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The vibronic structure of mixed ligand Os(IV) complexes II. Low lying ligand field levels of *trans*-$[OsCl_4I_2]^{2-}$, *fac*- and *mer*-$[OsCl_3I_3]^{2-}$

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Abstract

The title compounds were optically investigated by recording the 10 K absorption spectra of the Cs and n-tetrabutylammonium salts pressed in KBr pellets and the 10–20 K emission spectra of the complex ions doped into Cs_2SnCl_6. For d-d transitions the spectral region is limited to the range from about 4000-12000 cm-‘. The measured peaks are assigned to zero-phenon transitions (electronic origins) between states belonging to the $(t_{2g})^4$ subshell configuration and to corresponding vibronic transitions. For the better resolved spectra an assignment to symmetries of respective point groups can be obtained from selection rules using relative peak intensities. These results must be, however, considered as still tentative.

Introduction

In the preceding article of this series [1], the low temperature absorption and emission spectra of Os(IV) chloro complexes mono- and *cis* bi-substituted by bromine and iodine ligands were reported. Assignment to d-d transitions has been carried out applying selections rules of respective symmetries and results from ligand field calculations. The interpretation is based on assignments which have been reported for octahedral hexa-chloro and hexa-bromo complexes [2–6] using primarily symmetry arguments on the observed splitting pattern expected from the low symmetry and predictions obtained from ligand field parameters which were calculated for the high symmetry compounds. The same procedure can be applied also for other mixed halide Os(IV) complexes the preparations of which have been described by Preetz et al. [7–9]. Solution spectra of these compounds were reported earlier [IO], however, since MCD measurements indicated that the separation of isomers by electrophoresis was not complete [9], these spectra are recorded from geometrically contaminated compounds.

In the present work we prepared the Cs and n-tetrabutylammonium compounds of the three title compounds and measured their low temperature (10 K) absorption spectra; the 20 K emission spectra in the near infrared (NIR) region 4200-12 500 cm^{-1} were recorded from doped materials (in Cs_2SnCl_6). In this energy interval only d-d transitions between levels of mainly $(t_{2g})^4$ subshell configuration are expected [1–6] giving rise to a $^3T_{1g}$ multiplet (ground level) and to $^1T_{2g}$ and ^1E_g as first excited states. Since iodine complexes have ligand to metal charge transfer bands occurring already at low energy extending from about 11-12 000 cm^{-1} to higher frequency [11], the range where d-d transitions can be observed without larger interferences with charge transfer levels is very small. In the visible region the weak bands arising from ligand field transitions are, for the most part, covered by strong charge transfer transitions. Due to the close vicinity of charge transfer states, results obtained from ligand field calculations are not very reliable. For iodine complexes we came to the conclusion [1] that ligand field calculations cannot supply useful contributions to the assignment problem. The calculated low symmetry level sequences are likely to be changed by intermixing wave functions of charge transfer states into d orbital levels. We therefore will not report any theoretical results in the present paper, although many calculations have been carried out, since they did not lead to a satisfactory interpretation of the experiments. As a matter of fact, ligand field calculations for the high symmetry Os(IV) compounds are also not very reliable [4, 12–14] as long as assignments

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to higher levels which result from $(t_{2g})^3e_g$ or further excited configurations are not certain [15]. The mixing of charge transfer into ligand field levels can be large for many compounds but does not interfere with the group theoretically determined selection rules which are applied in the present case.

For a distinction of zero-phonon from vibronic transitions, the results of normal coordinate analyses are used which supply the symmetries of the normal modes and their vibrational quanta [16,17].

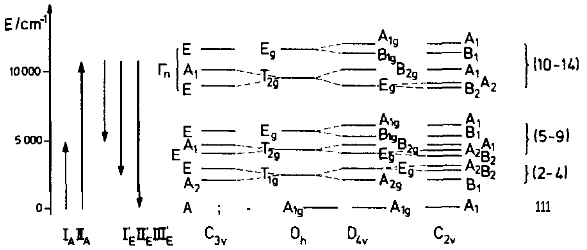

Fig. 1. Splitting of lowest octahedral d electron energy levels and the notations used for possible transitions.

