Luminescence Spectra of the Mixed Chloro-Bromo-Osmates(IV), $[OsCl_nBr_{6-n}]^{2-}$, $n = 1-5$

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The $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ luminescence spectra of mixed $Cs_2[OsCl_nBr_{6-n}]$, $n = 1-5$, have been measured between 15800 and 17000 cm^{-1} at 10 K. As a host lattice $Cs_2[TeCl_6]$ has been doped with purely isolated chloro-bromo-osmates(IV), including the geometrical isomers with $n = 2, 3, 4$. The assignments of the electronic transitions and their extensive vibronic structure are discussed.

Introduction

The luminescence intra-sub-shell transitions of the homoleptic complexes $[OsCl_6]^{2-}$ and $[OsBr_6]^{2-}$ [1] as well as of the heteroleptic species $[OsCl_5Br]^{2-}$ and cis-$[OsCl_4Br_2]^{2-}$ [2] have been studied in some detail. Only one paper reports on absorption and electronic Raman spectra of all mixed solid tetrabutylammonium salts $(TBA)_2[OsCl_nBr_{6-n}]$ [3]. The t_{2g}^4 configuration of Os(IV) in an octahedral field gives rise to the states $^3T_{1g}$, $^1T_{2g}$, ^1E_g, and $^1A_{1g}$ in order of increasing energy [1, 2]. The generated levels are split due to spin orbit coupling and lowered symmetry, observed as multiplets in the NIR regions 2600–3100, 4800–5400, 10500–11400, and 16000–17200 cm^{-1} [3].

The present work shows the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ transitions and their vibronic structure. They are observed in the region 16000–17200 cm^{-1} in electronic absorption and between 15800–17000 cm^{-1} in the luminescence spectra. The eight chloro-bromo-osmates(IV), $[OsCl_nBr_{6-n}]^{2-}$, $n = 1-5$, including the pairs of pure geometric isomers with $n = 2, 3, 4$ have been measured in $Cs_2[TeCl_6]$ as the host lattice at low temperature (10 K). The assignment of the distinct vibronic features is supported by the vibrational spectra and normal coordinate analysis [4].

Experimental

The chloro-bromo-osmates(IV) have been prepared and separated as previously described [4]. The samples of matrices, containing definite Os(IV) complexes, are prepared by treating a large excess (100–300 times) of $H_2[TeCl_6]$ in concentrated aqueous HCl with a very small amount of the particular Os(IV) species and precipitating homogenous crystalline solids by adding an excess of CsCl in aqueous HCl. By low temperature the ligand exchange against solvent molecules is minimized, but some times it is not possible to prevent it completely.

Luminescence spectra were measured at 10 K with a Jobin Yvon Raman spectrometer at various wavelengths of an argon-ion laser. Calibration was achieved by a neon lamp, which guarantees a wavenumber precision of 1 cm^{-1}. The samples are spread as a film on a smooth surface of a steel disk that is fixed in a closed-cycle helium cryocooler.

Results and Discussion

The measurement of well resolved $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ luminescence spectra of all chloro-bromo-osmates(IV)

Table 1. Symmetry and electronic origins $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ of $Cs_2[OsCl_nBr_{6-n}]$, $n = 0-6$, a = cis/fac, b = trans/mer, doped in $Cs_2[TeCl_6]$. In parenthesis: assignments from electronic absorption spectra [3].

n	Symmetry	$\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$	
6	O_h	16955 [8]	(17030)
5	C_{4v}	16816	(16860)
4a	C_{2v}	16608	(16695)
4b	D_{4h}	16653	(16750)
3a	C_{3v}	16412	(16445)
3b	C_{2v}	16445	(16585)
2a	C_{2v}	16263	(16340)
2b	D_{4h}	16382	(16400)
1	C_{4v}	16116	(16210)
0	O_h	16018 [8]	(16000)

