The above interpretations are supported by the results of the present study. As is apparent from Table III, the energy of activation for the Fephen^{2+} dissociation is considerably lower and the entropy of activation considerably more negative than the corresponding values for the Fe(phen)$_3{}^{2+}$ dissociation. In contrast to the Fe(phen)$_3{}^{2+}$ dissociation, the dissociation of Fephen^{2+} is not accompanied by a change in the spin state of the iron(II).[23] In both the cobalt(II) and nickel(II) systems, on the other hand, the activation energies and entropies for the dissociation of the mono complexes are similar to those for the dissociation of the tris complexes. These dissociations are not accompanied by changes in the spin states of the central metal ions.[12, 23, 24]

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The Electronic Structures and Spectra of Chromyl and Molybdenyl Ions

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The reflectance spectra of $(NH_4)_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5]$ are measured and interpreted in terms of a molecular orbital energy level scheme. As in VO^{2+}, substantial π-bonding between metal and oxygen in the oxycations CrO^{3+} and MoO^{3+} is assumed. The charge transfer transitions involve the excitation of an electron from the metal–oxygen π-bonding orbital into orbitals located mainly on the metal atom. The solution spectrum of $(NH_4)_2[MoOCl_5]$ in 10 *M* HCl is examined, and a comparison is made between the calculated and observed band intensities.

Introduction

Metal ions at the beginning of the transition series have a remarkable capacity to form oxycations with the general formula MO^{n+}. The vanadyl ion, VO^{2+}, is one of the simplest and most stable ions of this type. An electrostatic model of the vanadyl ion consists of V^{4+}, with the electronic structure [argon]$3d^1$, and an oxide ion. However, the spectral and magnetic properties of the vanadyl ion are understood best in terms of the molecular orbital theory; in particular, the most significant feature of the electronic structure of VO^{2+} seems to be the existence of considerable oxygen to metal π-bonding.[3]

The chromyl and molybdenyl ions, CrO^{3+} and MoO^{3+}, are electronically equivalent to VO^{2+}, since they can be formulated as containing $Cr^{5+}(3d^1)$ and $Mo^{5+}(4d^1)$. These ions are rather rare, and the only well characterized complexes containing CrO^{3+} and MoO^{3+} are of the types $M_2[CrOCl_5]$, prepared by Weinland and Fiederer,[4] and $M_2[MoOCl_5]$, prepared by James and Wardlaw[5] (M can be NH_4^+, Na^+, K^+, Rb^+, or Cs^+). In the present paper the molecular orbital level scheme derived for the vanadyl ion[3] will be used to interpret the electronic spectra of $(NH_4)_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5]$. The structure of solutions of Mo(V) also will be discussed.

Molecular Orbitals for Chromyl and Molybdenyl Ions.—The $[MOCl_5]^{2-}$ (M = Cr(V), Mo(V)) ions are assumed to have a tetragonal structure, with a notably short M–O bond, analogous to the known structure of $VOSO_4 \cdot 5H_2O$[6] (see Fig. 1). Thus the molecular field is dominated by the axial MO^{3+} interaction.

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

[4] R. F. Weinland and M. Fiederer, *Ber.*, **39**, 4042 (1906).

[5] R. H. James and W. Wardlaw, *J. Chem. Soc.*, 2145 (1927).

[6] M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo cimento*, **3**, 718 (1956).

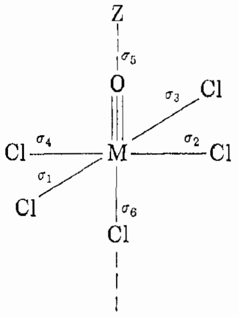

Fig. 1.—Structure of $(MOCl_5)^{2-}$.