Experimental

The compounds were prepared and separated according to the procedures described by Preetz and coworkers [7–9]. The *trans* isomers, i.e. *trans*-$[OsCl_4I_2]^{2-}$ and *mer*-$[OsCl_3I_3]^{2-}$, are preferably formed by virtue of the *trans* effect from $OsCl_6{}^{2-}$ reacting with HI; the *cis* isomers, in our case *fac*-$[OsCl_3I_3]$, are prepared from $OsI_6{}^{2-}$ by reaction with HCl. Complexes of certain ligand composition can be concentrated by employing distinct reaction times and temperatures. For separating the reaction mixtures the 2 N HCl solutions of the K or Rb salts are passed through an ion exchange column filled with DEAE-cellulose (Serva, capacity 0.8) at 0 °C temperature. For details see the preceding paper of this series [1] and the refs. quoted therein.

The absorption spectra were recorded from compounds incorporated in KBr pellets, the emission spectra from doped materials using Cs_2SnCl_6 as the host compound which are prepared by common precipitation with the Os complexes from HCl solutions. The optical equipment used was described in detail in ref. 1. For cooling, a flow-cryostat LT-3-110C was applied in the case of the absorption measurements; a Cryovac contact gas cryostat k 1104/so and a CSW 202 closed cycle system of Air Products were used for recording the emission spectra in the visible and NIR which allowed sample temperatures of 10 or 20 K, respectively, to be obtained.

Results and discussion

The low symmetry level schemes derived from the lowest octahedral states which result from group theoretical considerations are presented in Fig. 1 (all representations refer to respective double groups). The notations used for the absorption (A) and emission (E) spectra (transitions) agree with those introduced in the preceding article [1]. The emission spectra I_E to III_E of iodine complexes could not be obtained due to the interference with charge transfer transitions. In all cases the splitting resulting from low symmetry is small compared to spin-orbit coupling, therefore the spectra are observed in approximately the same regions as those of the octahedral complexes, e.g. in absorption near to 5000 (I,,) and 10 000 (II,) cm-‘, which correspond to transitions into E_g,T_{2g}(5–9) and E_g,T_{2g}(10-14) octahedral levels, respectively. The lowest level of the second group of states in low symmetry will be denoted in the discussion by Γ_n. The higher absorption (III_A) due to the A_{1g}(1.5) level which can be observed for chloro and bromo complexes close to 17 000 cm-’ is covered in iodo complexes by strong charge transfer bands [11, 13, 14].

Since all transitions below about 12 000 cm^{-1} belong to levels with predominantly $(t_{2g})^4$ configuration, the Stokes shifts are very small (cf. the discussion in ref. 1). For electronically allowed transitions the zero-phonon bands will be therefore the most intense in the spectra. Compounds with an inversion center in the point symmetry group as in the case of the *trans*-iodo complex must invoke a promotion (active) mode of odd symmetry for making a d-d transition electric dipole allowed. Here the vibrational side bands (vibronics) belonging to these modes may be more intensive or have similar intensity as the zero-phonon peaks, the latter obtaining intensity by magnetic dipole transitions (*vide infra*).

In Table 1 the selection rules for electric and magnetic dipole transitions of zero-phonon transitions are given which are obtained by group theory for the relevant point groups D_{4h}, C_{3v} and C_{2v}. For vibronically allowed transitions also the symmetry types of normal vibrations are added by which an electric dipole moment is induced.

Since absorption and emission spectra could not be obtained from the same material because of intensity problems (cf. ref. 1), a comparison of peak positions must take into account environmental effects on corresponding transitions. Throughout, the spectral resolution in absorption of the n-tetrabutylammonium (TBA) salts is distinctly higher than that of the Cs salts.

