The Preparations and the Electronic Spectra of Sexa-co-ordinate Molybdenum(III) Complexes

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It is interesting to compare the electronic spectra of the corresponding coordination compounds of molybdenum(III) and of chromium(III), both of which have a d^3-electronic configuration.

There have been a number of systematic studies of the spectra of chromium(III) complexes, and the band assignments have been well established,[1] as is schematically shown in Fig. 1, where quartet-quartet transitions are denoted with Roman numerals and quartet-doublet transitions, with letters of the alphabet.

In contrast with the case of chromium(III) complexes, however, such investigations of molybdenum(III) complexes have been so rare that only the hexachloro- and the pentachloroaquo-molybdate(III) ions appear to have been well investigated with regard to the inner d-shell bands. The absorption curves and the band assignments were reported by Jørgensen for these complexes.[1] According to these assignments and to the concept of

1) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962).

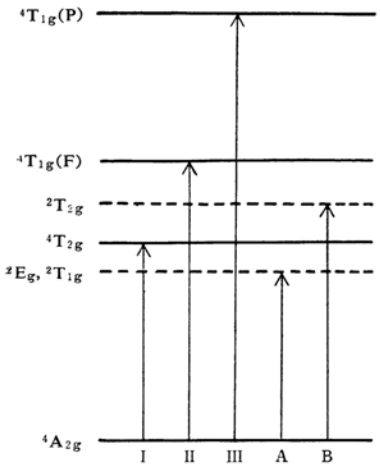

Fig. 1. Observed electronic transitions in d^3-system (Cr^{3+}) in octahedral field.

the spectrochemical series, the absorption spectra and band assignments by other authors for trichlorotripyridine- and "hexaquo-" molybdenum(III) complexes are doubtful.[2,3] Thus no systematic discussion of the electronic spectra of molybdenum(III) complexes has so far been presented because of a lack of available data.

The present paper is concerned with the preparation of and the electronic absorption spectra of several sexa-co-ordinate molybdenum(III) complexes, including three new compounds. Experimental results will be discussed, together with the available data on the corresponding chromium(III) complexes.

Experimental

Materials.—The following molybdenum(III) compounds were prepared: $K_3[MoCl_6]$, $(NH_4)_2[MoX_5(H_2O)]$, $[MoX_3(urea)_3]$, $[Mo(urea)_6]Br_3$, $[MoX_3(dmf)_3]$, $[MoCl_3(tu)_3]$ and $[MoX_3(py)_3]$ (where dmf=*N*, *N*-dimethylformamide, tu=thiourea, py=pyridine and X=Cl and Br). Among these compounds, $[MoBr_3(urea)_3]$, $[MoCl_3(dmf)_3]$ and $[MoBr_3(dmf)_3]$ are new compounds, while $[MoCl_3(urea)_3]$, $[Mo(urea)_6]Br_3$* and $[MoCl_3(tu)_3]$ have been briefly reported on by Russian authors.[4] No description, however, has yet been given of their preparation methods.

Trichlorotriureamolybdenum(III), $[MoCl_3(urea)_3]$.—Five grams of $(NH_4)_2[MoCl_5(H_2O)]$ and five grams of urea, ground together in a mortar, were added to 30 ml. of ethanol in a nitrogen atmosphere; the reaction mixture was then stirred continuously at 50—55°C. As the reaction proceeded, the color of the precipitate gradually changed from orange to yellow. After 3.5 hr. the product was filtered in air, washed with water until the filtrate became colorless and then with ethanol, and dried at 60°C. A yellow powder was obtained. Yield, 2.5 g. (43%).

This crude product was recrystallized with a concentrated aqueous solution of urea to give as a pure product yellow, tetragonal plates. The yield of the recrystallization was rather poor (less than 20%) because of the predominant decomposition,

Found: C, 9.42; H, 3.26; N, 21.77. Calcd. for $[MoCl_3(urea)_3]$: C, 9.42; H, 3.16; N, 21.97%.

Preparation in an aqueous medium was also possible.

