Luminescence Spectra of the Mixed Complexes $[TcCl_xBr_{6-x}]^{2-}$

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Reaction of $[TcCl_6]^{2-}$ with aqueous HBr followed by rapid precipitation of $Cs_2[SnCl_6]$ from the solution produces homogeneous crystalline solids which luminesce strongly under blue or ultraviolet excitation. Analysis of the spectra obtained at low temperatures with selective excitation shows the presence of nine of the ten expected stereoisomers of $[TcCl_xBr_{6-x}]^{2-}$ (x = 0—6). Similar results may be obtained by starting with $[TcBr_6]^{2-}$ in aqueous HCl. There is no evidence for the dominance of a *trans* effect in the substitution reaction.

Very little information is available concerning the formation and spectroscopic properties of mixed halogeno complexes of metal ions. Preparative procedures generally produce mixtures of several complexes which are not easily separated and the electronic absorption spectra of these mixtures are too complex for reliable analysis. Many hexahalogeno complexes of the heavier transition-metal ions luminesce strongly under blue or u.v. excitation at low temperatures to give spectra that are well resolved. Since the absorption spectra of these compounds are also well resolved, it seemed probable that the individual complexes in a mixture could be studied by measuring the highly resolved luminescence spectra under conditions where some of the complex ions are more strongly excited than others. In this paper we report a study of the mixed technetium complexes $[TcCl_xBr_{6-x}]^{2-}$.

The absorption spectrum of the $[TcCl_6]^{2-}$ ion has not been studied in detail. By analogy with the $[ReCl_6]^{2-}$ ion,[1] charge-transfer transitions are expected to dominate the high-energy region of the absorption spectra. We have shown that under u.v. excitation $[TcCl_6]^{2-}$ luminesces strongly due to the $\Gamma_7(^2T_{2g}) \longrightarrow \Gamma_8(^4A_{2g})$ transition. This ion however is almost transparent to 457-nm radiation and is therefore only very weakly excited by this wavelength. By contrast the $[TcBr_6]^{2-}$ ion is strongly excited by 514-nm and shorter-wavelength radiation due to the lower optical electronegativity of the bromide ion. It seemed possible therefore that there would be a progressive shift of the electronic absorption bands of the $[TcCl_xBr_{6-x}]^{2-}$ ion to shorter wavelength as x is changed from 0 to 6. We have also shown that the luminescence of the $[TcBr_6]^{2-}$ ion occurs some 700 cm^{-1} to low energy of that of the chloride complex and that both spectra are sufficiently well resolved for shifts of a few wavenumbers to be detected.[2] The shift of the electronic origin in the luminescence spectrum is caused by the slightly greater nephelauxetic effect of the bromide ligand. We anticipated that there would be a progressive shift in the position of the luminescence electronic origins as chloride was replaced by bromide. Ideally the selective excitation experiments should be performed using a dye laser, but in this work we found that an adequate differentiation of the complexes may be achieved using the various lines available from an argon-ion laser.

Experimental

The salts $Cs_2[TcCl_6]$ and $Cs_2[TcBr_6]$ were prepared as previously described.[2] A series of samples of $Cs_2[SnCl_6]$ containing the $[TcCl_xBr_{6-x}]^{2-}$ complexes were prepared by treating $Cs_2[TcCl_6]$ with a small quantity of concentrated aqueous HBr, adding the mixture to a large excess of $SnCl_4$ in aqueous HCl, and precipitating $Cs_2[SnCl_6]$ by adding excess of CsCl in aqueous HCl. A second series of samples were prepared similarly starting from $Cs_2[TcBr_6]$ in aqueous HCl. Preliminary spectral measurements showed that the first series contained significant amounts of the mixed complexes if the reaction was allowed to proceed for a few minutes at room temperature. The second series required reaction times of 1 d to 1 week. In no case was equilibrium reached.