TABLE 1. Selection rules for electric (+) and magnetic (MD) dipole transitions. For vibrationally induced transitions symmetries of normal vibrations are given

D_{4h}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g
A_{1g}	a_{2u},e_u	MD e_u	b_{2u},e_u	e_u	MD a_{2u}, b_{2u},e_u
A_{2g}		a_{2u},e_u	e_u	b_{2u},e_u	MD a_{2u}, b_{2u},e_u
B_{1g}			a_{2u},e_u	MD e_u	MD a_{2u}, b_{2u},e_u
B_{2g}				a_{2u},e_u	MD a_{2u}, b_{2u},e_u
E_g					MD a_{2u}, b_{2u},e_u

C_{3v}	A_1	A_2	E
A_1	+ a_1,e	a_2,e	+ a_1,a_2,e
A_2		+ a_1,e	+ a_1,a_2,e
E			+ a_1,a_2,e

C_{2v}	A_1	A_2	B_1	B_2
A_1	+ a_1,$b_{1,2}$	a_2,$b_{1,2}$	+ $a_{1,2}$,b_2	+ $a_{1,2}$,b_2
A_2		+ a_1,$b_{1,2}$	+ $a_{1,2}$,b_2	+ $a_{1,2}$,b_1
B_1			+ a_1,$b_{1,2}$	a_2,$b_{1,2}$
B_2				+ a_1,$b_{1,2}$

trans-[OsCl$_4$I$_2$]$^{2-}$ spectra (D_{4h})

The spectra of highest energy to be considered are those originating from II_A and III'_E transitions (Fig. 1). In the emission spectrum III'_E (Fig. 2) arising from Γ_n the main band is at 9980 cm^{-1} which has its equivalent in a broad band at about 10 000 cm^{-1} in absorption II_A, the spectrum of which containing other features at higher energy is extremely diffuse. The large intensity of the emission band cannot be entirely attributed to a magnetic dipole transition which in D_{4h} is allowed for an $E_g \rightarrow A_{1g}$ zero-phonon transition. A large contribution to the intensity is presumably due to vibronic (false) origins supplied by odd lattice modes or by the σ_{as}(Os–I) stretching mode $\nu_3(a_{2u})$ calculated from normal coordinate analysis at 93 cm^{-1} [17]. The smaller peak at 9765 cm^{-1} is also assigned to a false origin belonging to the π(Os–Cl) bending mode ν_4 of higher frequency [17] with the same symmetry a_{2u}. The weak features at 9480 and 9580 cm^{-1} at lower frequency cannot be assigned to the III'_E spectrum; they probably arise from I_E transitions [1] which should occur for iodo complexes at lower energy since the $A_{1g}(15)$ level primarily depending on d–d repulsion parameters is distinctly lowered [1, 3, 4] in the series of halogen complexes due to the increasing nephelauxetic effect [18].

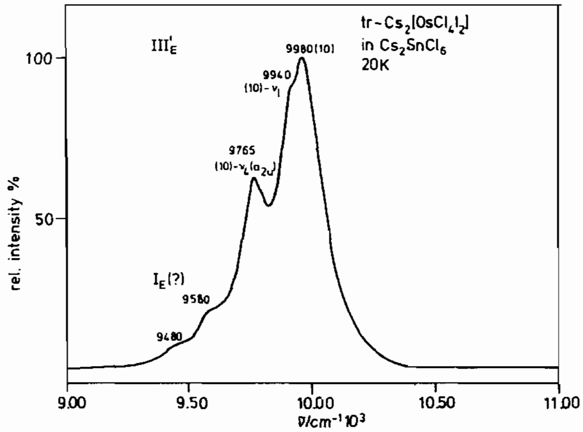

Fig. 2. $\Gamma_n \rightarrow A_1$ emission spectrum of doped *trans*-$Cs_2[OsCl_4I_2]$. Excitation achieved by all lines lower than 600 nm wavelength of a high pressure mercury lamp (cf. ref. 1).