In C_{4V} symmetry, the bonding in the molecule ion is described as follows: a strong σ bond of symmetry a_1 between the spσ oxygen hybrid orbital and the $[(n + 1)s + nd_{z^2}]$ metal hybrid orbital; two π-bonds of symmetry e between the oxygen $2p_x$ and $2p_y$ orbitals and the metal nd_{xz} and nd_{yz} orbitals, making a total of three metal–oxygen bonds in MO^{3+}; four σ bonds involving the $3p_z$ orbitals of the equivalent chlorines ($\sigma_1 - \sigma_4$) and the metal $[(n + 1)s - nd_{z^2}]$ (a_1), $(n + 1)p_x$ and $(n + 1)p_y$ (e) and $nd_{x^2-y^2}$ (b_2) orbitals; the axial chlorine (σ_6) is considered bonded to the remaining metal $(n + 1)p_z(a_1)$ orbital; finally, neglecting π-bonding between the metal and chlorine, the $nd_{xy}(b_2)$ metal orbital is non-bonding.

Using the $VO(H_2O)_5^{2+}$ calculation as a guide,[3] the relative ordering of the bonding and antibonding orbitals expected for $[MOCl_5]^{2-}$ is shown in Fig. 2. By placing the 17 valence electrons (10 from five Cl's, 6 from O, 1 from M) in the orbitals of lowest energy a ground state ${}^2B_2$ $[(Ia_1^b)^2 (IIa_1^b)^2 (b_1^b)^2 (e\sigma^b)^4 (IIIa_1^b)^2 (e\pi^b)^4 (b_2)]$ is obtained. It is convenient to divide the excited states into two classes: (1) those involving the promotion of the b_2 electron into e_π^*, b_1^*, and Ia_1^* levels and (2) those involving the promotion of an e_π^b electron into the b_2, $e\pi^*$, b_1^*, and Ia_1^* levels. Transitions to the excited states in the first category are the so-called crystal field transitions involving essentially d orbitals, and can be estimated to a good approximation as simply the energy differences in the one-electron molecular orbitals.

The second category includes the "charge transfer" transitions, that is, the promotion of an electron from the oxygen π orbital into the orbitals which belong mainly to the metal ion. Denoting the bonding σ orbitals as IC (inner core), the first charge transfer transition is ${}^2B_2[(IC)^{12} (e_\pi^b)^4(b_2)] \rightarrow {}^2E(II)[(IC)^{12}(e_\pi^b)^3(b_2)^2]$.

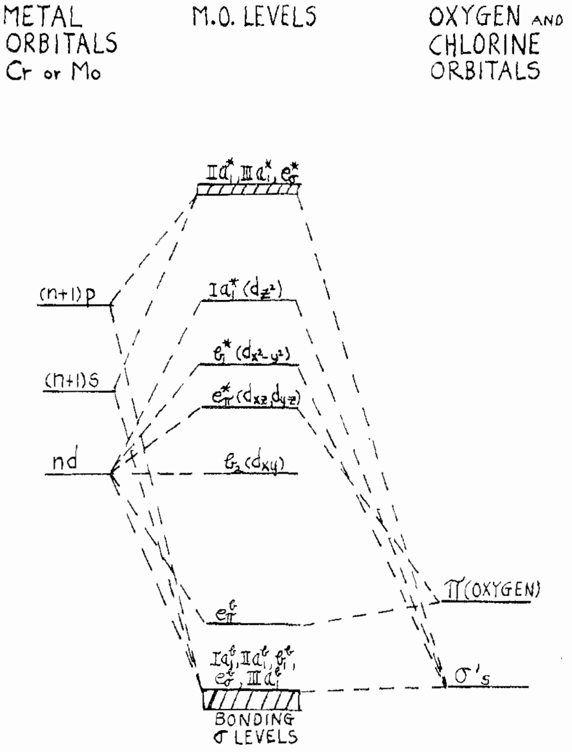

Fig. 2.—Relative energies of the one-electron molecular orbitals for the $(MOCl_5)^{2-}$ molecule ion.

