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

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The $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ luminescence spectra of mixed $Cs_2[TcCl_nBr_{6-n}]$, $n=1-5$, in various host crystals have been measured between 14 000 and 12 800 cm^{-1} at 10 K. For the first time host lattices have been doped with purely isolated chloro-bromo-technetates(IV), including the geometrical isomers with $n=2$, 3, 4. The assignments of the electronic transitions and their extensive vibronic structure are discussed.

Introduction

Whereas the intra-sub-shell transitions of $[TcCl_6]^{2-}$ and $[TcBr_6]^{2-}$ have been studied in some detail [1–5], only one paper reports on mixed complexes, concerning luminescence spectra of non-defined mixtures, which contain several species of $[TcCl_nBr_{6-n}]^{2-}$ in cubic host crystals of $Cs_2[SnCl_6]$ [6]. The t_{2g}^3 configuration of Tc(IV) in an octahedral crystal field gives rise to the states $^4A_{2g}$, ^2E_g, $^2T_{1g}$ and $^2T_{2g}$ in order of increasing energy. Due to spin-orbit coupling the T levels split into the double-group O_h^*, generating the components Γ_8, $\Gamma_6(^2T_{1g})$ and Γ_7, $\Gamma_8(^2T_{2g})$ [3]. The present work shows the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ luminescence spectra of the eight chloro-bromo-technetates(IV), $[TcCl_nBr_{6-n}]^{2-}$, $n=1-5$, including the pairs of pure geometrical isomers with $n=2$, 3, 4, measured in different host lattices at low temperature (10 K). The assignment of the destinct vibronic features is supported by the vibrational spectra and normal coordinate analysis [7].

Experimental

The chloro-bromo-technetates(IV) are prepared and separated as previously described [7]. The samples of matrices, containing definite Tc(IV) complexes, were prepared by treating a large excess (100–300 times) of $H_2[MX_6]$; (M = Sn, Te; X = Cl, Br) in concentrated aqueous HX with a very small amount of the particular Tc(IV) species and precipitating homogeneous crystalline solids by adding an excess of CsX in aqueous HX (X = Cl, Br). Low temperatures prevent substitution reactions of the sample with solvent molecules.

Luminescence spectra were measured at 10 K with a Jobin Yvon Raman spectrometer and various wavelengths of an argon-ion laser. Calibration was achieved by a neon lamp, which guarantees a wavenumber precision of 0.5 cm^{-1}. The samples are spread as a film on the smooth surface of a steel disk that is fixed in a closed-cycle helium cryocooler.

Results and Discussion

Well resolved $^2T_{2g} \rightarrow {}^4A_{2g}$ luminescence spectra of all chloro-bromo-technetates(IV) (Fig. 1) require different host lattices and low temperatures. An increase of sample temperature during excitation must be

Table 1. Symmetry and electronic origins $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ of $Cs_2[TcCl_nBr_{6-n}]$, $n=1-5$, a = cis/fac, b = trans/mer, doped in various host lattices M. In parenthesis: former assignment from [6].

n	Symmetry	M	$\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$
5	C_{4v}	$Cs_2[SnBr_6]$	13 898 (13 724)
4a	C_{2v}	$Cs_2[SnCl_6]$	13 725 (13 607)
4b	D_{4h}	$Cs_2[TeCl_6]$	13 671 (not observed)
3a	C_{3v}	$Cs_2[SnCl_6]$	13 607 (not observed)
3b	C_{2v}	$Cs_2[SnCl_6]$	13 582 (13 582)
2a	C_{2v}	$Cs_2[SnCl_6]$	13 478 (13 476)
2b	D_{4h}	$Cs_2[SnBr_6]$	13 492 (not observed)
1	C_{4v}	$Cs_2[SnCl_6]$	13 357 (13 354)