The transitions I'_E and I_A go into the same set of terminal states. The I'_E spectrum is very diffuse and shows a weak band at 5380 cm^{-1} and a broad band at 5280 cm^{-1} which dominates the spectrum. If the former is attributed to a zero-phonon transition, the strong band 100 cm^{-1} lower in energy could be of vibronic origin of the same transition with the a_{2u} Os–I vibration calculated at 93 cm^{-1} as promoting mode. The energy of this electronic state would be about 4600 cm^{-1} which is obtained from 10 000 cm^{-1}, i.e. Γ_n from II_A and III'_E, minus 5380 cm^{-1}. This number can be derived also from the I_A spectrum which has at the low energy flank a small band at 4710 cm^{-1}, when this is assigned to the false origin belonging to the 4600 cm^{-1} level (5), the transition into it being promoted by the same a_{2u} (93 cm^{-1}) mode. Since the TBA salt supplies a better resolved spectrum (Fig. 3) we prefer to use this where the absorption into level (5) occurs at 4640 cm^{-1} (for all TBA mixed halides corresponding absorptions peaks are found at slightly higher frequency compared to the Cs salts). All other bands and distinct shoulders in this spectrum towards higher energy can be assigned to vibronic transitions due to the promoting modes $\nu_3(a_{2u})$, $\nu_9(e_u)$ and $\nu_{10}(e_u)$ or (alternatively to the latter) $\nu_7(b_{2u})$ (cf. Table 2) which are measured

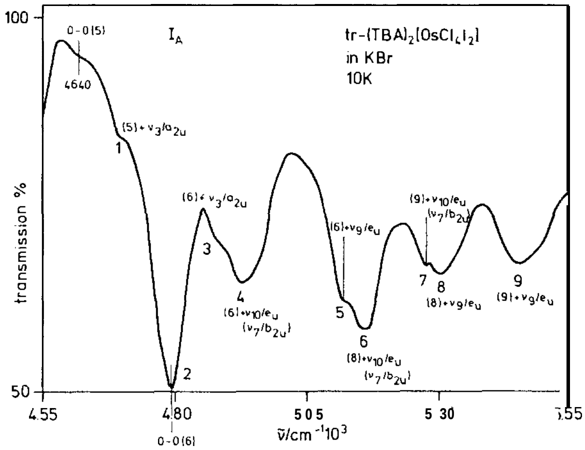

Fig. 3. $A_1 \rightarrow E,T_2(5–9)$ absorption spectrum of *trans*-$(TBA)_2[OsCl_4I_2]$ in KBr (2.2/123 mg).

TABLE 2. Assignments of band maxima (nos. 1-9) in the I, spectrum of *trans*-$[OsCl_4I_2]^{2-}$ (Fig. 3) to vibronic transitions and zero-phonon energies ν(O–O) calculated from frequency intervals

No.	Experimental	ν(O–O)			
		4640(5)	4800(6)	5010(8)	5130(9)
1	4740	$100\nu_3$			
2	4800		o - o		
3	4890		$90\nu_3$		
4	4950		$150\nu_{10}/\nu_7$		
5	5120		$320\nu_9$		
6	5160			$150\nu_{10}/\nu_7$	
7	5285				$155\nu_{10}/\nu_7$
8	5350			$330\nu_9$	
9	5450				$320\nu_9$

and/or calculated with frequencies close to those given in the Table. Only the main peak of Fig. 3 accordingly is due to a zero-phonon transition which obtains its intensity by the only possible magnetic dipole allowed $A_{1g} \rightarrow E_g$ transition (Table 1) and by promotion through odd lattice modes. This assignment is supported by the fact that this transition is the only one with three vibrational satellites which for a transition into Es are all vibronically allowed (cf. Table 1). Since the higher transitions combine only with e_u (or b_{2u}) modes they should be attributed to B_{1g} and B_{2g} states resulting from the $E_g,T_{2g}(5–9)$ level set. Therefore the lowest level at 4640 cm^{-1} can be assigned to A_{1g} (cf. Fig. 1).

The emission spectrum II'_E depicted in Fig. 4 shows several bands of different intensity. Since at low temperature only two electronic transitions $\Gamma_n(E_g) \rightarrow A_{2g}$ and $E_g(2–4)$ are expected which are magnetic dipole allowed, some peaks must be of vibronic nature. With the assignments given in Fig.