The energy of this transition is estimated as the $(b_2 - e_\pi^b)$ orbital energy difference, plus the repulsion energy expected from moving an electron from a delocalized π-molecular orbital into a non-bonding b_2 orbital localized on the metal ion. The magnitude of this repulsion energy probably is about 10,000 cm.$^{-1}$, an estimate based on the relative positions of the first charge transfer bands in VO^{2+} and VO^{3+}.[7] The next charge transfer transitions involve the promotion of an e_π^b electron into an e_π^* orbital, *i.e.*, ${}^2B_2[(IC)^{12}(e_\pi^b)^4(b_2)] \rightarrow [(IC)^{12}(e_\pi^b)^3(b_2)(e_\pi^*)]$. From the excited orbital configuration $[(IC)^{12}(e_\pi^b)^3(b_2)(e_\pi^*)]$ doublet states can be constructed which transform as A_1, A_2, B_1, and B_2 in C_{4V}. Of these excited states, only transitions to ${}^2B_2$'s are orbitally allowed in C_{4V}, so the ${}^2B_1$'s, ${}^2A_2$'s, and ${}^2A_1$'s will not be considered further. The energies of the ${}^2B_2 \rightarrow {}^2B_2(I)$ and ${}^2B_2 \rightarrow {}^2B_2(II)$ transitions are estimated as the $(e_\pi^* - b_2)$ orbital energy difference, which is obtained from the crystal field spectrum, plus the ${}^2B_2 \rightarrow {}^2E(II)$ transition energy, adjusted for repulsion differences between the ${}^2E(II)$ and the ${}^2B_2(I)$ and ${}^2B_2(II)$ excited states. These repulsion energy differ-

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(7) F. A. Miller and W. B. White, *Spectrochim. Acta*, **9**, 98 (1957).

TABLE I

PREDICTED ENERGIES OF THE ELECTRONIC TRANSITIONS FOR THE $[MOCl_5]^{2-}$ ION

Transition	Predicted energy
$^2B^2 \rightarrow {}^2E(I)$	$\epsilon(e\pi^* - b_2)$
$^2B_2 \rightarrow {}^2B_1$	$\epsilon(b_1^* - b_2)$
$^2B_2 \rightarrow {}^2A_1$	$\epsilon(Ia_1^* - b_2)$
$^2B_2 \rightarrow {}^2E(II)$	$\epsilon(b_2 - e\pi^b) + J(b_2, b_2) + 2J(e\pi^b, b_2) - 3J(e\pi^b, e\pi^b) + K(e\pi^b, e\pi^b) - K(e\pi^b, b_2)$
$^2B_2 \rightarrow {}^2B_2(I)$	$\epsilon(^2B_2 \rightarrow {}^2E(II)) + \epsilon(e\pi^* - b_2) + J(b_2, e\pi^*) - J(b_2, b_2) + 3[J(e\pi^b, e\pi^*) - J(e\pi^b, b_2)] + \frac{5}{2}K(e\pi^b, b_2) - \frac{1}{2}K(e\pi^b, e\pi^*) - K(b_2, e\pi^*)$
$^2B_2 \rightarrow {}^2B_2(II)$	$\epsilon(^2B_2 \rightarrow {}^2E(II)) + \epsilon(e_1^* - b_2) + J(b_2, e\pi^*) - J(b_2, b_2) + 3[J(e\pi^b, e\pi^*) - J(e\pi^b, b_2)] + \frac{3}{2}K(e\pi^b, b_2) - \frac{3}{2}K(e\pi^b, e\pi^*) + K(b_2, e\pi^*)$
$^2B_2 \rightarrow {}^2E(III)$	$\epsilon(^2B_2 \rightarrow {}^2E(II)) + \epsilon(b_1^* - b_2) + J(b_2, b_1^*) - J(b_2, b_2) + 3[J(e\pi^b, b_1^*) - J(e\pi^b, b_2)] + \frac{5}{2}K(e\pi^b, b_2) - \frac{1}{2}K(e\pi^b, b_1^*) - K(b_2, b_1^*)$
$^2B_2 \rightarrow {}^2E(IV)$	$\epsilon(^2B_2 \rightarrow {}^2E(II)) + \epsilon(b_1^* - b_2) + J(b_2, b_1^*) - J(b_2, b_2) + 3[J(e\pi^b, b_1^*) - J(e\pi^b, b_2)] + \frac{3}{2}K(e\pi^b, b_2) - \frac{3}{2}K(e\pi^b, b_1^*) + K(b_2, b_1^*)$