Luminescence spectra were measured as previously described.[3]

Results

The ten possible species of the type $[TcCl_xBr_{6-x}]^{2-}$ (x = 0—6) together with their point-group symmetries are listed in Table 1. In addition to the progressive shift in the position of the electronic origin with x noted above, two other factors may be used to identify the particular species. First we expect that in centrosymmetric complexes the magnetic dipole-allowed electronic origins will be relatively weak compared with the vibronic structure as is observed for the compounds with $x = 0$ or 6. In non-centrosymmetric compounds the electronic origins become electric dipole-allowed and are likely to be approximately one order of magnitude more intense than the vibronic bands. Secondly we expect to resolve splittings of the ground state in the low-symmetry complexes. No information is available on the likely magnitude of these splittings in technetium(IV) compounds, but we note that the ground-state splitting is of the order of 100 cm^{-1} in $[ReF_6]^{2-}$ in non-cubic crystals[4] and this splitting is proportional to the square of the spin-orbit coupling constant. Splittings of some tens of wavenumbers might then be expected for the mixed complexes which would be easily resolved at low temperatures. Furthermore crystal-field arguments enable the relative magnitude of the low-symmetry splittings to be estimated. If the low-symmetry perturbation of the octahedral field is expanded in

Table 1. Symmetry and position of the luminescence electronic origins in mixed $[TcCl_xBr_{6-x}]^{2-}$ complex ions

Complex ion	Symmetry	$^2T_{2g} \longrightarrow {}^4A_{2g}$ origin in $Cs_2[SnCl_6]$ (cm^{-1})
$[TcCl_6]^{2-}$	O_h	14 027
$[TcCl_5Br]^{2-}$	C_{4v}	13 724
cis-$[TcCl_4Br_2]^{2-}$	C_{2v}	13 607
trans-$[TcCl_4Br_2]^{2-}$	D_{4h}	Not observed
mer-$[TcCl_3Br_3]^{2-}$	C_{3v}	13 588, 13 577
fac-$[TcCl_3Br_3]^{2-}$	C_{2v}	Not observed
cis-$[TcCl_2Br_4]^{2-}$	C_{2v}	13 479, 13 472
trans-$[TcCl_2Br_4]^{2-}$	D_{4h}	Not observed
$[TcClBr_5]^{2-}$	C_{4v}	13 354
$[TcBr_6]^{2-}$	O_h	13 249

Table 2. Assignment of the bands in Figure 1 and 2

Band	Wavenumber/cm^{-1}	Species	Comment	Band	Wavenumber/cm^{-1}	Species	Comment
1	13 851	$[TcCl_6]^{2-}$	ν_6, ν_4 unresolved	15	13 307	*trans*-$[TcCl_4Br_2]^{2-}$	Vibration ?
2	13 724	$[TcCl_5Br]^{2-}$	Origin	16	13 272	*trans*-$[TcCl_2Br_4]^{2-}$	Vibration ?
3	13 671	$[TcCl_6]^{2-}$	ν_3	17	13 265	*trans*-$[TcCl_2Br_4]^{2-}$	Vibration ?
4	13 607	*cis*-$[TcCl_4Br_2]^{2-}$	Origin	18	13 243	*cis*-$[TcCl_2Br_4]^{2-}$	Vibration 299 cm^{-1}
5	13 588	*mer*-$[TcCl_3Br_3]^{2-}$	Origin	19	13 230	$[TcClBr_5]^{2-}$	Vibration 134 cm^{-1}
6	13 577	*mer*-$[TcCl_3Br_3]^{2-}$	Origin	20	13 191	$[TcBr_6]^{2-}$	Vibration 58 cm^{-1}
7	13 501	$[TcCl_5Br]^{2-}$	Vibration 223 cm^{-1}	21	13 161	$[TcClBr_5]^{2-}$	Vibration 193 cm^{-1}
8	13 472	*cis*-$[TcCl_2Br_4]^{2-}$	Origin	22	13 156	$[TcBr_6]^{2-}$	ν_6
9	13 434	*mer*-$[TcCl_3Br_3]^{2-}$	Vibration 148 cm^{-1}	23	13 136	*cis*-$[TcCl_2Br_4]^{2-}$	Vibration 336 cm^{-1}
10	13 408	*mer*-$[TcCl_3Br_3]^{2-}$	Vibration 194 cm^{-1}	24	13 134	$[TcBr_6]^{2-}$	ν_4
11	13 399	$[TcCl_5Br]^{2-}$	Vibration 325 cm^{-1}	25	13 070	$[TcBr_6]^{2-}$	Host ν_3
12	13 372	*cis*-$[TcCl_4Br_2]^{2-}$	Vibration 239 cm^{-1}	26	12 999	$[TcBr_6]^{2-}$	ν_3
13	13 354	$[TcClBr_5]^{2-}$	Origin	27	12 945	$[TcBr_6]^{2-}$	$\nu_6 + \nu_1$
14	13 326	*trans*-$[TcCl_4Br_2]^{2-}$	Vibration ?	28	12 922	$[TcBr_6]^{2-}$	$\nu_4 + \nu_1$