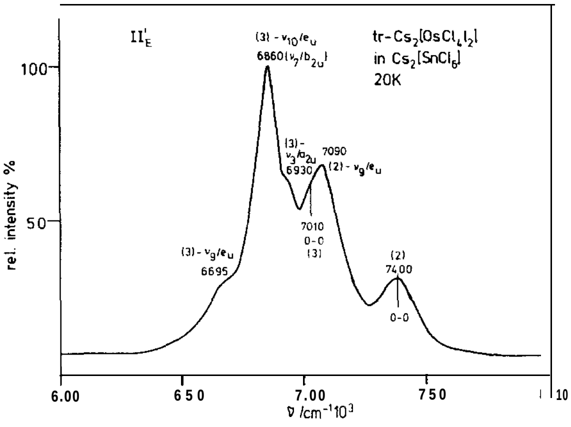

Fig. 4. $\Gamma_n \rightarrow T_1$ emission spectrum of doped *trans*-$Cs_2[OsCl_4I_2]$. Excitation achieved as for the spectrum in Fig. 2.

TABLE 3. Energies and assignments of d electron levels for *trans*-$[OsCl_4I_2]^{2-}$ obtained from zero-phonon transitions

Cs salt	TBA salt	Symmetry D_{4h}	Level no.
9980	10040	E_g	(10)Γ_n
	5130	B_{1g},B_{2g}[a]	(9)
5020	5010	B_{2g},B_{1g}	(8)
4810	4800	E_g	(6)
4610	4640	A_{1g}	(5)
3000		A_{2g},E_g	(3)
2600		E_g,A_{2g}	(2)

“Alternative assignment.

4 the spectrum can be well rationalized. From the electronic origins at about 7010 and 7400 cm^{-1} as well as the 10 000 cm-’ level determined from spectrum II_A, the energies of the low symmetry levels arising from the octahedral $T_{1g}(2–4)$ are calculated as 2600 and 3000 cm^{-1}. An assignment to the possible symmetries, A_{2g} and E,, cannot be obtained. In Table 3 the level assignments proposed from D_{4h} selection rules are collected which for some cases can be given only alternatively. On the basis of the experimental results reported, all these assignments must be considered, however, as tentative.

fac-$[OsCl_3I_3]^{2-}$ spectra (C_{3v})

The emission spectrum III'_E essentially consists of a narrow band at 9745 cm-’ indicating that only a single electronic transition is present which arises from the lowest state Γ_n of the $E_g,T_{2g}(10–14)$ level group. The only other feature, i.e. a shoulder at 9580 cm-‘, can be assigned to a vibrational sideband to this transition due to a δ(Cl–Os–I) vibration ν_{10} of e symmetry which is measured in the far IR spectrum at 159 cm-’ [16]. The absorption spectrum

II_A of the Cs salt is very diffuse. It has two broad bands near 10 000 and 10 400 cm-’ which are not very characteristic. The corresponding TBA spectrum II_A (Fig. 5) is also poorly resolved but contains more information: at least five absorption features can be detected which in this region are due to the levels (10-14) which belong to the symmetries A_1 and two E in the point group C_{3v} (cf. Fig. 1). If these absorptions are all assigned to zero-phonon transitions, the spectrum would indicate a molecular symmetry lower than C_{3v}, the two degenerate E levels being further split into two components. Since the energy differences between the low and high energy components are smaller (100 and 65 cm-‘, respectively) than the others, the two corresponding pairs could be due to transitions into the E levels. Some of the weak features can, however, be alternatively explained by vibrational side bands, the vibrational modes obtained from the far IR spectrum having quanta up to 300 cm^{-1} (cf. ref. 17). Due to the poor resolution a more reliable assignment is not possible.

The I_A and I'_E spectra are also very diffuse and show only a few bands. The I_A spectrum of the Cs salt has merely one broad band with 4740 cm-’ at the absorption maximum, while the corresponding spectrum of the TBA salt (Fig. 6) is again better resolved. It exhibits two peaks which are only 50 cm-’ apart. Since for octahedral complexes, Os&*-(X= Cl, Br), the levels E_g and $T_{2g}(5–9)$ also differ by only 90–100 cm^{-1} [3–6] we can conclude that the two peaks of the low symmetry compound are also due to zero-phonon transitions into two terminal states belonging to the same group of levels. The low symmetry field is seen to be manifested by the smaller slope on the low frequency flank of the spectrum where the second transition into the other of the two C_{3v} components of T_{2g} could be hidden.