TABLE II

REFLECTANCE SPECTRA OF $VOSO_4 \cdot 5H_2O$, $(NH_4)_2[CrOCl_5]$, AND $(NH_4)_2[MoOCl_5]$

	Band maxima in cm.$^{-1}$[a]						
Compound	$^2B_2 \rightarrow {}^2E(I)$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2E(II)$	$^2B_2 \rightarrow {}^2B_2(I)$	$^2B_2 \rightarrow {}^2B_2(II)$	$^2B_2 \rightarrow {}^2E(III)$	$^2B_2 \rightarrow {}^2E(IV)$
$VOSO_4 \cdot 5H_2O$	13,000	16,000	41,700	50,000[b] (46,200)			
$(NH_4)_2[CrOCl_5]$	12,900	23,500	40,000[c]	(44,400)			
$(NH_4)_2[MoOCl_5]$	13,800	23,000	26,700	32,100 (32,000)	35,700 (37,000)	41,700[c] (44,350)	(47,250)

[a] Calculated values are given in parentheses, for $J(b_2, e_\pi^*) - J(b_2, b_2) = -7000$ cm.$^{-1}$, $J(b_2, b_1^*) - J(b_2, b_2) = -4900$ cm.$^{-1}$, $J(e_\pi{}^b, e_\pi^*) - J(e_\pi{}^b, b_2) = J(e_\pi{}^b, b_1^*) - J(e_\pi{}^b, b_2) = 0$, $K(b_2, e_\pi^*) = 3500$ cm.$^{-1}$, $K(b_2, b_1^*) = 2450$ cm.$^{-1}$, $K(e_\pi{}^b, b_2) = K(e_\pi{}^b, e_\pi^*) = K(e_\pi{}^b, b_1^*) = 1000$ cm.$^{-1}$. [b] For an aqueous solution of $VOSO_4 \cdot 5H_2O$, 0.01 M in H_2SO_4; see ref. 3. [c] Shoulder.

ences can be expressed in terms of the usual coulomb and exchange integrals (see Table I).

The next charge transfer transitions are $^2B_2[(IC)^{12}(e_\pi{}^b)^4(b_2)] \rightarrow {}^2E(III)$, $^2E(IV)[(IC)^{12}(e_\pi{}^b)^3(b_2)(b_1^*)]$ and the transition energies are equal to the $(b_1^* - b_2)$ orbital energy difference, again obtainable from the crystal field spectrum, plus the $^2B_2 \rightarrow {}^2E(II)$ transition energy, adjusted as above for repulsion differences in the $^2E(II)$ and the $^2E(III)$ and $^2E(IV)$ excited states.

This process can be continued until all possible charge transfer transitions are obtained, but those given above are the ones whose energies are expected to fall within the readily accessible ultraviolet and visible spectral regions. A summary of the transitions (both crystal field and charge transfer) and their predicted energies in terms of orbital and repulsion differences is given in Table I.

The Spectrum of CrO^{3+}.—The maxima in the reflectance spectrum of $(NH_4)_2[CrOCl_5]$ are given in Table II, along with the band assignments. Assignments of the spectrum of $VOSO_4 \cdot 5H_2O$ are given for purposes of comparison. Consistent with the energy levels tabulated in Table I, the two bands found in the visible spectrum of $(NH_4)_2[CrOCl_5]$ are assigned to the transitions $^2B_2 \rightarrow {}^2E(I)$ and $^2B_2 \rightarrow {}^2B_1$, respectively. The third crystal field transition ($^2B_2 \rightarrow {}^2A_1$) is not observed, apparently being hidden under the first charge transfer band as in $VOSO_4 \cdot 5H_2O$. The first charge transfer transition ($^2B_2 \rightarrow {}^2E(II)$) is observed as a shoulder at about 40,000 cm.$^{-1}$.

