are sufficiently smaller than K_t that the necessary simplifying assumptions were satisfactory for the treatment of the isotopic exchange.

Additional observations for this system are to be noted. Since the equilibrium constant was not known precisely, the treatment of the exchange data was rerepeated with values of K_t taken as 2×10^{-3} and 4×10^{-3} M. In neither case did the calculation indicate any different type of rate law, but the rate constants k_2 and k'_c were changed accordingly. In other experiments a change in hydrogen ion concentration over the range of 0.01 to 0.243 gave no change in the observed half-time. When some of the solutions were exposed to light, a precipitate had formed within an 8-day aging period, whereas the solutions were stable for at least several weeks in the dark. The sensitivity to light was apparently influenced by the presence of sulfate since solutions of $K[Pt(C_2H_4)Cl_3]$ in dilute HCl have been stored for months in the light with no evidence of decomposition. One exchange solution, aged in the dark but exposed to light upon the addition of Cl^{36}, appeared to have an initial rate 25% higher than the same solution in the dark. However, the solution in the light decomposed before the completion of the exchange.

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The Visible and Ultraviolet Spectra of Some Molybdenum Complexes[1]

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The visible and ultraviolet spectra have been examined for several complexes of the type $MoOCl_3 \cdot 2L$ (L = oxygen donor), and for $MoCl_5 \cdot (C_6H_5)_3AsO$ and $NH_4MoOCl_4 \cdot CH_3CN$. In all cases the ligand field bands observed at approximately 14,000 and 23,000 cm.$^{-1}$ are believed to be due to a strong tetragonal field created by the oxygen atom. The spectrum of Mo(V) in a field of six Cl^- ligands was obtained by examining KCl pellets of KCl–$MoCl_5$ melts. A single asymmetric band was observed in the visible region at 24,100 cm.$^{-1}$ and assigned to the transition $^2T_2 \rightarrow {}^2E$ in $MoCl_6^-$. The compound $[(CH_3)_4N]_2MoCl_6$ was prepared and characterized by conductance, magnetic moment, and visible and infrared spectra. Two bands which probably are due to ligand field transitions were observed in the visible spectrum at approximately 22,000 and 25,800 cm.$^{-1}$.

Introduction

Some attention has been accorded the electronic spectra of d^1-type oxycations. Ballhausen and Gray[2] published a complete study of oxovanadium(IV), and the spectra of several of its complexes have been reported from this Laboratory.[3] Gray and Hare[4] have reported the electronic structures and spectra of the CrO^{3+} and MoO^{3+} ions. The preparation of several MoO^{3+} compounds has been reported earlier by us,[5] and a report of their visible spectra seemed a suitable extension of the work. In addition we set out to prepare a salt of the $MoCl_6^-$ ion in order to examine the spectrum of a d^1 ion in an undistorted octahedral field.

The spectra of the MoO^{3+} compounds were all very much like that of $MoOCl_5^{2-}$, as reported by Gray and Hare,[4] and earlier by Jørgensen.[6] In each case, the octahedrally coördinated species was observed to be subjected to strong tetragonal distortion due to the molybdenyl oxygen. Distortions to still lower symmetry than C_{4v} by non-equivalent ligands other than the oxygen atom seemed unimportant.

Various attempts to prepare the $MoCl_6^-$ ion led to the preparation of the compounds $[(CH_3)_4N]_2MoCl_6$ and $NH_4MoOCl_4 \cdot CH_3CN$, whose spectra subsequently were studied. Finally, $MoCl_5$ was fused in the presence of excess dry powdered KCl, and the resulting mixture pressed into a translucent KCl pellet. The spectrum of this material indicates that the molybdenum exists as the $MoCl_6^-$ ion in the melt.

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted. Molybdenum pentachloride was obtained from Climax Molybdenum Company.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Molybdenum and chlorine were determined in the manner described previously.[5]

Measurement of Magnetic Susceptibility.—Magnetic susceptibilities were determined by the Gouy method as described previously.[5]

The μ_{eff} values for Mo in the KCl–$MoCl_5$ melts presented a special problem. After a sample of the powdered melt was subjected to the usual susceptibility measurements, the contents of the tube were analyzed for Mo. The calculations of the μ_{eff} value assumed that all the Mo existed as $KMoCl_6$ and that KCl made up the residue of the sample weight.