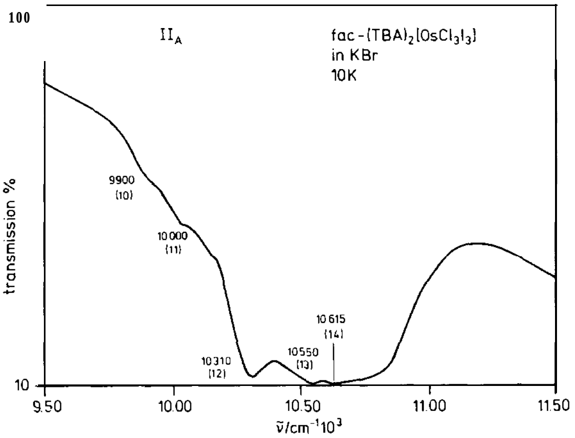

Fig. 5. $A_1 \rightarrow E,T_2(10–14)$ absorption spectrum of *fac*-$(TBA)_2[OsCl_3I_3]$ in KBr (2.7/122 mg).

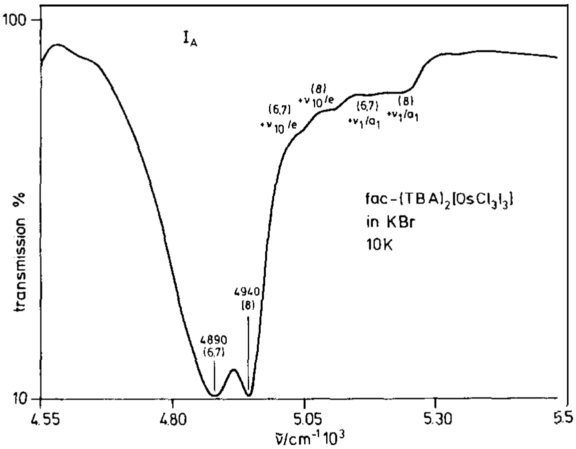

Fig. 6. $A_1 \rightarrow E,T_2(5–9)$ absorption spectrum of *fac*-$(TBA)_2[OsCl_3I_3]$ in KBr (2.7/122 mg).

The weak absorption features at higher energy can be interpreted by vibrational side bands due to $\nu_1(a_1)$ and v,,(e) modes which are measured in the far IR at 298 and 159 cm-‘, respectively [16]. The I'_E spectrum of the Cs salt has only one broad peak at 5145 cm^{-1} attributed to transitions into levels of parent $E_g,T_{2g}(5–9)$ states. Since the difference to 9745 cm^{-1} from III'_E predicts one (or more) levels at 4600 cm^{-1}, the transition(s) observed in I'_E must go to lower level(s) of $E_g,T_{2g}(5–9)$ in view of the fact that from I_A a level at 4740 cm^{-1} from the same parent states has been derived.

The emission spectrum II'_E has a main band at 7105 cm^{-1} and three shoulders towards lower energy which can be assigned to vibrational side bands due to ν_8, ν_{10} and ν_6 (listing with increasing frequency) of *e* symmetry [16]. Since apparently only one electronic transition can be detected we must assume that the levels A_2 and E(2–4), the transitions from $\Gamma_n(E)$ being allowed, are nearly degenerate. This is predicted by theory when holohedral symmetry [1] is present where the effective octahedral ligand field has octahedral symmetry [19]. With the Γ_n level obtained from III'_E the resulting energy of A_2 and E is calculated to be 2640 cm^{-1}. Table 4 summarizes the results which can be derived from the present spectra.

mer-$[OsCl_3I_3]^{2-}$ *spectra* (C_{2v})

For this complex only the spectra I_A, II_A and II'_E could be recorded, the others were too weak or diffuse to be evaluated. Since the symmetry is very low most of the transitions are allowed, therefore little can be said about level assignments on the basis of selection rules.