Tribromotriureamolybdenum(III), $[MoBr_3(urea)_3]$.—A saturated aqueous solution of urea was prepared at room temperature. Five grams of $(NH_4)_2[MoBr_5(H_2O)]$ and three grams of urea were dissolved in as small an amount as possible of the urea solution in a nitrogen atmosphere, and then the mixture was stirred continuously at 48—50°C. After about 15 min. a crystalline precipitate began to separate. For an additional 30 min. the stirring was continued; then the mixture was cooled to room temperature, poured into about 50 ml. of water in air, and stirred for about 15 min. The precipitate was filtered, washed with water and with ethanol, and dried at 60°C. Yield, 1.3 g. (28%).

Found: C, 7.02; H, 2.24; N, 16.78. Calcd. for $[MoBr_3(urea)_3]$: C, 6.99; H, 2.34; N, 16.29%.

This compound, which consists of fine, orange microcrystals, is soluble in a warm aqueous solution of urea with decomposition, but insoluble in cold water and in common organic solvents.

Hexaureamolybdenum(III) Bromide, $[Mo(urea)_6]Br_3$.—The initial procedure was the same as that described for $[MoBr_3(urea)_3]$. When the orange precipitate of $[MoBr_3(urea)_3]$ had separated out, the temperature of the reaction mixture was raised to 70°C. Soon the precipitate was dissolved, and about 10—20 min. after the dissolution a pale-colored crystalline precipitate separated slowly from the dark brown solution. When the amount of the precipitate no longer increased, the stirring was stopped and the mixture was allowed to cool at room temperature. The crystals, which separated abundantly, were filtered in air, washed with ethanol, and dried at 60°C. Yield, 2.2 g. (35%).

For the elemental analyses the crude crystals were added to a large amount of ethanol at 40°C and stirred continuously for 20 min., filtered, washed with cold ethanol, and dried at 30°C under reduced pressure over phosphorus pentoxide for half a day.

Found: C, 10.48; H, 3.75; N, 23.83. Calcd. for $[Mo(urea)_6]Br_3$; C, 10.35; H, 3.48; N, 24.15%.

The pale greenish yellow pillar-shaped crystals thus obtained were soluble in water with decomposition but insoluble in common organic solvents.

Trichlorotris(N, N-dimethylformamide)molybdenum(III), $[MoCl_3(dmf)_3]$.—To 50 ml. of a purified *N*, *N*-dimethylformamide[5] 15 g. of $(NH_4)_2[MoCl_5(HO_2)]$

2) E. König and H. L. Schläfer, *Z. phys. Chem., N. F.* **26**, 371 (1960).

3) H. Hartmann and H.-J. Schmidt, *Z. phys. Chem., N. F.*, **11**, 234 (1957).

* In the Russian paper it is described as a dihydrate, $[Mo(urea)_6]Br_3 \cdot 2H_2O$.

4) V. B. Evdokimov, V. V. Zelentsov, I. D. Kolli, Wen-Hsia T'ang and V. I. Spitsyn, *Dokl. Akad. Nauk S. S. S. R.*, **145**, 1282 (1962).

5) D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

were added. The mixture was then stirred continuously for 12 hr. at 30—35°C in a nitrogen atmosphere. The insoluble red precipitate of the starting molybdate salt was slowly displaced by a white precipitate of ammonium chloride until the red color disappeared in the precipitate at the end of the reaction. This was separated with a glass filter, and the dark-brown filtrate was concentrated to a thick paste under reduced pressure below 35°C and preserved in an ice-box for several days. When the crystallization of the paste did not occur spontaneously, one of the following procedures was taken: (1) scratching by means of a magnetic stirrer, (2) dissolving the paste in ethanol at 50°C, followed by cooling the solution with an ice-bath as soon as possible and scratching,* or (3) dissolving the paste in ethanol or in acetone at room temperature and then preserving it in an ice-box for a few weeks. The yellow product separated was filtered and washed with ethanol. Yield of the crude product was about 60%. As the crude product was often contaminated with ammonium chloride, purification was performed by procedure 2 for the elemental analyses. The yellow powder produced was filtered, washed with ethanol several times, and dried at 35°C under reduced pressure over phosphorus pentoxide for 100 min. All the procedures were carried out in an oxygen-free atmosphere so far as possible.