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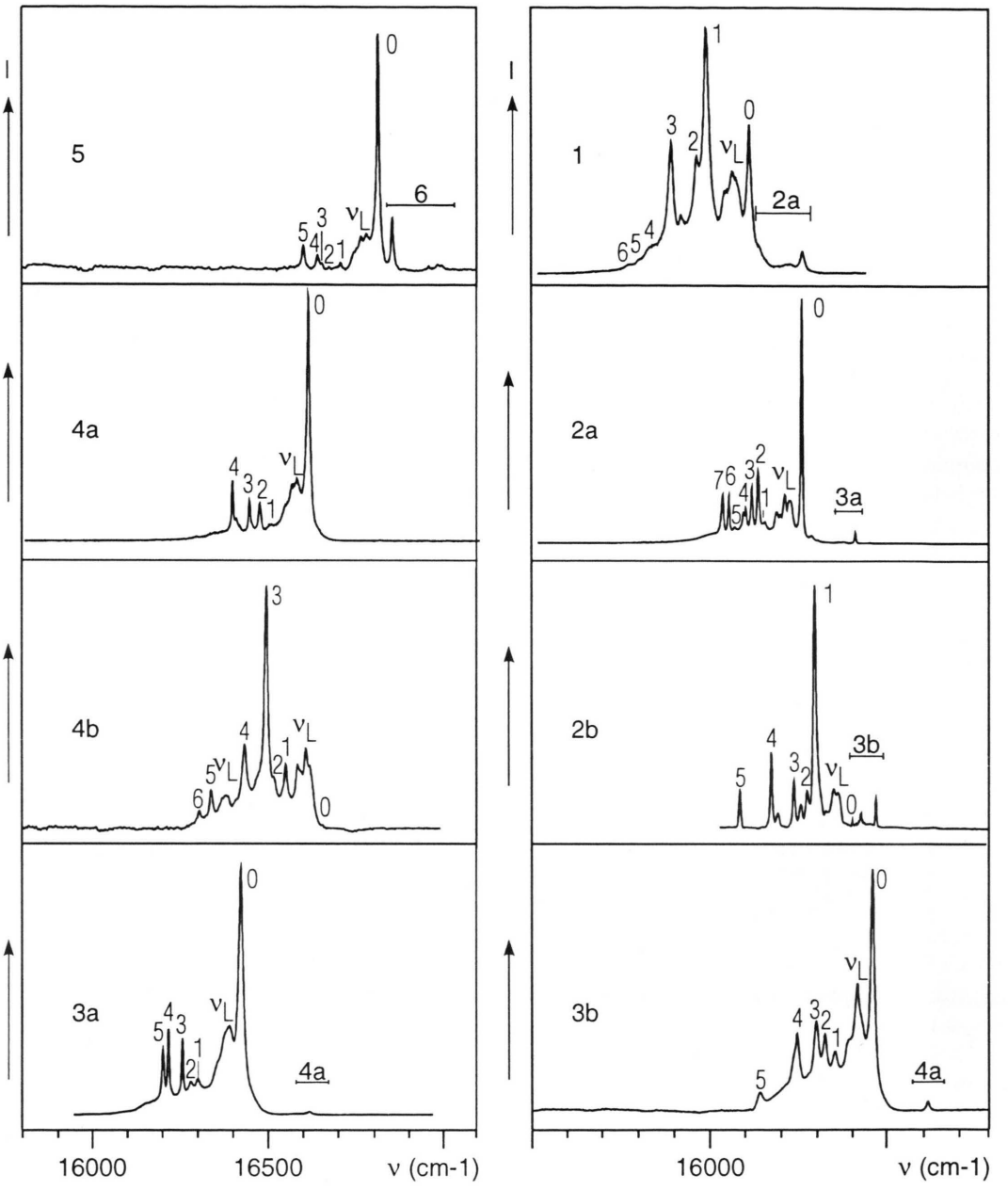

Fig. 1. $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ luminescence spectra of $Cs_2[OsCl_nBr_{6-n}]$, $n = 1-5$, in the host lattice $Cs_2[TeCl_6]$ at 10 K, $\lambda_0 = 488$ nm. For assignments see Tables 1 and 2.

Figure 1) requires the host lattice $Cs_2[TeCl_6]$ and low temperature. An increase of sample temperature during excitation must be strictly avoided because the population of the stimulated vibronic states produces broader emission lines [6]. The electronic origins of the different $[OsCl_nBr_{6-n}]^{2-}$ shift to higher wavenumbers with increasing n. In addition to this nephelauxetic effect, a luminescence shift due to the host material is observed if the 0-0-transitions are compared to the data resolved from electronic absorption spectra [3, 7], Table 1. The decisive factor for the intensities depends on the point group symmetry of the different complex

Table 2. Assignment of the luminescence bands in Figure 1. In parenthesis: vibrational frequencies of pure $(TBA)_2[OsCl_nBr_{6-n}]$*, $n = 1-5$, [4] or of the host lattice [5].