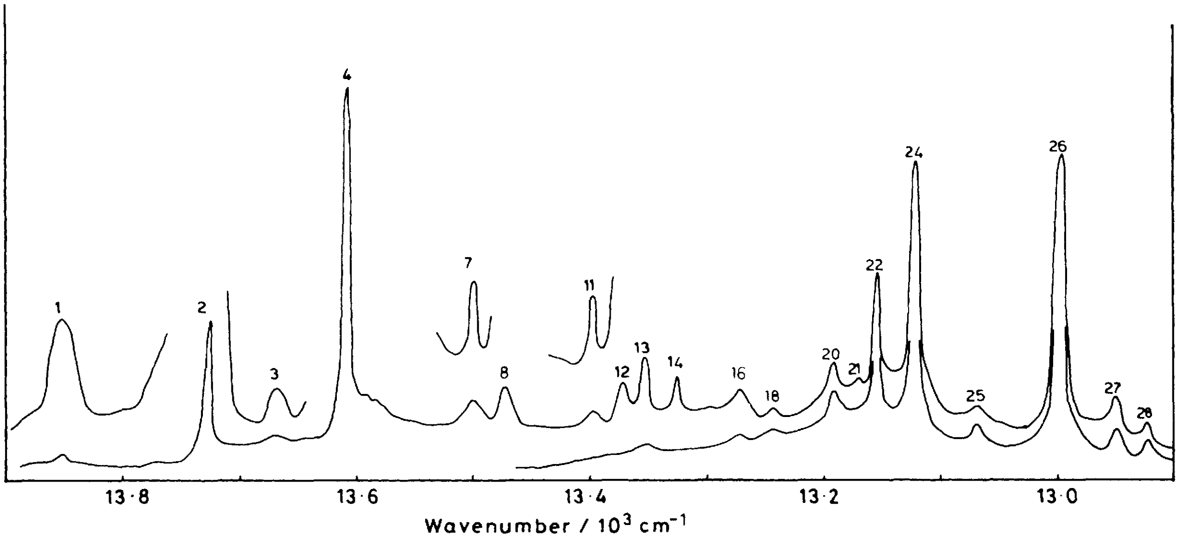

Figure 1. The 457-nm excited luminescence spectrum of $[TcCl_xBr_{6-x}]^{2-}$ in $Cs_2[SnCl_6]$ at 10 K

spherical harmonics, only the second- and fourth-order terms can contribute to the energies of states derived from a d^3 configuration.[5] The crystal field along a given axis is then equal to the arithmetic mean of the contributions due to the ligands on that axis. This gives rise to the concept of holohedrised symmetry.[6] The ground-state splitting is linearly dependent on the low-symmetry crystal-field parameters.[7] The ground-state splitting is expected to be approximately the same (but of opposite sign) in the mono- and *cis*-disubstituted species and about twice as large in *trans*-disubstituted ions. Similarly the splitting in the *fac*-trisubstituted ion will be small but that of the *mer*-trisubstituted ion will be larger than that of the *cis*-disubstituted species.