Conductance Measurements.—Conductivities were measured in nitrobenzene solution at 25° in the manner described elsewhere.[7] The concentrations were approximately 10^{-3} M.

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[1] Presented at the Eastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, Nov., 1962.

[2] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[3] S. M. Horner, S. Y. Tyree, and D. L. Venezky, *ibid.*, **1**, 844 (1962).

[4] H. B. Gray and C. R. Hare, *ibid.*, **1**, 363 (1962).

[5] S. M. Horner and S. Y. Tyree, Jr., *ibid.*, **1**, 122 (1962).

[6] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

[7] D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

Infrared spectra were run on a Perkin-Elmer Infracord, using KCl pellets.

Preparation of Complexes.—All operations were performed in a nitrogen atmosphere, unless otherwise stated.

$NH_4MoOCl_4 \cdot CH_3CN$.—An excess of dry powdered NH_4Cl was added to a freshly-prepared red-brown solution of $MoCl_5$ in CH_3CN. The flask was stoppered after swirling and allowed to stand. The solution slowly turned green, and after a short time a finely divided green precipitate was observed, suspended in the solution above the undissolved NH_4Cl. The green suspension was decanted and evaporated further. The green precipitate was filtered and dried in a current of nitrogen. A later experiment using undried NH_4Cl gave a rapid reaction, the solution turning green immediately and the green precipitate forming in larger quantities. As many as six decantations were needed to separate the precipitate from undissolved NH_4Cl. The compound turns orange-brown rapidly on exposure to moist air, and is soluble in CH_3CN.

Anal. Calcd.: Mo, 30.67; Cl, 45.32. Found (on different preparations): Mo, 30.57, 30.28; Cl, 45.30, 45.21.

$[(CH_3)_4N]_2MoCl_6$.—Four g. of powdered, freshly dried $(CH_3)_4NCl$ was suspended in 50 ml. of warm CH_3CN. Two g. of $MoCl_5$ was added to the suspension. Enough $MoCl_5$ dissolved to turn the solution red-brown. Upon agitation, a yellow precipitate formed, which mixed with the other two solids suspended in the flask. The mixture was triturated until no solid $MoCl_5$ remained, by which time the solution had turned green, and a considerably larger amount of the yellow precipitate had formed. The residue was filtered, triturated with ethanol to dissolve any excess of $(CH_3)_4NCl$, refiltered, and washed with ethanol and CH_2Cl_2. The yellow product was sucked dry on the filter in air since it proved to be stable in air.

The same procedure was used in a later experiment, substituting CH_2Cl_2 for CH_3CN. The reaction occurred more slowly, requiring 3–4 hr. for all of the $MoCl_5$ to react, and the supernatant liquid did not turn green as the yellow powder formed. Otherwise the results were the same.

In each case the yellow powder was insoluble in CH_3CN, CH_2Cl_2, and acetone. It dissolved very slowly in ethanol to give a yellow solution, which, on standing overnight, darkened and turned brown. It was instantly dissolved in H_2O, giving a greenish brown solution which turned blue rapidly. In all cases chemical analyses and infrared spectra indicated that some solvent was retained in the lattice, as the compounds were dried in a current of air or nitrogen, but not under vacuum. Approximately one-half mole of CH_3CN per formula weight of compound was retained, and somewhat less in the CH_2Cl_2 case.

Anal. Calcd. for $[(CH_3)_4N]_2MoCl_6 \cdot 0.5CH_3CN$: N, 7.34; Cl, 44.56; Mo, 20.09; C, 22.64; H, 5.38. Found: N, 7.39; Cl, 44.76; Mo, 20.03; C, 23.28; H, 5.28. Calcd. for $[(CH_3)_4N]_2MoCl_6 \cdot {}^1/_3CH_2Cl_2$: Cl, 43.87; Mo, 19.78. Found: Cl, 43.64; Mo, 19.85.

Preparation of Pellets Containing $KMoCl_6$ for Spectral Measurements.—The KCl used was prepared by fusing reagent grade KCl at 800°, cooling in a 110° oven, grinding to a fine powder in an agate mortar, and storing in a desiccator. The $MoCl_5$ used was freshly opened and stored in a nitrogen-filled drybox.