The II, spectrum of the Cs salt has on the low frequency side a broad band peaking at 9920 cm-’

TABLE 4. Energies and assignments of d electron levels for *fac*-$[OsCl_3I_3]^{2-}$ obtained from zero-phonon transitions

Cs salt	TBA salt	Symmetry C_{3v}	Level no.
10370	10615	E	(14)
	10550		(13)
10000	10310	A_1	(12)
9745	10000	E	(11)
	9900		(10)Γ_n
4740	4940	E	(8)
(4600)	4890	A_1+E	(5–7)
2640		A_2+E	(2–4)

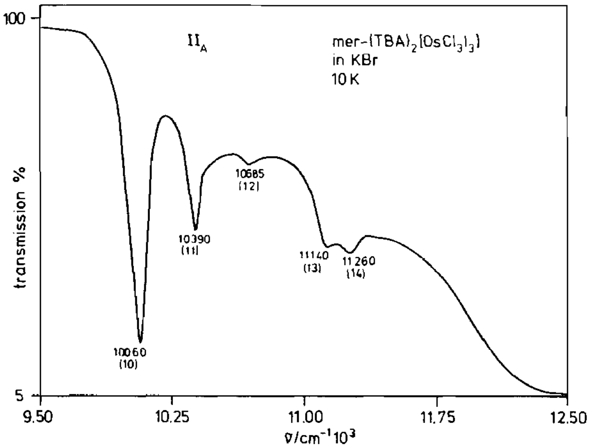

Fig. 7. $A_1 \rightarrow E,T_2(10–14)$ absorption spectrum of *mer*-$(TBA)_2[OsCl_3I_3]$ in KBr (3.0/121 mg).

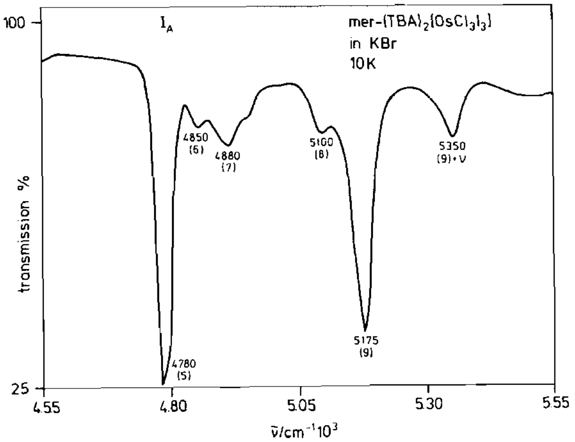

Fig. 8. $A_1 \rightarrow E,T_2(5–9)$ absorption spectrum of *mer*-$(TBA)_2[OsCl_3I_3]$ in KBr (3.0/121 mg).

TABLE 5. Energies of d electron levels for *mer*-$[OsCl_3I_3]^{2-}$ obtained from zero-phonon transitions (level energies of (2–4) cannot be determined due to poor spectral resolution)

Cs salt	TBA salt	Level no.
	11260	(14)
	11140	(13)
	10685	(12)
	10390	(11)
9920	10060	(10)Γ_n
4975	5175	(9)
	5100	(8)
4830	4880	(7)
	4850	(6)
4710	4780	(5)

which by comparison with the other Os complex spectra in this region will be due to transitions into lower states of the $E_g,T_{2g}(10–14)$ level series. The TBA salt spectrum (Fig. 7) is better resolved exhibiting five distinct bands of different intensity the number of which corresponds to the number of possible levels predicted by group theory when considering the octahedral parent states in this region and reducing the symmetry down to C_{2v}. In the I_A spectrum (Fig. 8) five or six peaks can be distinguished which at this energy must belong to a total of five origins due to the $E_g,T_{2g}(5–9)$ level set. Since in O_h symmetry these energy levels differ by only 90–100 cm^{-1} [3–6], the peak at 5350 cm^{-1} which lies somewhat apart from the others, may be assigned to a vibrational side band belonging to level (9) localized at 5175 cm^{-1}. For comparison, there are the modes $\nu_5 = 166(a_1)$, $\nu_9 = 157(b_1)$ and $\nu_{13} = 180(b_2)$ cm^{-1} measured in the far IR spectrum [17] which agree well with the energy interval of 175 cm^{-1} obtained from two peaks in the absorption spectrum. Since the transition $A_1 \rightarrow A_2$ is electric dipole forbidden (cf. Table 1), one of the five zero-phonon transitions should give rise to a smaller intensity. As there are, however, three smaller absorptions aside from the two stronger peaks, a level assignment to symmetry types cannot be obtained.