Found: C, 26.13: H, 5.21; N, 10.36. Calcd. for $[MoCl_3(dmf)_3]$: C, 25.64; H, 5.02; N, 9.97%.

This compound is soluble with decomposition in water, ethanol, acetone, pyridine and chloroform, but insoluble in benzene; the color changes after a few days in moist air.

Tribromotris(N, N-dimethylformamide)molybdenum(III), $[MoBr_3(dmf)_3]$—Five grams of $(NH_4)_2[MoBr_5(H_2O)]$ were dissolved in 17 ml. of purified *N, N*-dimethylformamide; the mixture was then stirred continuously at 29—31°C for 6 hr. in a nitrogen atmosphere. After about 15 min. the color of the solution became blood-red. Near the end of the reaction, the white precipitate of ammonium bromide separated. This was filtered rapidly in air, and the filtrate was concentrated at 30°C under reduced pressure in an atmosphere of carbon dioxide until just enough of the solvent remained to moisten the crystalline product. All the contents were then poured into about 50 ml. of water, and the suspension was stirred for 20 min. at room temperature. The orange crystalline substance was filtered, washed with water and with methanol, and dried at about 30°C under reduced pressure over calcium chloride. Yield, 1.4 g. (28%).

Found: C, 19.55; H, 3.79; N, 7.97. Calcd. for $[MoBr_3(dmf)_3]$: C, 19.48; H, 3.81; N, 7.57%.

The orange-red hexagonal microcrystalline plates of the compound are soluble in chloroform, where they rapidly decompose; soluble in water and in acetone only with difficulty, and insoluble in ethanol and in ether. The color of the compound changes when it is left in moist air for several days.

Trichlorotrithioureamolybdenum(III), $[MoCl_3(tu)_3]$.—Fifteen grams of $(NH_4)_2[MoCl_5(H_2O)]$ and ten grams of thiourea were ground together in a mortar, added to about 200 ml. of ethanol, and the mixture was stirred continuously at 50°C for 20 hr. in a nitrogen atmosphere. The color of the solution gradually became dark brown. Then the reaction mixture was left at room temperature for 10 hr., and filtered. The crude precipitate was washed with cold and warm water until the reddish color faded from the filtrate; it was then washed with ethanol and dried at 60°C for several minutes. Yield, 8.5 g. (43%).

Found: C, 8.58; H, 2.84; N, 19.30. Calcd. for $[MoCl_3(tu)_3]$: C, 8.38; H, 2.81; N, 19.54%.

This compound, obtained as an orange-yellow microcrystalline powder, is soluble in *N, N*-dimethylformamide with decomposition, slightly soluble in water and in pyridine, and insoluble in common organic solvents. The compound is stable in air, at least for several days.

Other Compounds. — $K_3[MoCl_6]$, $(NH_4)_2[MoCl_5(H_2O)]$ and $(NH_4)_2[MoBr_5(H_2O)]$ were prepared according to the method of Hartmann and Schmidt[3] with slight modifications.

$[MoCl_3(py)_3]$ was prepared according to the method described in the literature.[6]

Found: C, 40.93; H, 3.35; N, 9.56. Calcd. for $[MoCl_3(py)_3]$: C, 40.98; H, 3.44; N, 9.56%.

$[MoBr_3(py)_3]$ was obtained by almost the same method as that used for $[MoCl_3(py)_3]$.

Found: C, 32.23; H, 2.34; N, 7.54. Calcd. for $[MoBr_3(py)_3]$: C, 31.44; H, 2.64; N, 7.33%.