In order roughly to predict the positions of the other charge transfer bands, it is necessary to have values for the J(coulomb) and K(exchange) integrals listed in Table I. The values which were used in the calculations are given in footnote *a* of Table I, and were arrived at by using the following rules: (1) Coulomb and exchange integrals between M.O.'s which are essentially localized on the same atom, *e.g.*, $J(b_2, b_1^*)$, are expressed in terms of Slater–Condon parameters calculated for the pure atomic orbitals. The estimates $F_2(d, d) = 700$ cm.$^{-1}$ and $F_4(d, d) = 70$ cm.$^{-1}$ then are used to obtain the listed values. (2) Coulomb integrals between M.O.'s which essentially are localized on different atoms, *e.g.*, $J(e_\pi{}^b, b_2)$, are small. Since these coulomb integrals occur in pairs in the energy expressions in Table I, the pair differences are set equal to zero. (3) Exchange integrals between M.O.'s which essentially are localized on different atoms are smaller than the "same atom" exchange integrals of rule 1, and arbitrarily are set equal to 1000 cm.$^{-1}$.

Using J's and K's calculated in the above way, and with $\Delta E({}^2B_2 \rightarrow {}^2E(II)) = 40,000$ cm.$^{-1}$, $(e\pi^* - b_2) = 12,900$ cm.$^{-1}$, the second charge transfer transition (${}^2B_2 \rightarrow {}^2B_2(I)$) is expected at about 44,400 cm.$^{-1}$. Unfortunately, accurate reflectance measurements could not be obtained for energies higher than 43,000 cm.$^{-1}$, preventing the prediction from being checked for CrO^{3+}.

Aqueous solutions of $(NH_4)_2[CrOCl_5]$ decompose rapidly, even when acidified up to 10 M HCl, and thus no attempt was made to obtain a solution spectrum.

The Spectrum of MoO^{3+}.—The results of the determination of the reflectance spectrum of $(NH_4)_2[MoOCl_5]$ are summarized in Table II. The visible spectrum is remarkably similar to that of $(NH_4)_2[CrOCl_5]$, showing bands at 13,800 cm.$^{-1}$, assigned to ${}^2B_2 \rightarrow {}^2E(I)$, and at 23,000 cm.$^{-1}$, assigned to ${}^2B_2 \rightarrow {}^2B_1$. Again the ${}^2B_2 \rightarrow {}^2A_1$ transition apparently is masked by the charge transfer spectrum. The first charge transfer band is observed at 26,700 cm.$^{-1}$ and is assigned to the transition ${}^2B_2 \rightarrow {}^2E(II)$. For the values of the coulomb and exchange integrals given in *a* of Table II, and taking $\epsilon(e_\pi^* - b_2) = 13,800$ cm.$^{-1}$ and $\epsilon(b_1^* - b_2) = 23,000$ cm.$^{-1}$ from the visible spectrum, the positions of the other charge transfer bands are calculated and listed in Table II in parentheses. The agreement between theory and experiment is quite good.

The fact that the molecular orbital energy level scheme derived[3] for $VO(H_2O)_5{}^{2+}$ is able to account satisfactorily for the electronic spectra of $(NH_4)_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5]$ is good evidence that the CrO^{3+} and MoO^{3+} ions are present as the dominating structures in these latter two cases. The qualitative correlation of the charge transfer and crystal field spectra for $VO(H_2O)_5{}^{2+}$ and $MoOCl_5{}^{2-}$ must be emphasized. Thus the first charge transfer band is due to a transition to the configuration in which two electrons are paired in the $b_2(d_{xy})$ orbital. For the other charge transfer bands of interest the excited states have one of these two electrons in a different orbital, and therefore the repulsion energies of these states are much less. These observations are consistent with the relative positions of the first few charge transfer bands in $VO(H_2O)_5{}^{2+}$ and $MoOCl_5{}^{2-}$. If electron repulsions were negligible the spacing between the first and second charge transfer bands would be equal to the energy of the first crystal field band, or 13,000 cm.$^{-1}$ for $VO(H_2O)_5{}^{2+}$ and 13,800 cm.$^{-1}$ for $MoOCl_5{}^{2-}$. The fact that these two bands are much more closely spaced, 8300 cm.$^{-1}$ for $VO(H_2O)_5{}^{2+}$ and 5400 cm.$^{-1}$ for $MoOCl_5{}^{2-}$, supports the argument presented above. Thus we estimate that the repulsion energy of the configuration $b_2{}^2$ is greater than $b_2e_\pi{}^*$ by 4700 cm.$^{-1}$ for $VO(H_2O)_5{}^{2+}$ and by 8400 cm.$^{-1}$ for $MoOCl_5{}^{2-}$.