No.	$\bar{\nu}$ [cm^{-1}]	Δ cm^{-1}	Assignment
D_{4h}, trans-$Cs_2[OsCl_4Br_2]/Cs_2[ReCl_6]$, 4b			
0	16653	0	Origin (not obs.)
1	16547	106 (97)	$+\nu_{11}, E_u$
2	16511	142 (134)	$+\nu_4, A_{2u}$
3	16493	160 (157)	$+\nu_{10}, E_u$
4	16430	223 (217)	$+\nu_3, A_{2u}$
5	16336	317 (307)	$+\nu_9, E_u$
6	16303	350 (157+186)	$+\nu_{10}+\nu_2, A_{1g}$
D_{4h}, trans-$Cs_2[OsCl_2Br_4]/Cs_2[TeCl_6]$, 2b			
0	16382	0	Origin (not obs.)
1	16282	100 (98)	$+\nu_{10}, E_u$
2	16261	121 (125)	$+\nu_6$ (host), T_{2u} [5]
3	16224	158 (141)	$+\nu_{11}, E_u$
4	16161	221 (216)	$+\nu_9, E_u$
5	16074	308 (306)	$+\nu_3, A_{2u}$
C_{4v}, $Cs_2[OsCl_5Br]/Cs_2[TeCl_6]$, 5			
0	16816	0	Origin
1	16708	108 (106)	$+\nu_{11}, E$
2	16678	138 (138)	$+\nu_9, E$
3	16656	160 (160)	$+\nu_{10}, E$
4	16645	171 (166)	$+\nu_7, B_2$
5	16603	213 (205)	$+\nu_3, A_1$
C_{4v}, $Cs_2[OsClBr_5]/Cs_2[TeCl_6]$, 1			
0	16116	0	Origin
1	15994	122 (117)	$+\nu_7, B_2$
2	15967	149 (144)	$+\nu_{11}, E$
3	15924	192 (188)	$+\nu_1, A_1$
4	15897	219 (217)	$+\nu_2, A_1/+\nu_8, E$
5	15812	304 (307)	$+\nu_3, A_1$
6	15786	330 (217+106)	$+\nu_2+\nu_4, A_1/+\nu_8+\nu_4$
C_{3v}, fac-$Cs_2[OsCl_3Br_3]/Cs_2[TeCl_6]$, 3a			
0	16412	0	Origin
1	16291	121 (118)	$+\nu_5, A_2$
2	16271	141 (133)	$+\nu_{10}, E$
3	16248	164 (163)	$+\nu_3, A_1/+\nu_8, E$
4	16207	205 (198)	$+\nu_7, E$
5	16190	222 (219)	$+\nu_2, A_1$
C_{2v}, mer-$Cs_2[OsCl_3Br_3]/Cs_2[TeCl_6]$, 3b			
0	16455	0	Origin
1	16347	108 (105)	$+\nu_{14}, B_2$
2	16321	134 (132)	$+\nu_{13}, B_2$
3	16297	158 (156)	$+\nu_{11}, B_1$
4	16243	212 (210)	$+\nu_4, A_1$
5	16138	317 (210+105)	$+\nu_4+\nu_{14}$
C_{2v}, cis-$Cs_2[OsCl_4Br_2]/Cs_2[TeCl_6]$, 4a			
0	16608	0	Origin
1	16501	107 (99)	$+\nu_6, A_1/+\nu_{15}, B_2$
2	16469	139 (139)	$+\nu_5$ (host), T_{2g} [5]
3	16440	168 (160)	$+\nu_7, A_2$
4	16392	216 (210)	$+\nu_3, A_1$

Table 2. (Continued).

No.	$\bar{\nu}$ [cm^{-1}]	Δ cm^{-1}	Assignment
C_{2v}, cis-$Cs_2[OsCl_2Br_4]/Cs_2[TeCl_6]$, 2a			
0	16263	0	Origin
1	16161	102 (94)	$+\nu_7, A_2$
2	16141	122 (119)	$+\nu_{15}, B_2$
3	16124	139 (138)	$+\nu_{11}, B_1$
4	16107	156 (159)	$+\nu_6, A_1$
5	16076	187 (180)	$+\nu_1, A_1$
6	16060	203 (196)	$+\nu_{12}, B_2$
7	16043	220 (217)	$+\nu_9, B_1$

* The influence of different cations, $(TBA)^+$ and Cs^+, has to be noted.

ions. In centro-symmetric species the magnetic dipol-allowed electronic origins are very weak ($\sim 1/100-1/1000$) compared with the electronic dipol-allowed zero-phenon transitions of compounds without center of inversion.

The $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ luminescence exhibits for all species of the series $[OsCl_nBr_{6-n}]^{2-}$ a distinct vibronic structure, Fig. 1, Table 2. Whereas the main quantum yield of low-symmetry complexes, except of $[OsClBr_5]^{2-}$, is accumulated in the zero-phonon transition, in centrosymmetric species Laporte's rule forces weak electronic origins. This restriction is ruled out by coupling with normal vibrations of odd parity (A_{2u}, E_u). The progression with such modes enables the calculation of the not observed origins for trans-$[OsCl_4Br_2]^{2-}$ and trans-$[OsCl_2Br_4]^{2-}$, Table 2. For the species without center of inversion dominant 0-0-luminescence is observed due to the loss of parity, similar to the mixed chloro-bromo-complexes of technetium(IV) [9]. In some cases the spectra reveal that it was not possible to avoid ligand exchange during preparation of the samples. For example 2b contains small amounts of 3b, and 1 is contaminated with traces of 3a, Figure 1. Guest species as well as the host material participate in vibronic coupling when a resonance between vibronic origins of the two compounds takes place [7]. Very weak emissions in a short interval ($30-70$ cm^{-1}) to both electronic and main vibronic origins correlate with lattice vibrations ν_L and vibron-phonon modes [1].

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