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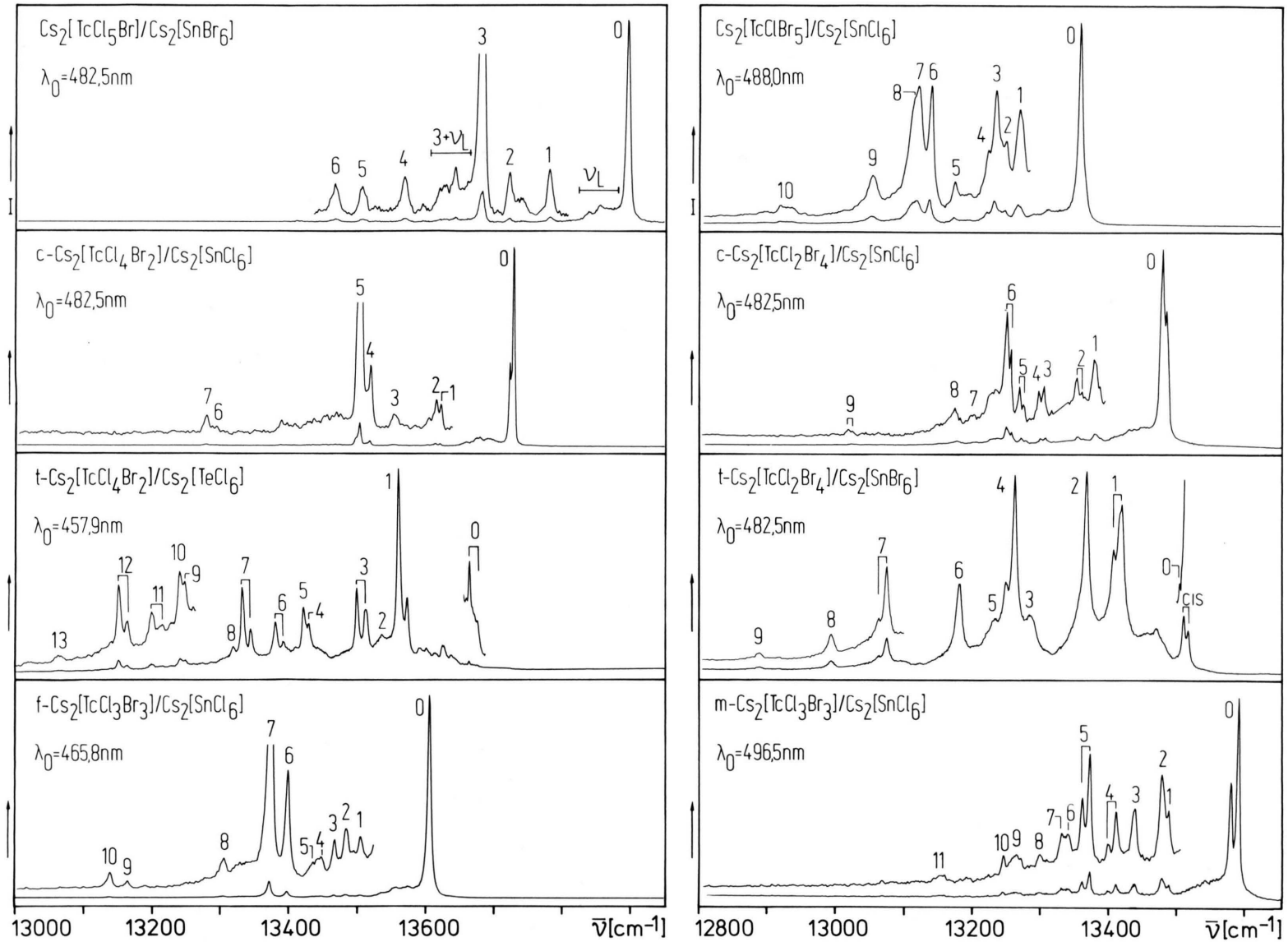

Fig. 1. $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ luminescence spectra of $Cs_2[TcCl_nBr_{6-n}]$, $n=1-5$, in various host lattices at 10 K.

Table 2. Ground-state splittings ($^4A_{2g}$) [cm^{-1}] of $Cs_2[TcCl_nBr_{6-n}]$, $n=1-5$, a = cis/fac, b = trans/mer.

n	1	2a	2b	3a	3b	4a	4b	5
[cm^{-1}]	<2	6	12	<2	11	6	12	<2

Table 3. Assignment of the luminescence bands in Figure 1. In parenthesis: vibrational frequencies of pure $(TBA)_2[TcCl_nBr_{6-n}]$* [7] or host lattices [16–18].