In each run, $MoCl_5$ was ground in an agate mortar in a drybox with a 5- to 10-fold excess of dry KCl. The mixture was placed in a 50-ml. round-bottomed flask fitted with a ball joint and heated on a heating mantle until the $MoCl_5$ melted. The cooled black, clinker-like mass then was ground again in an agate mortar and diluted with still more dry KCl. (The color of the finely ground melt is always a very dark green, whereas when pure $MoCl_5$ is ground with KCl, the resulting mixture is red.) The finely ground melt was loaded into a pellet die, lining both top and bottom of the die with pure KCl powder. The mixture was pressed for about 5 min. at 22,000 p.s.i. The resulting pellet was always a translucent green. All operations prior to removing the pellet from the die were in a nitrogen atmosphere. After removing it from the press, the pellet was mounted in a pellet holder[8] fabricated in our instrument shop to fit a Cary Model 14 recording spectrophotometer. The spectrum immediately was scanned from 2,000 to 10,000 Å. The pellet was exposed to the atmosphere for no longer than 3 min. prior to scanning its spectrum. The spectrum of each pellet was rerun immediately, and some were rerun after being allowed to stand in air for several hours or days.

In a modification of the above experiment some KCl–$MoCl_5$ mixtures were heated in a Vycor tube above the melting point of KCl. A stream of nitrogen into the mouth of the tube prevented back-wash of air. Some $MoCl_5$ sublimed to the cooler portion of the tube, but the fused melt always remained black even on heating at 800° for 1 hr. The powder obtained by grinding the melt again was dark green, and pellets were prepared as described above.

Measurements of Visible Spectra of Complexes.—The complexes were weighed directly into nitrogen-filled 25-ml. volumetric flasks. The flasks subsequently were filled to the mark with CH_2Cl_2 which had been dried over $CaCl_2$. The spectra of the solutions were run on a Cary Model 14 recording spectrophotometer, using 1-cm. quartz cells. Duplicate calculations of extinction coefficients on different solutions of the same complex gave fair agreement. The concentrations of the solutions varied from approximately 3×10^{-3} to 3×10^{-2} *M*.

Results

Table I[9] lists the absorption bands and their extinction coefficients for the ligand field spectra of the compounds studied. The assignments for the transitions in the MoO^{3+} compounds are based on Ballhausen and Gray's molecular orbital model for the vanadyl ion.[2] For the species containing $MoCl_6^{2-}$ and $MoCl_6^-$, the transitions are based on a simple molecular orbital model for a pure octahedral field.

Table II lists the results of appropriate physical measurements on the compounds $NH_4MoOCl_4 \cdot CH_3CN$ and $[(CH_3)_4N]_2MoCl_6 \cdot 0.5CH_3CN$.

The visible and ultraviolet spectra of the KCl–$MoCl_5$ melts, that of crystalline $(NH_4)_2MoOCl_5$ as reported by Gray and Hare,[4] and that of $[(CH_3)_4N]_2MoCl_6 \cdot 0.5CH_3CN$ are listed in Table III. In both the $MoCl_6^{2-}$

TABLE I

Compound	λ, Å. (shoulder)	ν, cm.$^{-1}$	ε, molar	Assignment
$MoOCl_3 \cdot (C_6H_5)_3AsO \cdot (CH_3)_2CO$	7190	13,900	57.3	${}^2B_2 \rightarrow {}^2E$ (I)
	(6000)	(16,700)		${}^2B_2 \rightarrow {}^2E$ (I)
	(4230)	(23,600)	51.0	${}^2B_2 \rightarrow {}^2B_1$
$MoOCl_3 \cdot 2(CH_3)_2CO$[a]	7220	13,800	20.5	${}^2B_2 \rightarrow {}^2E$ (I)
	4290	23,300	25.2	${}^2B_2 \rightarrow {}^2B_1$
$MoOCl_3 \cdot 2(C_6H_5)_3AsO$	7350	13,600	51.6	${}^2B_2 \rightarrow {}^2E$ (I)
	(6250)	(16,000)		${}^2B_2 \rightarrow {}^2E$ (I)
	4420	22,600	37.6	${}^2B_2 \rightarrow {}^2B_1$
$MoCl_5 \cdot (C_6H_5)_3AsO$	7250	13,800	20.8	${}^2B_2 \rightarrow {}^2E$ (I)
	4400	22,700	11.2	${}^2B_2 \rightarrow {}^2B_1$
$MoOCl_3 \cdot 2(CH_3)_2SO$	7230	13,800	19.0	${}^2B_2 \rightarrow {}^2E$ (I)
	4410	22,700	9.4	${}^2B_2 \rightarrow {}^2B_1$
$MoOCl_3 \cdot 2(C_6H_5)_3PO$	7430	13,500	18.9	${}^2B_2 \rightarrow {}^2E$ (I)
	4490	22,300	11.2	${}^2B_2 \rightarrow {}^2B_1$
$NH_4MoOCl_4 \cdot CH_3CN$[b]	7440	13,400	18.0	${}^2B_2 \rightarrow {}^2E$ (I)
	4450	22,500	16.5	${}^2B_2 \rightarrow {}^2B_1$
$KMoCl_6$[c]	4150	24,100	. . .	${}^2T_2 \rightarrow {}^2E$
$[(CH_3)_4N]_2MoCl_6 \cdot 0.5 CH_3CN$[c]	(4500)	(22,200)	. . .	${}^3T_1 \rightarrow {}^3T_2$
	(3875)	(25,800)	. . .	either ${}^3T_1 \rightarrow {}^3A_2$ or ${}^3T_1 \rightarrow {}^3T_1$ (P)

