

THE $\Gamma_1-\Gamma_1$ INTRACONFIGURATIONAL ELECTRONIC TRANSITION WITHIN t_{2g}^4
OF THE CHLORO-BROMO MIXED HALOGENO COMPLEXES OF Os(IV)

Akio URUSHIYAMA

Department of Chemistry, Faculty of Science, Rikkyo University,
Nishiikebukuro, Toshima-ku, Tokyo 171

The electronic spectra of the chloro-bromo mixed halogeno complex anions, $[\text{OsBr}_x\text{Cl}_{6-x}]^{2-}$ ($x=0-6$), in K_2SnCl_6 matrix were measured in the region of 16000-18000 cm^{-1} . In this region, intraconfigurational electronic transition within t_{2g}^4 was observed in the absorption and emission measurements. The mixed halogeno complex anions showed band features markedly different from those of the complexes in O_h symmetry.

A number of studies have been carried out on the electronic spectra of the intraconfigurational d-d transition with metal complexes in O_h site symmetry.¹⁾ However, few spectroscopic measurements have been reported on the spectra of the complexes in reduced site symmetry.²⁾ This communication presents the absorption and emission spectra of the $\Gamma_1[{}^3T_{1g}(O_h)]-\Gamma_1[{}^1A_{1g}(O_h)]$ intraconfigurational electronic transition within t_{2g}^4 of the mixed halogeno complex anions, $[\text{OsBr}_x\text{Cl}_{6-x}]^{2-}$ ($x=0-6$). The spectra were observed to have markedly different patterns from those of the complexes in O_h site symmetry.

Pure chloro-bromo mixed halogeno complex anions, $[\text{OsBr}_x\text{Cl}_{6-x}]^{2-}$ ($x=0-6$), were isolated from the reaction mixtures according to the procedures of Preetz et al.³⁾ These complex anions were doped into crystals of K_2SnCl_6 for measurements. The absorption spectra measured at 80 K and the emission spectra measured at 20 K upon Hg 365 nm line excitation are illustrated in the figure. The infrared absorption bands of the complex salts in the 200-700 cm^{-1} region

are also shown in the table. In the present study, no emission was observed with the complexes containing more than four Br^- ligands.

The $\Gamma_1[{}^3\text{T}_{1g}(\text{O}_h)] - \Gamma_1[{}^1\text{A}_{1g}(\text{O}_h)]$ intraconfigurational transition of $[\text{OsCl}_6]^{2-}$ in single crystals of K_2PtCl_6 ^{1a)}, Cs_2ZrCl_6 ^{1a,1c)}, Cs_2HfCl_6 ^{1b)} and $[\text{OsBr}_6]^{2-}$ in Cs_2ZrBr_6 ^{1d)} has been studied by many workers. The absorption spectra of $[\text{OsCl}_6]^{2-}$ and $[\text{OsBr}_6]^{2-}$ in the present K_2SnCl_6 matrix were in good agreement with those in Cs_2ZrCl_6 or Cs_2ZrBr_6 already reported. However, some additional lines, which are assigned to $\nu_4 + \nu_{\text{lattice}}$, $\nu_4 + \nu_2$, and $\nu_4 + \nu_2 + \nu_{\text{lattice}}$, were clearly observed in the emission spectra of $[\text{OsCl}_6]^{2-}$. An assignment of the vibrational modes which appeared in the emission spectrum of $[\text{OsCl}_6]^{2-}$ is given in the figure.

The distinctive feature of the spectra is an enhanced intensity of the 0-0 line in the mixed ligand complexes. The 0-0 lines should be observed in the same positions for the absorption and emission spectra in the case of the intraconfigurational d-d transition, and thus the 0-0 line could readily be assigned. Even when the emission spectra could not be detected, the positions of the 0-0 line could be identified by careful inspection of the absorption spectra. The transmission spectra of the doped single crystals could be measured by means of the microspectroscopic technique.⁴⁾ The molar extinction coefficient of the 0-0 line of $[\text{OsBrCl}_5]^{2-}$ was estimated to be ~ 100 at 80 K, while that of the vibronically allowed ν_4 line of $[\text{OsCl}_6]^{2-}$ was estimated to be ~ 8 at the same temperature. Doped crystals large enough for the microscopic

Table. Infrared Absorption Bands of $\text{Cs}_2\text{OsBr}_x\text{Cl}_{6-x}$ ($x=0-6$)

Compound	Symmetry	Absorption Bands (cm^{-1})
Cs_2OsCl_6	O_h	316
$\text{Cs}_2\text{OsBrCl}_5$	C_{4v}	330, 310, 295, 212
cis- $\text{Cs}_2\text{OsBr}_2\text{Cl}_4$	C_{2v}	324, 308, 297, 218, 203
trans- $\text{Cs}_2\text{OsBr}_2\text{Cl}_4$	D_{4h}	310, 226
fac- $\text{Cs}_2\text{OsBr}_3\text{Cl}_3$	C_{3v}	317, 295, 224, 202
mer- $\text{Cs}_2\text{OsBr}_3\text{Cl}_3$	C_{2v}	308, 295, 225, 210
cis- $\text{Cs}_2\text{OsBr}_4\text{Cl}_2$	C_{2v}	309, 294, 222
trans- $\text{Cs}_2\text{OsBr}_4\text{Cl}_2$	D_{4h}	309, 224
$\text{Cs}_2\text{OsBr}_5\text{Cl}$	C_{4v}	302, 223
Cs_2OsBr_6	O_h	223

spectroscopy could not be obtained in the case of the complexes containing more than two Br^- ligands because of their instabilities in aqueous solution. Hence, the extinction coefficients were known only in a qualitative sense because the mull method was necessary for the measurements. However, distinct 0-0 lines were observed for most mixed ligand complexes.