No.	$\bar{\nu}$ [cm^{-1}]	Δ [cm^{-1}]	Assignment
D_{4h}, trans-$Cs_2[TcCl_4Br_2]/Cs_2[TeCl_6]$			
0	13 677/13 665	0	Origin
1	13 575/13 563	102 (91)	ν_{11}, E_u
2	13 537	128 (125)	ν_6, host
3	13 514/13 501	164 (144)	ν_{10}, E_u
4	13 430	235 (91+138)	$\nu_{11}+\nu_8, E_g$
5	13 423	242 (243)	ν_3, A_{2u}
6	13 393/13 381	284 (91+174)	$\nu_{11}+\nu_2, A_{1g}$
7	13 345/13 333	332 (320)	ν_9, E_u
8	13 320	345 (144+174)	$\nu_{10}+\nu_2$
9	13 250	415 (229+174)	$\nu_{11}+\nu_8+\nu_2$
10	13 243	422 (243+174)	$\nu_3+\nu_2$
11	13 212/13 200	464 (91+348)	$\nu_{11}+2\nu_2$
12	13 164/13 153	512 (320+174)	$\nu_9+\nu_2$
13	13 064	607 (439+138)	$\nu_{11}+2\nu_2+\nu_8$
D_{4h}, trans-$Cs_2[TcCl_2Br_4]/Cs_2[SnBr_6]$			
0	13 498	0	Origin
1	13 415/13 404	94 (91)	ν_{10}, E_u
2	13 364	145 (124)	ν_{11}, E_u
3	13 278	226 (222)	ν_3, host
4	13 258/13 246	252 (242)	ν_9, E_u
5	13 229/13 217	281 (91+187)	$\nu_{10}+\nu_1, A_{1g}$
6	13 178	331 (124+187)	$\nu_{11}+\nu_1$
7	13 070/13 059	439 (242+187)	$\nu_9+\nu_1$
8	12 989	515 (124+374)	$\nu_{11}+2\nu_1$
9	12 883	625 (242+374)	$\nu_9+2\nu_1$
C_{4v}, $Cs_2[TcCl_5Br]/Cs_2[SnBr_6]$			
0	13 898	0	Origin
1	13 784	114 (112)	ν_{11}, E
2	13 724	174 (161)	ν_{10}, E
3	13 683	215 (210)	ν_3, A_1
4	13 570	328 (323)	ν_1, A_1
5	13 508	390 (161+210)	$\nu_{10}+\nu_3$
6	13 470	428 (2×210)	$2\nu_3$
C_{4v}, $Cs_2[TcClBr_5]/Cs_2[SnCl_6]$			
0	13 357	0	Origin
1	13 265	92 (91)	ν_{11}, E
2	13 246	111 (105)	ν_9, E
3	13 230	127 (112)	ν_4, A_1
4	13 219	138 (136)	ν_{10}, E
5	13 170	187 (181)	ν_1, A_1
6	13 135	222 (218)	ν_2, A_1
7	13 116	241 (242)	ν_8, E
8	13 110	247 (243)	ν_2, host
9	13 049	308 (310)	ν_3, A_1
10	12 915	442 (2×218)	$2\nu_2$
C_{3v}, fac-$Cs_2[TcCl_3Br_3]/Cs_2[SnCl_6]$			
0	13 607	0	Origin
1	13 506	101 (88)	ν_9, E
2	13 484	123 (108)	ν_4, A_1
3	13 467	140 (130)	ν_{10}, E
4	13 444	163 (157	ν_8, E
5	13 437	170 (168)	ν_5, host
6	13 399	208 (202)	ν_7, E
7	13 373	234 (229)	ν_2, A_1
8	13 303	304 (299)	ν_6, E
9	13 164	443 (202+229)	$\nu_7+\nu_2$
10	13 138	469 (2×229)	$2\nu_2$
C_{2v}, mer-$Cs_2[TcCl_3Br_3]/Cs_2[SnCl_6]$			
0	13 587/13 576	0	Origin
1	13 485	102 (92)	ν_6, A_1
2	13 475	107 (107)	ν_6, host
3	13 436	151 (135)	ν_5, A_1
4	13 407/13 396	180 (170)	ν_3, A_1
5	13 369/13 358	218 (212)	ν_4, A_1
6	13 337	250 (92+135)	$\nu_6+\nu_5$
7	13 326	259 (107+135)	ν_6, host $+\nu_5$
8	13 293	294 (289)	ν_2, A_1
9	13 258	324 (107+212)	ν_6, host $+\nu_4$
10	13 241	346 (2×170)	$2\nu_3$
11	13 149	433 (2×212)	$2\nu_4$
C_{2v}, cis-$Cs_2[TcCl_4Br_2]/Cs_2[SnCl_6]$			
0	13 728/13 722	0	Origin
1	13 620	105 (107)	ν_6, host
2	13 615	113 (104)	ν_6, A_1
3	13 553	172 (172)	ν_4, host
4	13 517	211 (202)	ν_{13}, B_2
5	13 502	226 (218)	ν_3, A_1
6	13 290	438 (202+218)	$\nu_{13}+\nu_3$
7	13 277	451 (2×218)	$2\nu_3$
C_{2v}, cis-$Cs_2[TcCl_2Br_4]/Cs_2[SnCl_6]$			
0	13 481/13 475	0	Origin
1	13 383/13 377	98 (87)	ν_4, A_1
2	13 357/13 351	124 (110)	ν_5, A_1
3	13 303	175 (172)	ν_4, host
4	13 296	179 (170)	ν_1, A_1
5	13 273/13 267	208 (201)	ν_{12}, B_2
6	13 252/13 245	229 (225)	ν_2, A_1
7	13 199	279 (170+87)	$\nu_1+\nu_4$
8	13 167	311 (309)	ν_3, host
9	13 023/13 017	458 (2×225)	$2\nu_2$