Furthermore, it is very striking that the separation between the second–third[8] and the fourth charge transfer bands for $MoOCl_5{}^{2-}$ is very nearly equal to the separation of the first and second crystal field bands (9200 cm.$^{-1}$), suggesting that the configurations $b_2e_\pi{}^*$ and $b_2b_1{}^*$ differ only slightly in repulsion energy.

The emerald green solution of $(NH_4)_2[MoOCl_5]$ in 10 M HCl is stable and the spectrum is shown in Fig. 3.[9] This solution spectrum is very much like the reflectance spectrum of $(NH_4)_2[MoOCl_5]$, and it may be concluded that the species in 10 M HCl is either the $[MoOCl_5]^{2-}$, or something of a very similar structure such as $[MoOCl_4(H_2O)]^-$; at least the main features of the molybdenyl spectrum are retained. The structure of solutions containing Mo^{5+} is more complicated at HCl concentrations lower than 10 M. There is good evidence that both paramagnetic and diamagnetic dimers are present in solution in the region be-

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(8) The second and third charge transfer bands both arise from the one electron transition $e\pi^b \rightarrow e_\pi{}^*$.

(9) This same spectrum also has been obtained by (a) G. P. Haight, Jr., *J. Inorg. & Nuclear Chem.*, in press, and (b) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

TABLE III

OSCILLATOR STRENGTHS FOR THE ELECTRONIC TRANSITIONS OF $[MoOCl_5]^{2-}$ AND $[VC(H_2O)_5]^{2+}$

	For $[MoOCl_5]^{2-}$			For $[VO(H_2O)_5]^{2+}$		
Transition	Band maxima (cm.$^{-1}$) in 10 M HCl	Calcd. $f \times 10^4$	Obsd. $f \times 10^4$	Band maxima (cm.$^{-1}$) in dil. H_2SO_4	Calcd. $f \times 10^4$	Obsd. $f \times 10^4$
$^2B_2 \rightarrow {}^2E(I)$	14,050	1.4	2.4	13,000	3.9	1.1
$^2B_2 \rightarrow {}^2B_1$	22,500	orbitally forbidden	1.6	16,000	orbitally forbidden	0.45
$^2B_2 \rightarrow {}^2E(II)$	28,200	15	60	41,700	26.4	50.3
$^2B_2 \rightarrow {}^2B_2(I)$ $^2B_2(II)$	32,200	75	730	50,000	89.4	150
$^2B_2 \rightarrow {}^2E(III)$ $^2E(IV)$	41,700	55	1400	...	...	...

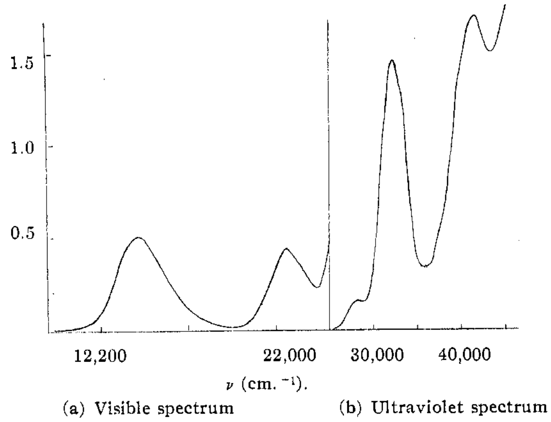

Fig. 3.—The electronic absorption spectrum of $(NH_4)_2$-$[MoOCl_5]$ in 10 M HCl: (a) 0.0315 M complex; (b) 0.000315 M complex.

tween 2 and 7 M HCl.[9a] Detailed electron spin resonance and magnetic susceptibility studies are presently being carried out on these solutions, and will be published separately.[10]

The oscillator strengths (f's) of the orbitally allowed transitions have been calculated using the dipole length operator, and these values are given in Table III along with the f values observed for the spectrum of MoO^{3+} in 10 M HCl. Details of the calculation are given in the Appendix. The calculated and observed band intensities for $VO(H_2O)_5{}^{2+}$ are included in Table III for comparison.