Measurements.—Electronic absorption spectra in the solid state were measured with a Hitachi EPU-2A spectrophotometer equipped with a diffuse reflectance attachment, and the spectra in solution, with a Beckman DU spectrophotometer. A Hitachi EPS-2 self-recording spectrophotometer was employed for the measurement of $[Mo(urea)_6]Br_3$ in solution.

The infrared absorption spectra measurements of the three molybdenum(III) compounds containing urea and of hexaureachromium(III) chloride were made in the rock salt region by the KBr disk technique.

All the measurements of the ultraviolet and infrared spectra were carried out at room temperature.

Results and Discussion

The Ultraviolet Spectra and the Structures of the Molybdenum(III) Complexes. — The main results of the ultraviolet measurements are given in Figs. 2—4 and in Table I. There are common features through all these absorption spectra: each spectrum has two sharp bands of a lower intensity near 9000 cm^{-1} and 15000 cm^{-1} and two more intense broad bands of a similar type in the higher wave number region, though these bands are partly embedded under

* This complex is rapidly decomposed in ethanol at 50°C.

6) H. B. Jonassen and L. J. Bailin, *Inorg. Syn.*, 7, 140 (1963).

much more intense bands in some spectra. This observation gives support to Jørgensen's band assignments, which are shown in Figs. 1—2,[1] and to the octahedral configuration in all these complexes. The corresponding bands of the molybdenum(III) compounds have been similarly assigned.

The absorption spectra of ammonium pentabromoaquomolybdate(III) were measured in the solid state, in 3 N hydrobromic acid and in 12 N hydrobromic acid (Fig. 2). The I- and II-bands in the 12 N hydrobromic acid solution are shifted by about 1000 cm^{-1} to a lower wave number compared with those in the solid state, and they show almost no change during the measurement. On the other hand, the corresponding bands in the 3 N hydrobromic acid solution are shifted to a higher wave number and show a considerable time dependency. The same behavior was observed among the spectra of the corresponding chlorocomplexes, such as $(NH_4)_2[MoCl_5(H_2O)]$ and $K_3[MoCl_6]$ (Fig. 2). Table I summarizes the corresponding band maxima in these spectra. From these observations it may be concluded that the spectra of $(NH_4)_2[MoBr_5(H_2O)]$ in 12 N hydrobromic acid and of $K_3[MoCl_6]$ in 12 N hydrochloric acid are due to the $[MoBr_6]^{3-}$ ion and to the $[MoCl_6]^{3-}$ ion respectively, and that considerable decomposition takes place in the 3 N hydrobromic acid solution of the bromomolybdate complex.

Since $[Mo(urea)_6]Br_3$ is rapidly decomposed, even in a concentrated aqueous solution of urea (about 4 mol. urea), the spectrum was obtained within 15 min. after dissolution. Both the I- and II-bands are considerably (about 1000 cm^{-1}) shifted to a lower wave number compared with those of the solid state. Therefore, any structure in which the bromide ion is directly attached to the molybdenum ion is improbable for the compound in the solid state. Moreover, the pronounced intensity of the B-band common to the other bromide-containing complexes is not obvious in the spectra of the hexaurea compound. It is, therefore most likely that this contains the $[Mo(urea)_6]^{3+}$ ions.

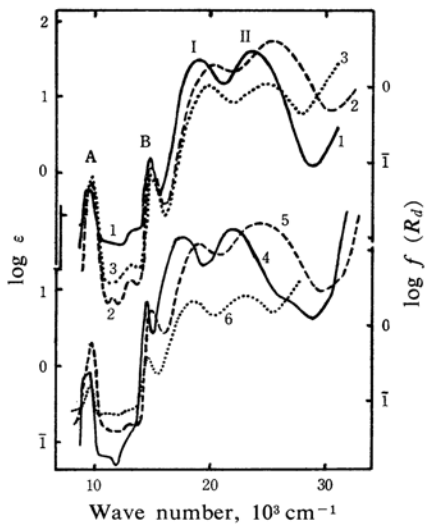

Fig. 2. Absorption spectra of: 1, $K_3[MoCl_6]$ in 12 N HCl; 2, in 3 N HCl; 3, $(NH_4)_2[MoCl_5(H_2O)]$ in solid state; 4, $(NH_4)_2[MoBr_5(H_2O)]$ in 12 N HBr; 5, in 3 N HBr; 6, in solid state.