[a] Measured in acetone solution. [b] Measured in CH_3CN solution. [c] KCl pellet.

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[8] The design for the pellet holder was obtained from Prof. J. V. Quagliano, Florida State University, Tallahassee, Florida.

[9] A portion of the data in Table I was presented at the 7th International Conference on Coördination Chemistry, Stockholm, Sweden, June, 1962.

Table II

	μ_{eff}, B.M.	Λ molar, ohm^{-1} cm.^{2} mole^{-1}	Infrared spectra Pertinent obsd. band, cm.$^{-1}$	Assignment
$NH_4MoOCl_4 \cdot CH_3CN$	1.68	28	990	Mo–O
			2290	CN^-
			1405	CH_3
			3300	CH_3
$[(CH_3)_4N]_2MoCl_6$	2.44	56	3050	CH_3
			1440, 1470	CH_3
	(Prepared in CH_3CN)		2300	CN^-
	(Prepared in CH_2Cl_2)		880	$-CCl_2$

and $MoCl_6^-$ species the intensities of the absorption bands decreased with decreasing wave number. It was impossible to obtain the band at 41,000 cm.$^{-1}$ on the same graph as the ligand field bands, since it was much more intense. Although it was difficult to estimate the level of a hypothetical base line for reference, the band at 24,100 cm.$^{-1}$ in $KMoCl_6$ was less intense than the one at 32,800 cm.$^{-1}$ by at least a factor of three, possibly by much more.

The bands listed for $KMoCl_6$ after exposure to air are those which developed after the first time the spectrum was scanned. On the rerun, some indications of the original charge transfer bands usually were still present, but were largely swamped out by the intensity of the band at 32,500 cm.$^{-1}$.

Discussion

The similarity of the visible spectra of all the molybdenyl complexes indicates that the tetragonal distortion imposed by the molybdenyl oxygen is by far the most important deviation from cubic symmetry. The change of the type of oxygen donor ligand, and even the substitution of five Cl^- ligands for three Cl^- and two oxygen donor ligands, seems to have little effect on the position of the absorption bands.

Also, it is noteworthy that the spectrum of $MoCl_5 \cdot (C_6H_5)_3AsO$ is practically identical with those of complexes containing the MoO^{3+} species. The transition at 13,800 cm.$^{-1}$ involves molecular orbitals arising from the oxygen atom in molybdenyl compounds, according to the model of Ballhausen and Gray.[2] Since the energy of this transition is not appreciably different in $MoCl_5 \cdot (C_6H_5)_3AsO$ from that in the molybdenyl complexes, the Mo–O distance in the former is obviously very short, comparable to that of a molybdenyl compound. It has been noted earlier[5] that the As–O stretching frequency undergoes an unusually large shift upon complexing with $MoCl_5$. This fact substantiates the idea that the As atom almost loses its oxygen entirely to the Mo atom. When $(C_6H_5)_3PO$ was used as a donor, the Mo atom completely abstracted the oxygen atom, always forming molybdenyl complexes.[5] Apparently the slight difference in properties between phosphorus and arsenic is sufficient to permit the isolation of $MoCl_5 \cdot (C_6H_5)_3AsO$, but not of the corresponding phosphine oxide.