The II'_E emission spectrum has a strong band at 6810 and two smaller peaks at 7040 and 6640 cm^{-1}. While the two features at higher energy may be assigned to zero-phonon transitions into levels (2) and (3) of T_{1g}, the low frequency peak can be either due to the third zero-phonon transition (4) of T_{1g} or to a vibrational side band belonging to the origin of (3). The actual energies of C_{2v} levels which would be calculated by subtraction from the lowest peak of II_A cannot be obtained due to the poor resolution of the Cs salt spectrum. Table 5 compiles the data obtained for the level energies of *mer*-$[OsCl_3I_3]^{2-}$ which result from the discussion above. An assignment to symmetry types on the basis of intensity relations is not feasible.

Conclusions

Comparing intraconfigurational absorption and emission spectra conveniently allows the determination of the energies of low-lying d-electron levels. For a distinction of zero-phonon transitions from vibrational side bands, it is useful to know the vibrational quanta and symmetries from normal coordinate analyses. Band assignments to symmetry types of low symmetry point groups should start from corresponding results on octahedral systems and use relative peak intensities for distinguishing transitions between levels split by low symmetry fields.

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References

1 D. Strand, R. Linder and H.-H. Schmidtke, Mol. *Phys.,* 71 (1990) 1075.

2 S. M. Khan, H. H. Patterson and H. Engstrom, Mol. *Phys.,* 35 (1978) 1623.

3 C. D. Flint and A. G. Paulusz, *Mol. Phys., 41* (1980) 907.

4 B. A. Kozikowski and T. A. Keiderling, *Mol. Phys.,* 40 (1980) 477.

5 H.-H. Schmidtke and D. Strand, *Inorg. Chim. Acta,* 62 (1982) 153.

6 B. A. Kozikowski and T. A. Keiderling, *J. Phys.* Chem., 87 (1983) 4630.

7 W. Preetz, H. J. Walter and E. W. Fries, *Z. Anorg. Allg. Chem.,* 402 (1973) 180.

8 W. Preetz, A. Scheffler and H. Homborg, *Z. Anorg. Allg. Chem., 406* (1974) 92.

9 G. Barka and W. Preetz, Z. *Anorg. Allg.* Chem., 433 (1977) 147.

10 C. K. Jorgensen, W Prectz and H. Homborg, *Inorg. Chim. Acta, 5* (1971) 223.

11 S. P. Piepho, W. H. Inskeep, P. N. Schatz, W. Preetz and H. Homborg, Mol. *Phys., 30* (1975) 1569.

12 P. A. Dorain, H. H. Patterson and P. C. Jordan, *J. Chem. Phys.,* 49 (1968) 3845.

13 G. C. Allen, R. Al-Mobarak, G. A. M. El-Sharkawy and K. D. Warren, *Inorg. Chem., II* (1972) 787.

14 W. H. Inskcep, R. W. Schwartz and P. N. Schatz, *Mol. Phys., 25* (1973) 805.

15 T. Schonherr, R. Wernicke and H.-H. Schmidtke, *Spectrochim. Acta, Part A, 38* (1982) 679.

16 H.-H. Schmidtkc, C. Grzonka and T. Schonherr, *Spectrochim. Acta, Part A, 45 (1989)* 129.

17 C. Grzonka, *Diploma Thesis.* University of Düsseldorf, 1987.

18 C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes,* Pergamon, Oxford, 1962.

19 C. E. Schäffer and C. K. Jdrgensen, *Kgl. Danske Videnskab. Selskab. Mad. Fys. Medd., 34 (1965) No. 13.*