TABLE I. SPIN-ALLOWED BANDS OF SOME MOLYBDENUM(III) COMPLEXES

Complex	Condition	Band maxima and assignments I	II
$K_3[MoCl_6]$	in 12 N HCl	19.15	23.8
$(NH_4)_2[MoCl_5(H_2O)]$	Solid	19.95	24.15
$K_3[MoCl_6]$	in 3 N HCl	20.5	25.35
$(NH_4)_2[MoBr_5(H_2O)]$	in 12 N HBr	17.7	22.0
	Solid	18.55	23.2
	in 3 N HBr	19.05	24.25
$[Mo(urea)_6]Br_3$	Solid	25.9	31.0

wave number, 10^3 cm^{-1}

It may obviously be concluded, on the basis of absorption spectra and chemical properties, that the two trihalotriurea complexes are not $[MoX_6]$ $[Mo(urea)_6]$ but $[MoX_3(urea)_3]$ (Figs. 2 and 3). The infrared absorption spectra of these three urea-containing compounds and of $[Cr(urea)_6]Cl_3$ were, therefore, measured in order to obtain further information on their molecular structure. The results are summarized in Table II.

Penland et al.[7] have studied the infrared spectra of many transition metal-urea complexes and found a method to determine the species of atom by which the central metal ion is coordinated in each of the complexes. This consists mainly of comparisons of NH-stretching frequencies and of CO-stretching frequencies coupled with NH_2 bending. According to this method, it may be concluded from Table II that urea is coordinated through the oxygen atom to the metal atom in the molybdenum complexes as well as in the chromium complex.

The trichloro- and tribromo-triureamolybdenum(III) have almost the same infrared patterns, while the pattern of hexaureamolybdenum(III) bromide is quite similar to that of hexaureachromium(III) chloride. The main differences between the spectra of these two

7) R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

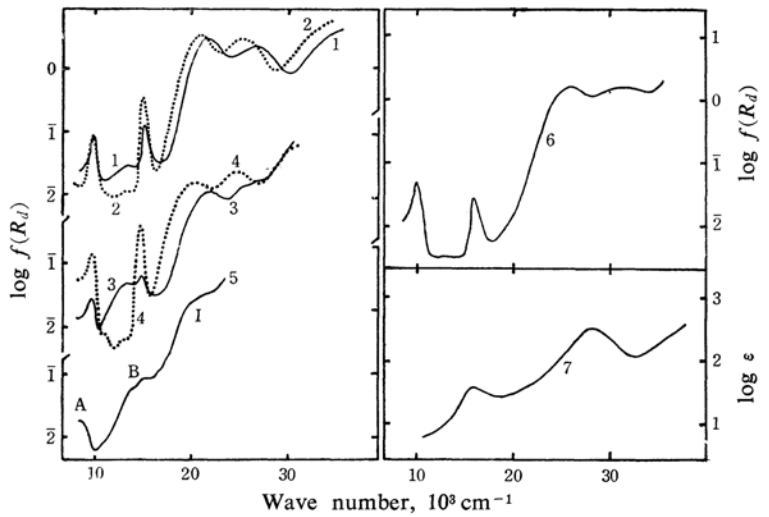

Fig. 3. Absorption spectra of: 1, $[MoCl_3(urer)_3]$; 2, $[MoBr_3(urea)_3]$; 3, $[MoCl_3(dmf)_3]$; 4, $[MoBr_3(dmf)_3]$; 5, $[MoCl_3(tu)_3]$; 6, $[Mo(urea)_6]Br_3$; 7, Mo^{3+} in 4 N H_2SO_4 (Ref. 3).