A series of attempts were made to isolate a compound containing the $MoCl_6^-$ ion. When either dry LiCl or KCl was combined with $MoCl_5$ dissolved in CH_3CN, in the manner described in the Experimental section, no reaction was observed. Oven-dried NH_4Cl, however, reacted very slowly to form the green solid $NH_4MoOCl_4 \cdot CH_3CN$, and moist NH_4Cl reacted very rapidly to give the same product. No comparable reaction was observed using CH_2Cl_2 as the solvent. Obviously H_2O must be present to hydrolyze the $MoCl_5$ to a molybdenyl species.

When $(CH_3)_4NCl$ was used as a chloride donor with $MoCl_5$ solutions, a reaction was observed with both CH_3CN and CH_2Cl_2 as solvents. In each case reduction to Mo(IV) occurred. As it seems rather unlikely that CH_2Cl_2 would act as a reducing agent, although CH_3CN could do so, it is probable that the tetramethylammonium ion itself must be involved in the reduction. However, it is possible to isolate green crystals from $MoCl_5$ solutions in CH_3CN. The nature of these crystals was not determined in this Laboratory, but we have been informed[10] that they are $MoCl_4 \cdot 2CH_3CN$. The latter fact suggests that the reaction to yield $MoCl_6^{-2}$ proceeds more rapidly in CH_3CN than in CH_2Cl_2 because the solvent itself can function as a reducing agent. Professor Fowles[10] also has isolated compounds containing $MoCl_6^{2-}$ from reactions in liquid SO_2.

An alternative explanation of the reduction is supplied by the work of Pearson and Garner.[11] They found that chlorine is evolved when $MoCl_5$ is dissolved in CCl_4. Such dissociation in CH_2Cl_2 and CH_3CN would account for lower chlorides of molybdenum in the solution.

In the method used to obtain a spectrum of $MoCl_6^-$, it was of course impossible to isolate pure $KMoCl_6$. However, we feel confident that the spectrum obtained is that of $MoCl_6^-$. The most potent argument is the complete absence of a band in the 13,000–14,000 cm.$^{-1}$ region, which is the one involving the π-orbitals of the molybdenyl oxygen. There should be only a single transition observed in such a d^1 ion, the transition from the non-bonding t_{2g} orbital to the antibonding e_g orbital. Only one absorption band was observed in our $KMoCl_6$ pellets which can be assigned reasonably as a ligand field band, the band at 24,100 cm.$^{-1}$. Since pellets were used no extinction coefficients could be calculated, but the band was definitely less intense than the ones at higher energies.

Some asymmetry, too weak to be called a shoulder, and centered roughly around 21,300 cm.$^{-1}$, was observed in the 24,100 cm.$^{-1}$ band. Since the asymmetry was at a wave length 200 Å. too long to be attributed to molybdenyl absorption, it probably is evidence of Jahn–Teller distortion in $MoCl_6^-$. Two bands separated by 3000–3500 cm.$^{-1}$ in Ti^{3+} compounds have been ascribed to Jahn–Teller splitting,[6] so the effect in $MoCl_6^-$ is of a reasonable magnitude. It has been pre-

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[10] G. W. A. Fowles, private communication.

[11] I. M. Pearson and C. S. Garner, *J. Phys. Chem.*, **65**, 690 (1961).

TABLE III

POSITION OF ABSORPTION BANDS, CM.$^{-1}$

$KMoCl_6$, freshly prepared	41,150	36,430	32,800	28,250	24,100	...
$KMoCl_6$ pellet after standing in open air			32,550		21,160	13,330
$(NH_4)_2MoOCl_5$[2]	41,700	35,700	32,100	26,700	23,000	13,800
$[(CH_3)_4N]_2MoCl_6$	41,300	36,760	33,900	28,400	25,800	22,200

dicted[12] that splitting due to spin-orbit coupling will not be negligible in a second-row transition element. The spin-orbit coupling constant for the Mo^{5+} free ion is about 1000 cm.$^{-1}$.[13] We consider that this splitting is of too small a magnitude to account for the above asymmetry, and furthermore is not likely to be seen in light of the half-width of the principal band.

When the pressed pellets were allowed to stand in moist air for a day or two, certain changes were observed in the spectrum. A very intense band developed in the region of 32,550 cm.$^{-1}$, and weaker bands appeared at about 22,000 and 13,330 cm.$^{-1}$. The changes indicate that the $MoCl_6^-$ ion was slowly hydrolyzed to a molybdenyl compound, since the two ligand field bands which appeared are quite comparable to those in the spectra of molybdenyl compounds.