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

strictly avoided because the population of stimulated vibronic states produces broader emission lines [8]. Due to the weak spin-orbit coupling of Tc(IV), only from the Γ_7 level a phosphorescence transition arises, in contrast to similar complexes of Re(IV) [9]. The electronic origins of the different $[TcCl_nBr_{6-n}]^{2-}$ shift to higher wavenumbers with increasing n, Table 1. In addition to this nephelauxetic effect, a luminescence shift by different host materials is observed [10, 11]. In some cases this matrix influence is stronger than the zero-phonon energy difference of stereoisomers, i.e. cis- and trans-$[TcCl_2Br_4]^{2-}$ (Figure 1).

According to the point-group symmetries of the complex ions, two other factors influence the zero-phonon transitions of different species. First, in centrosymmetric complexes the magnetic dipole-allowed electronic origins are relatively weak ($\approx 1/50$) compared with the electric dipole-allowed zero-phonon transitions of the compounds without inversion symmetry. Secondly, double bands in the luminescence spectra of the mixed complexes indicate ground-state splittings due to lowered symmetries [12]. The small values of these splittings correspond to the expected weak spin-orbit coupling in Tc(IV) complexes (Table 2). Calculations [13] yield a linear dependence of the $\Gamma_8(^4A_{2g})$ ground-state splittings on the low-symmetry crystal-field parameters and verify the observed data. Whereas the splittings in cis-$[TcCl_4Br_2]^{2-}$ and cis-$[TcCl_2Br_4]^{2-}$ are the same (but of opposite sign), the splittings of trans isomers are twice as large (and of opposite sign) than in corresponding cis isomers. The photochemical and photophysical reactivity of compounds with d^3 centres [14] requires attention during the irradiation of Tc(IV) complexes. The cis-contamination in the luminescence spectrum of trans-$Cs_2[TcCl_2Br_4]$ (Fig. 1) is caused by an intramolecular photoisomerization during the preparation. Due to the stability of the solid cesium salts in the present case the spectroscopic measurements are not disturbed by photoreactions.