The vibrational fine structures of the bands were found to be rather complicated. However, some of the lines may be assignable on the basis of the infrared absorption data in the table.

It was found that the positions of the 0-0 lines shift towards the lower wavenumber side with increase in the number of Br^- ligand in the mixed ligand complexes. The $\Gamma_1[{}^3T_{1g}(\text{O}_h)] - \Gamma_1[{}^1A_{1g}(\text{O}_h)]$ transition is estimated to be of $15B+5C+\xi_{5d}$ in energy by first-order approximation. Hence, this finding is consistent with the fact that the interelectronic repulsion and the effective

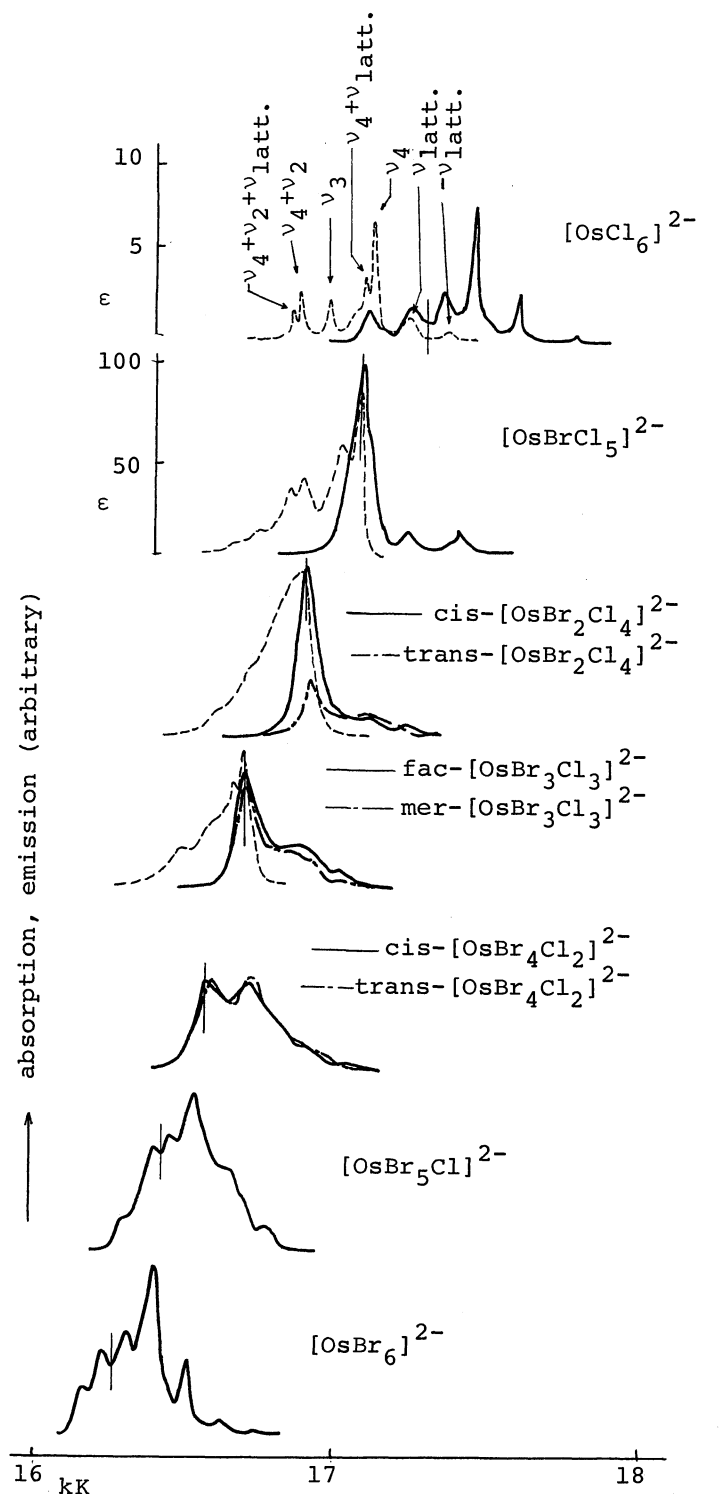


Figure. Electronic spectra of the chloro-bromo mixed halogeno complexes of Os(IV) (— and — — —: absorption spectra at 80 K, — — — —: emission spectra at 20 K). The emission spectra and the positions of the 0-0 line indicated with vertical lines are shown for cis isomers.

spin-orbit coupling in the bromocomplexes are known to be reduced more than in the chlorocomplexes.

REFERENCES

- 1) (a) P. B. Dorain, H. H. Patterson, and P. C. Jordan, *J. Chem. Phys.*, 49, 3845 (1968); (b) A. R. Reinberg, *Phys. Rev. B*, 3, 41 (1971); (c) S. B. Piepho, J. R. Dickinson, J. A. Spencer, and P. N. Schatz, *Mol. Phys.*, 24, 609 (1972); (d) J. L. Nims, H. H. Patterson, S. M. Khan, and C. M. Valencia, *Inorg. Chem.*, 12, 1602 (1973).
- 2) C. D. Flint and A. P. Matthews, *J. Chem. Soc. Faraday II*, 1973, 69, 419.
- 3) (a) Von E. Blasius and W. Preetz, *Z. anorg. allgem. Chem.*, 335, 16 (1965); (b) W. Preetz, *ibid.*, 348, 151 (1966); (c) W. Preetz and J. L. Nadlar, *ibid.*, 410, 48 (1974).
- 4) A. Urushiyama, Y. Itoh, M. Nakahara, and Y. Kondo, *Bunko Kenkyu*, 22, 151 (1973).

(Received August 5, 1976)