of the O_h point group according to which the mode transforms is given in parentheses. The Raman and infrared spectra of $CsMoCl_6$ have not been reported. However, Adams, Gebbie, and Peacock[12] have measured the far-infrared spectrum of Cs_2MoCl_6 and have found ν_3 325 cm^{-1} and ν_4 170 cm^{-1}. Horner and coworkers[13] have found for the cesium salts of niobium and tantalum that on going from the 4+ to the 5+ oxidation state ν_3 increases by 20 cm^{-1} and ν_4 remains constant. If the same changes were to hold for molybdenum we would estimate ν_3 345 cm^{-1} and ν_4 170 cm^{-1}. The ν_6 mode from the considerations of Krynauw and Pistorius[14] we would estimate to be in the region 100–130 cm^{-1}.

Pollack[15] has shown that for a substance like Cs_2ZrCl_6 with an antifluorite, face-centered cubic lattice, there are three lattice modes of t_{1u}, t_{1g}, and t_{2g} symmetries. The t_{1u} mode is infrared active and is labeled as ν_7, the *reststrahlen* mode. When a small amount of the molybdenum complex is present in the Cs_2ZrCl_6 lattice, ν_7 is not expected to change from the undoped value. For dilute $Cs_2(Os,Zr)Cl_6$ mixed crystals the ν_7 energy has been found to be 48 cm^{-1}.

Three progressions are present in the observed absorption spectrum shown in Figure 1 and these are labeled as A*n*, B*n*, and C*n*. The average energy spacing between peaks A*n* and B*n* is 121 cm^{-1}, between B*n* and C*n* is 115 cm^{-1}, and between C*n* and A*n* is 56 cm^{-1}. Comparing the values for the ground electronic state vibrational modes with the energy differences between the various peaks, we find the most reasonable assignment is to choose peak A1 as the ν_7 mode, B1 as the ν_4 mode, A2 as the $(\nu_7 + \nu_1)$ mode and as the ν_3 mode, and B2 as the $(\nu_4 + \nu_1)$ mode. The peaks beyond B2 are repetitive. If ν_4 is assumed to be 170 cm^{-1}, then ν_7 is 49 cm^{-1}, ν_3 is 340 cm^{-1}, and ν_1 is 292 cm^{-1}. Further, with ν_7 being 49 cm^{-1}, then peak C1 may be assigned as 5 ν_7, C2 as $(5\ \nu_7 + \nu_1)$, and so on. The peak corresponding to 3 ν_7 should appear about where the strong ν_4 peak is located and there is some evidence of a shoulder on peaks B3, B4, and B5 at the correct energy. There is not any evidence of the odd ν_6 mode in this spectrum. All of the assignments are given in Table I.

Temperature Dependence of the Spectrum.—If the vibronic assignments are correct, one would expect that as the temperature of the crystal is increased from 4°K to room temperature, two effects should occur. First, various hot bands should appear in the spectrum as the odd vibrational modes of the ground electronic state are populated. In particular, we should expect

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the appearance of a vibronic line at about 23,730 cm^{-1} corresponding to the annihilation of a lattice phonon. At about 30°K a weak, broad line did appear at the predicted energy ±5 cm^{-1}. Second, it is known[16] that the oscillator strength of a vibronically allowed transition should increase as a function of increasing temperature according to

$$f(T) = f(0°\mathrm{K}) \coth (h\nu/2kT) \qquad (1)$$

where $f(0°\mathrm{K})$ is the oscillator strength at 0°K, $f(T)$ is the oscillator strength at temperature T, and ν is the electronic ground-state frequency of the intensity-producing normal mode. The experimental data displayed in Figure 2 show that as the crystal temperature is increased from 4°K to 136°K, the oscillator strength increases in accordance with eq 1 by a factor of 1.5 corresponding to ν 150 cm^{-1}. This value is only in rough agreement with the energy of the strongly appearing ν_4 mode for two reasons: first, there is the difficulty in estimating relative oscillator strengths with photographic plates; second, other intensity-producing normal modes besides the ν_4 mode occur weakly in the spectrum and eq 1 should really be represented by a sum over all the odd modes. Above 136°K all vibronic structure disappears.