The presented luminescence spectra measured on pure mixed ligand complexes (Fig. 1) demonstrate the shortcomings of a previous work [6]. It is not surprising that superimposed spectra of mixtures, containing several compounds in different ratios, effect improper assignments. Particular difficulties arise from the different zero-phonon intensities of the various Tc(IV) complexes. A preferential electronic stimulation of a special compound is not possible, even if different excitation lines are used. Thus, and due to the lack of suitable host materials the weak origins of the centrosymmetric complexes 2b and 4b have not been observed. The zero-phonon transitions of 4a and 3a are mixed up with those of 5 and 4a, Table 1. Furthermore, the conclusion that there is no trans directing influence in the monosubstituted complexes of Tc(IV) [6, 15] is disproved by the preparation of pure stereoisomers in stereospecific ligand exchange reactions of $[TcBr_6]^{2-}$ with HCl and $[TcCl_6]^{2-}$ with HBr [7].

The $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ phosphorescence exhibits for all species of the series $[TcCl_nBr_{6-n}]^{2-}$ a destinct vibronic structure, Table 3. Whereas the quantum yield of the low-symmetry complexes is accumulated in the zero-phonon transitions, in centrosymmetric species Laporte's rule forces very weak electronic origins. This restriction is ruled out only by coupling with normal vibrations of odd parity (A_{2u}, E_u), Figure 1. Only these promoting modes generate triple products with the participating electronic states $^2T_{2g}$, $^4A_{2g}$ and the electric-dipole operator (A_{2u}, E_u), which contain A_{1g}. The promoting-mode origins are accompanied by two progressions to lower energy, built with A_{1g} and E_g vibrations. For the non-centrosymmetric species a dominant 0–0-luminescence is observed due to the loss of parity. The vibronic patterns appear weak, but conspiciously in all cases the most intense band stems from a coupling with the Tc–Br stretching mode of non-symmetric Cl–Tc–Br axes [7]. Guest species as well as the host material participate in vibronic coupling when a resonance between vibronic origins of the two compounds takes place [11]. Very weak emissions in a short interval (30–70 cm^{-1}) to both electronic and main vibronic origins (i.e. $Cs_2[TcCl_5Br]/Cs_2[SnBr_6]$, Fig. 1) correlate with lattice vibrations ν_L and vibron-phonon modes [3, 4].

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[1] Chr. K. Jørgensen and K. Schwochau, Z. Naturforsch. **20a,** 65 (1965).
[2] H. J. Schenk and K. Schwochau, Z. Naturforsch. **28a,** 89 (1973).
[3] C. D. Flint and P. Lang, J. Lumin. **24/25,** 301 (1981).
[4] C. D. Flint and P. F. Lang, J. Chem. Soc. Faraday Trans. II, **82,** 465 (1986).
[5] E. N. Vasil'ev and A. V. Karyakin, Zh. Anal. Khim. **41,** 818 (1986).
[6] C. D. Flint and P. F. Lang, J. Chem. Soc. Dalton Trans. **1986,** 921.
[7] W. Preetz and A. Wendt, Z. Naturforsch. **46b,** 1496 (1991).
[8] J. Degen, H. Kupka, and H.-H. Schmidtke, Chem. Phys. **117,** 165 (1987).
[9] H. H. Patterson, J. L. Nims, and C. M. Valencia, J. Mol. Spectrosc. **42,** 567 (1972).
[10] A. M. Black and C. D. Flint, J. Chem. Soc. Faraday Trans. II, **1977,** 877.
[11] R. Wernicke and H.-H. Schmidtke, Mol. Phys. **37,** 607 (1979).
[12] M. Bettinelli, L. di Sipio, G. Ingletto, A. Montenero, and C. D. Flint, Mol. Phys. **56,** 1033 (1985).
[13] R. M. MacFarlane, J. Chem. Phys. **47,** 2066 (1967).
[14] A. W. Adamson, J. Phys. Chem. **71,** 798 (1967).
[15] C. D. Flint and P. F. Lang, J. Chem. Soc. Dalton Trans. **1987,** 1929.
[16] M. Debeau and H. Poulet, Spectrochim. Acta **25A,** 1553 (1969).
[17] D. M. Adams and D. M. Morris, J. Chem. Soc. A **1967,** 2067.
[18] H. Poulet, C. Belgodere, and M. Debeau, C. R. Acad. Sci. Paris **B 267,** 290 (1968).