On two of the pellet preparations the melt was heated strongly under nitrogen in a Vycor tube above the melting point of KCl. Even on prolonged heating for over 1 hr. at 800°, the color of the melt remained black. It would appear that some interaction stabilized the $MoCl_5$ to prevent it from all subliming away. The spectrum of the cooled melt was apparently the same as those of samples which had been heated only to the melting point of $MoCl_5$. However, a determination of the magnetic moment on the powdered melt gave a μ_{eff} of 2.7 Bohr magnetons. Another sample which was heated to just the fusion of the KCl had a μ_{eff} of 2.5 Bohr magnetons. A sample heated only to the melting point of $MoCl_5$ had a normal spin-only moment of 1.68 Bohr magnetons. These magnetic moments indicate that when the sample was heated strongly, some thermal dissociation to Cl_2 and lower valence states of Mo occurred. The lack of change in the spectrum is not too surprising, since reasonably small impurities of Mo(III) or (IV) would markedly increase the paramagnetism of the sample. Also, the bands observed in all the pellet spectra were extremely broad, and not well resolved. The half-width δ^- of the 24,100 cm.$^{-1}$ band was on the order of 3000 cm.$^{-1}$, and often this band appeared only as a shoulder on a broader charge transfer band. Thus absorption bands due to impurities of lower molybdenum chlorides would, in all probability, be hidden under the broad bands of the $KMoCl_6$ species. However, in the spectrum of the sample which was heated most strongly, with $\mu_{eff} = 2.7$ B.M., small indications of shoulders did appear at approximately 26,000 and 22,000 cm.$^{-1}$. These positions are comparable to the bands in the $MoCl_6^{2-}$ compound. This observation supports the postulate that the Mo(V) underwent some reduction upon heating in the KCl melt. It seems probable that some of the molybdenum still existed as $MoCl_6^-$, even after strong heating, since the absorption bands corresponded almost exactly with those of melts which had had more gentle treatment.

TABLE IV

Ion	$MoCl_6^{3-}$	$MoCl_6^{2-}$	$MoCl_6^-$
10 *Dq* (cm.$^{-1}$)	19,200[a]	22,200	24,100

[a] H. Hartman and H. L. Schläfer, *Angew. Chem.*, **66**, 768 (1954).

Jørgensen[6] predicted the energy of the $t_{2g} \rightarrow e_g$ transition in the hypothetical $MoCl_6^-$ ion would be about 30,000 cm.$^{-1}$. Although our observed value of 24,100 cm.$^{-1}$ is somewhat lower, the comparison is not unreasonable. For a d^1 ion in an octahedral field, the $t_{2g} \rightarrow e_g$ transition energy of course corresponds to 10 *Dq*, the ligand field splitting. For the same ligands, the magnitude of this splitting increases with increasing charge on the central ion. The band at 19,200 cm.$^{-1}$ in the spectrum of $MoCl_6^{3-}$ has been assigned to the transition $^4A_2 \rightarrow {}^4T_2$. This transition corresponds to the promotion of one electron from the t_{2g} to the e_g level, or to 10 *Dq*. Two bands which probably are due to ligand field transitions were observed in the pellet spectrum of $MoCl_6^{2-}$ at 22,200 and 25,800 cm.$^{-1}$. The lower energy almost surely corresponds to the first spin-allowed transition for a d^2 ion, $^3T_1 \rightarrow {}^3T_2$. The band at 25,800 cm.$^{-1}$ might be either of the other two spin-allowed transitions, $^3T_1 \rightarrow {}^3A_2$ or $^3T_1 \rightarrow {}^3T_1$ (P), the former, a two-electron transition, being unlikely. These assumptions give a value of 22,200 cm.$^{-1}$ for the value of 10 *Dq* for the $MoCl_6^{2-}$ ion. Table IV shows a comparison of the observed magnitudes of ligand field splitting for $MoCl_6^{n-}$ species as the formal valence of the Mo atom increases. There is a fairly regular progression, as one might predict.

In view of the foregoing arguments, the assignment of $^2T_2 \rightarrow {}^2E$ for the 24,100 cm.$^{-1}$ band in $KMoCl_6$ seems a reasonable one.

Acknowledgment.—This work was supported by the Office of Naval Research.

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[12] A. D. Liehr, *J. Phys. Chem.*, **64**, 43 (1960).

[13] Kindly pointed out by a referee.