The absolute values of f calculated in this way are certainly of the right magnitude, but it is more significant that the predicted intensity ratios of the bands are in good agreement with experiment.

Experimental

Preparation of $(NH_4)_2[MoOCl_5]$.—This compound was prepared by the electrolytic reduction of a Mo(VI) solution as reported by James and Wardlaw.[5] The compound was purified twice by dissolving it in water and reprecipitating with HCl. The resulting green solid was separated and dried *in vacuo* over NaOH.

Preparation of $(NH_4)_2[CrOCl_5]$.—Reduction of a Cr(VI) solution with HCl as described by Weinland and Fiederer[4] was used to prepare this compound. The resulting garnet red solid was separated and dried *in vacuo* over NaOH. No purification was possible since dissolution of this compound results in its decomposition.

Spectra.—The reflectance spectra were obtained with a Beckman DU spectrophotometer fitted with a standard reflectance attachment, using MgO as the standard. Because of the hygroscopic nature of the solids, precautions were taken to eliminate moisture during the determinations. The solution spectrum was recorded using a Zeiss PMQ-2 spectrophotometer.

Acknowledgments.—The authors express their appreciation to Professor C. J. Ballhausen for encouragement during the course of this work. We also thank Professor G. P. Haight, Jr., for several helpful suggestions.

Appendix

The predicted values for the oscillator strengths of the absorption bands of $[MoOCl_5]^{2-}$ were calculated using the expression[11]

$$f = 1.085 \times 10^{-5} (\nu_{\text{cm.}^{-1}})[\text{av}_{\text{I}}\ \Sigma_{\text{II}} |\int \psi_{\text{I}}^* \vec{r}\, \psi_{\text{II}} d\tau|^2] \quad (1)$$

where $\nu_{\text{cm.}^{-1}}$ is the frequency of the band, ψ_{I} and ψ_{II} are, respectively, the proper orbital functions for the initial and final states involved in the transition, and $\vec{r} = ix + jy + kz$. The one-electron molecular orbitals are assumed to have the form

$$\psi(\text{M.O.}) = c_1\Phi(\text{metal}) + c_2\Phi(\text{ligand}) \quad (2)$$

where Φ(metal) and Φ(ligand) are the proper combinations of atomic orbitals for the M.O. in question. For radial functions of the type

$$\Phi(R) = Nr^{n-1}e^{-\mu r} \quad (3)$$

where N is the normalization constant for the

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(10) C. Hare, I. Bernal, and H. B. Gray, to be published.

(11) C. J. Ballhausen, *Progr. in Inorg. Chem.*, **2**, 251 (1960).

exponential factor μ and n is the principal quantum number for the atomic orbital, eq. 1 simplifies as follows for the transitions of $[MoOCl_5]^{2-}$

A. $^2B_2 \longrightarrow {}^2E(I), f = 1.085 \times$

$$10^{-5}\,(\nu_{cm^{-1}})\left[\frac{[N_{2p}c_2{}^{e\pi^*}}{2N_{3dxy}{}^{\mu 2p}}\right]^2 \times 2[S(3d_\delta{}^{\mu 2p}, 4d\delta)]^2 \quad (4)$$

B. $^2B_2 \longrightarrow {}^2E(II), f = 1.085 \times$

$$10^{-5}\,(\nu_{cm.^{-1}})\left[\frac{N_{2p}c_2{}^{e\pi^b}}{2N_{3dxy}{}^{\mu 2p}}\right]^2 \times 2[S(3d_\delta{}^{\mu 2p}, 4d\delta)]^2 \quad (5)$$