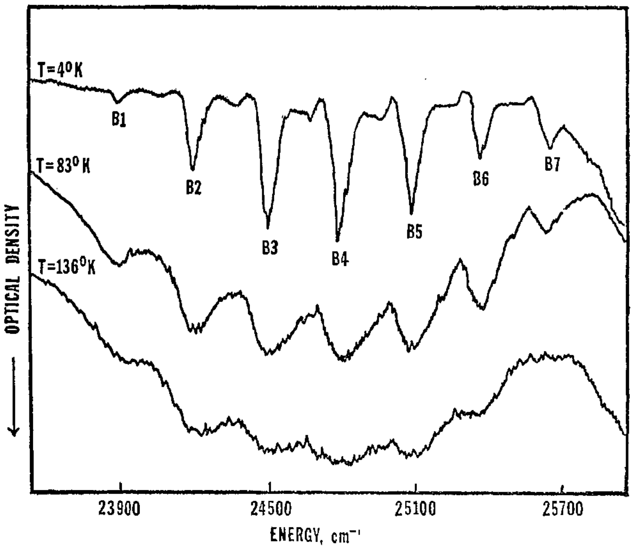

Figure 2.—Microphotometer tracing of the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2E_g)$ electronic transition at 4, 83, and 136°K. The spectrum in this figure is from a different crystal specimen than the spectrum in Figure 1. The hot band at 23,730 cm^{-1} is too weak to be seen in these microphotometer tracings.

Jahn–Teller Effect.—The crystal structure of Cs_2ZrCl_6 is that of K_2PtCl_6 with four Cs_2ZrCl_6 units per unit cell in an antifluorite cubic arrangement.[17] This may be visualized as a cubic lattice of cesium ions in which every other body-centered position is occupied by a $ZrCl_6^{2-}$ ion. When $MoCl_6^-$ substitutes for $ZrCl_6^{2-}$, we would expect from previous studies on CaF_2[18] that charge compensation is achieved by interstitial substitution of a Cl$^-$ ion at the center of a vacant cube.

The low-temperature $MoCl_6^-$ spectrum does not show any evidence of a static Jahn–Teller effect with the $\Gamma_8(^2E_g)$ state distorted by vibrational-electronic coupling and the symmetry of the complex lowered to D_{4h} or D_{2h}. A medium-strength dynamic Jahn–Teller effect is not present since there is no progression in the e_g Jahn–Teller-active mode in a double-humped pattern.[19] The spectrum in Figure 1 corresponds to a progression in the ν_1 symmetric stretching mode where the equilibrium internuclear separation for the $\Gamma_8(^2E_g)$ excited state is about 0.1 Å greater than in the $\Gamma_8(^2T_{2g})$ ground state.[20] There is little anharmonicity present because the spacing between the sharp Bn peaks remains relatively constant for n = 1, 7. Finally, if a weak dynamic Jahn–Teller effect is present for the $\Gamma_8(^2E_g)$ state, Zeeman measurements should provide a means for study since the g value of this state is about 2. The theory has been developed by Ham.[21] Experiments of this type are presently being undertaken.

Comparison with Previous Results.—Horner and Tyree[4] observed the optical spectrum of $KMoCl_6$ at room temperature. The half-width of the 24,100-cm^{-1} band was of the order of 3000 cm^{-1} and often this appeared only as a shoulder on a broader charge-transfer band. This is in marked contrast to the highly resolved spectrum at 4°K for the $MoCl_6^-$ ion in the Cs_2ZrCl_6 host lattice shown in Figure 1. Also, Brisdon and Walton[5,6] have reported the $^2T_{2g} \rightarrow {}^2E_g$ transition for tetraethylammonium hexachloromolybdate(V) to correspond to two rather broad peaks at 15,400 and 21,700 cm^{-1}. This difference between the spectrum of the potassium or cesium salts and the tetraethylammonium salt is not too surprising since the molar magnetic susceptibility[22] for the WCl_6^- ion at 80°K differs by a factor of 4 for the cesium *vs.* the tetraethylammonium cation. Magnetic data are not available for the corresponding molybdenum compounds. Evidently, tetraethylammonium hexachloromolybdate(V) is strongly distorted from cubic symmetry.

The energy separation between the ground electronic state $\Gamma_8(^2T_{2g})$ and the excited state $\Gamma_8(^2E_g)$ is, for $Dq \gg$ spin–orbit interaction, equal to $10Dq$ plus one-half the spin–orbit interaction.[23] Since the spin–orbit interaction is about 500 cm^{-1} for the hexachloromolybdate(V) ion,[6] $10Dq$ is 23,500 cm^{-1}. In comparison, Horner and Tyree reported $10Dq$ as equal to 24,100 cm^{-1}.

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