TABLE II. INFRARED ABSORPTION MAXIMA OF THE UREA COMPLEXES OF Mo(III) AND Cr(III)

$[MoCl_3(urea)_3]$	$[MoBr_3(urea)_3]$	$[Mo(urea)_6]Br_3$	$[Cr(urea)_6]Cl_3$*	Assignments
3460 s	3450 s	3430 s	3440 s	free NH str.
3350 s	3340 s	3320 s	3340 s	
—	—	3210m	3190m	?
1660 sh	1660 sh	1660 sh	1660 sh	CO str.
1627 s	1627 s	1620 s	1623 s	$+NH_2$bend.
1130m	1130m	1160m	1165m	NH_2 rock.

Wave number, cm^{-1}
Abbreviations: s, strong; m, medium; sh, shoulder
* Our measurement virtually reproduced the Penland's data for this compound (Cf. Ref. 7).

couples are found in the bands near 3200 cm^{-1} and near 1150 cm^{-1}. The former band is found only in the spectra of the hexaurea complexes; a corresponding band has also been found in hexaureairon(III) chloride.[7] On the other hand, both the frequency and the shape of the latter NH_2 rocking band are the same within each of the two pairs of compounds, but they are differentiated between the two pairs. These observations also support the presence of the $[Mo(urea)_6]^{3+}$ species in the hexaureamolybdenum(III) bromide.

Although the electronic absorption spectrum of the trichlorotris(*N*, *N*-dimethylformamide)-molybdenum(III) has some ambiguous features, which may be related to the difficulty of preparation (Fig. 3), the wave numbers of both the I- and II-bands of the two *N*, *N*-dimethylformamide complexes are not essentially different from those of the two corresponding triurea complexes, so the former two complexes, as well as the latter two, may be regarded as having the configuration $[MoX_3O_3]$.

The spectrum of trichlorotrithioureamolybdenum(III) appears to show at least four bands in the near infrared and visible region. These bands may be assigned to the A, B and I transitions, as is shown in Fig. 3. According to this assignment and to the spectrochemical series, this complex may be concluded to be of the $[MoCl_3S_3]$ type.

The spectra of trichlorotripyridinemolybdenum(III) have already been investigated by König and Schläfer[2]; one of them is shown in Fig. 4. However, our measurements for this compound gave slightly different absorption curves (Fig. 4), which show the spectral features common to the other sexa-co-ordinate molybdenum(III) complexes. The I- and the II-bands are most probably embedded under the much more intense charge transfer bands, because a part of the I-band appears on the lower wave number side of the charge transfer band in the spectra of the tribromotripyridinemolybdenum(III) (Fig. 4). A considerable splitting of the B-band was observed in the spectra of the two complexes, both in solution and in the solid state. On the contrary, a broad band at 12500 cm^{-1} in the spectra of the trichlorotripyridine complex has an enhanced

TABLE III. LIGAND FIELD PARAMETERS, Dq AND B, AND NEPHELAUXETIC RATIO β OF SOME OCTAHEDRAL COMPLEXES OF Mo(III) AND Cr(III)

		6 Br^-	6 Cl^-	6 urea	6 H_2O
Mo^{3+}	Dq	1.77	1.91_5	2.59	—
	B	0.39_0	0.42_1	0.45_3	—
	β	0.64	0.69	0.74	—
Cr^{3+}	Dq	—	a 1.318 b 1.38_5	c 1.60	c 1.74
	B	—	a 0.575 b 0.61_1	c 0.660	c 0.725
	β	—	a 0.62 b 0.67	c 0.72	c 0.79

Dq and B: $10^3\,cm^{-1}$

a) These values for $[Rh(ph)_3][CrCl_6]$ are quoted from Ref. 8.

b) These values were calculated from the unpublished spectral data for $K_3[CrCl_6]$ in Ref. 9.

c) These values are quoted from Ref. 1.