C. $^2B_2 \longrightarrow {}^2B_2(I), {}^2B_2(II), f = 1.085 \times 10^{-5}(\nu_{cm.^{-1}}) \times$

$$\left[\frac{2(c_1{}^{e_\pi{}^b}c_2{}^{e_\pi{}^*} + c_1{}^{e_\pi{}^*}c_2{}^{e_\pi{}^b})N_{2p}}{N_{3dxz,yz}{}^{\mu 2p}}\right]^2 \times [S(3d_\pi{}^{2p}, 4d_\pi)]^2 \quad (6)$$

D. $^2B_2 \longrightarrow {}^2E(III), {}^2E(IV), f = 1.085 \times 10^{-5}\,(\nu_{cm.^{-1}}) \times$

$$2\left\{\left[\frac{N_{3p}c_1{}^{e_\pi{}^b}c_2{}^{b_1{}^*}S(4d_\pi{}^{\mu 3p}, 4d_\pi)}{N_{4dxz,yz}{}^{\mu 3p}}\right]^2 + 2\left[\frac{N_{2p}c_1{}^{b_1{}^*}c_2{}^{e_\pi{}^b}S(3d_\delta{}^{\mu 2p}, 4d_\delta)}{2N_{3dxy}{}^{\mu 2p}}\right]^2\right\} \quad (7)$$

Notation: N_{np} is a normalization constant for an atomic p orbital; $N_{nd}{}_{\mu_{(n-1)p}}$ is a normalization constant for a nd orbital with a $\mu_{(n-1)p}$ radial exponential factor; $S(nd^{\mu_{(n-1)p}}, 4d)$ is a two-atom overlap integral between a nd ligand orbital with radial exponential factor $\mu_{(n-1)p}$, and a molybdenum 4d orbital; finally, $c_{1 \text{ or } 2}{}^{M.O.}$ is an atomic orbital coefficient of eq. 2 for a particular molecular orbital (see Fig. 2).

The predicted f's of Table III are obtained from eq. 4–7 by evaluating the overlap integrals for μ values calculated using Slater's rules, and further assuming $c_1{}^* = c_2{}^b = 0.92$, $c_1{}^b = 0.40$, and $c_2{}^* = -0.40$, in agreement with the coefficients arrived at in the $VO(H_2O)_5{}^{2+}$ calculation.[3] The Mo–O distance is taken as 2 Å., and the Mo–Cl distance is taken to be 2.3 Å.

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Binuclear Intermediates in the Reaction between Uranium(VI) and Chromium(II)[1]

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It has been found that at least one binuclear intermediate forms rapidly when Cr(II) and U(VI) are mixed in acid solutions near 0°. The spectrum of the intermediate indicates that it is a substituted Cr(III) species. The intermediate reacts with Tl(III) and V(IV) at rates which are first order in the intermediate concentration but zero order in the concentration of oxidizing agent. In the absence of other reactants the intermediate decomposes to give U(IV), U(VI), and Cr(III) with apparent half-times at 0° ranging between 4 and 8 min. Chemical, optical and kinetic evidence have been found for the presence of significant amounts of a second, more reactive, intermediate in the system.

Introduction

A study of the reaction between U(VI) and Cr(II) in aqueous solution was undertaken to provide further information on the factors which influence the rates of reactions between positive ions. Cr(II) is a particularly interesting reducing agent since the product, Cr(III), is substitution inert.[2]

The kinetics of two other reductions of U(VI) already have been studied: the reaction with Sn(II) in HCl solutions[3] and with Fe(II) in H_3PO_4 solutions.[4] In both of these examples the reactions occur in strongly complexing media. Cr(II), however, is strong enough to reduce U(VI) in perchlorate solutions.

In the present work it has been found that the reaction between U(VI) and Cr(II) is complicated in that the reactants disappear much faster than the final products appear. When the reactants are mixed in acid solutions near 0° a very rapid reaction occurs which gives a bright bottle-green solution. This is followed by a slower reaction to give a darker green solution, characteristic of the final products, U(IV) and Cr(III). This paper gives the details of the evidence for the existence of intermediates in the reaction and also presents some chemistry of the intermediates.

The formation of intermediates in oxidation–

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission and was presented in part at the 138th National A.C.S. Meeting, New York, N. Y., September, 1960.

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