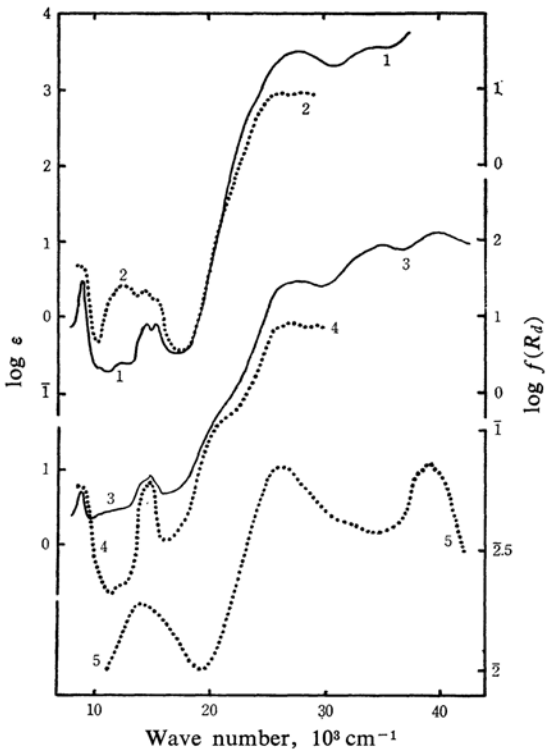

Fig. 4. Absorption spectra of: 1, $[MoCl_3(py)_3]$ in CH_2Cl_2; 2, in solid state; 3, $[MoBr_3(py)_3]$ in CH_2Cl_2; 4, in solid state; 5, $[MoCl_3(py)_3]$ in solid state, copied from Ref. 2.

intensity only in the solid state. More detailed investigations will be necessary to explain these phenomena.

Spectrochemical Series and Nephelauxetic Series.—From our spectral data the spectrochemical series for molybdenum(III) complexes was obtained as:

$$py \gtrsim (urea, dmf, and\ tu) > Cl^- > Br^-$$

This agrees with the series for complexes of other transition metal ions.

Using the wave numbers of the I- and II-bands, the Racah's parameter B's of interelectronic repulsion were calculated for the three octahedral molybdenum(III) complexes. From these values nephelauxetic ratios β' were then obtained by assuming $B=0.61(10^3\,cm^{-1})$ for free molybdenum(III) ions, in accordance with the findings of Jrgøensen.[1] The results are tabulated in Table III. For the purpose of comparing these parameters for $3d^3$- and $4d^3$-complexes, the corresponding values for three octahedral chromium(III) complexes are also given in Table III.[1,8,9] The following nephelauxetic series were obtained:

$Br^- > Cl^- >$ urea for molybdenum(III) complexes, and Cr(III) > Mo(III) for the same ligands.

These series are in good agreement with those for the chromium(III) and other transition metal complexes.[1]

Approximating the transition energies for the first and the second spin-forbidden bands as $9B+3C$ and $15B+5C$ respectively, Racah's parameters C' were calculated for the three molybdenum(III) complexes. These give ratios C/B between 4 and 5.

Hartmann and Schmidt[3] regarded the spectra of the green solutions obtained by the electrolytic reduction of diluted solutions of molybdenum oxide in various mineral acids as due to the "hexaquomolybdenum(III) ion"; a typical spectrum is shown in Fig. 3. This is apparently not a spectrum of the genuine hexaquomolybdenum(III) ion, in the light of the present investigation.

Summary

Several sexa-co-ordinate molybdenum(III) compounds containing some of chloride ions, bromide ions, urea, thiourea N,N-dimethylformamide and pyridine as ligands have been

8) W. E. Hatfield, R. C. Fay, C. E. Pfluger and T. S. Piper, *J. Am. Chem. Soc.*, 85, 265 (1963).

9) M. Nakahara, private communication.

10) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 9, 753 (1954).

prepared, and their electronic absorption spectra determined.

It has been shown that the spectrum of the sexa-co-ordinate molybdenum(III) compound generally has two spin-forbidden and two spin-allowed bands. The ligand field parameters of the octahedral molybdenum(III) complexes have been calculated and compared with those of the corresponding chromium(III) complexes.

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