Figure 1 shows the luminescence spectrum (excited at 457 nm) of a sample prepared from $Cs_2[TcBr_6]$ by treatment with HCl for about 1 week. All the features to low wavenumber of 13 230 cm^{-1} (lines 20—28) are identical in position and relative intensity to features in the luminescence spectrum of $[TcBr_6]^{2-}$. Moreover the relative intensity of these lines is independent of the exciting wavelength. To high wavenumber of these bands a number of other quite sharp bands are observed, the relative intensity of which varies with the exciting wavelength. Two very weak bands at 13 851 and 13 671 cm^{-1} (lines 1 and 3) are of similar wavelength to those of the strongest features in the luminescence spectrum of $[TcCl_6]^{2-}$ and they are not observed with longer-wavelength exciting lines. The remaining lines are therefore probably due to the mixed compounds. Since this sample contains a large amount of unreacted $[TcBr_6]^{2-}$ their assignment will be discussed using another sample prepared by treating $[TcCl_6]^{2-}$ with HBr for a short period (Figure 2, Table 2).

In the luminescence spectrum [excited at 457 nm, Figure 2(*a*)] of this sample bands due to both the hexachloro species and the hexabromo species are weak. This however does not indicate a low concentration of the hexachloro species because this ion is only very weakly excited by that wavelength. The concentration of the hexabromo species is however low. The two most intense features in Figure 2(*a*) (lines 2 and 4) are also observed strongly with 472-nm excitation [Figure 2(*b*)] but with different relative intensities. They become progressively weaker relative to the other bands as the excitation wavelength is further increased. No other strong bands in the spectra have the same variation in intensity with excitation wavelength as these two features and they are therefore assigned as electronic origins of two distinct non-centrosymmetric mixed species. Moreover since they are at higher wavenumber than the features due to other mixed species it is probable that the species contain a small number of bromide ligands. We therefore assign these bands as the electronic origins of $[TcCl_5Br]^{2-}$ and *cis*-$[TcCl_4Br_2]^{2-}$ respectively. The ground-

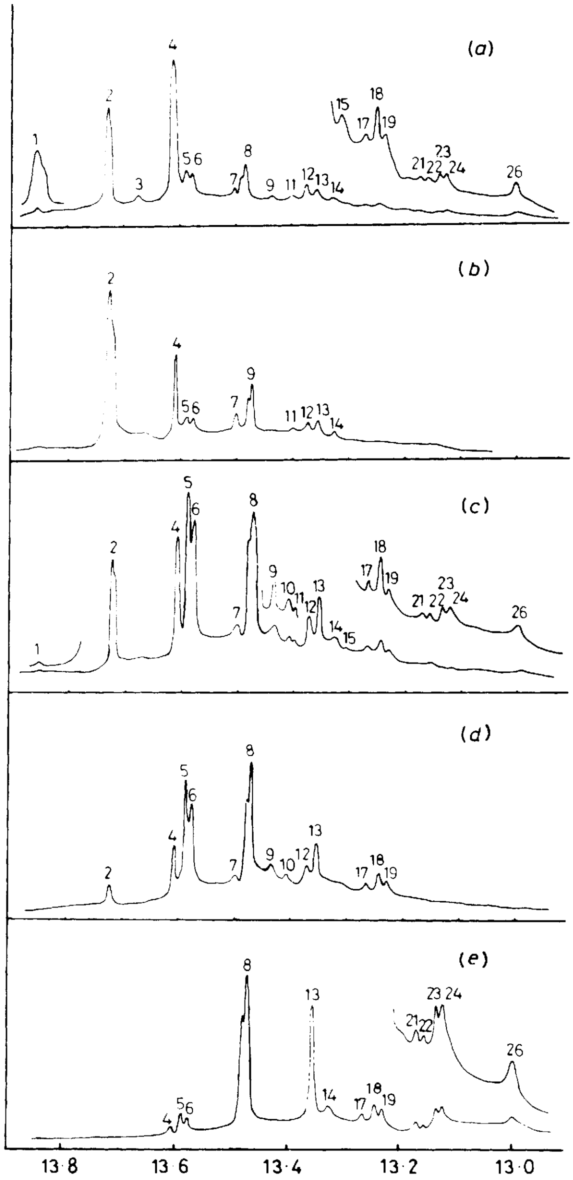

Figure 2. As Figure 1 but with excitation at 457 (*a*), 472 (*b*), 488 (*c*), 496 (*d*), and 514 nm (*e*)

state splitting is expected to be of similar magnitude but different sign in these two species but in neither case is it resolved.

Under 488-nm excitation two split bands at 13 577, 13 588 cm^{-1} and 13 479, 13 472 cm^{-1} which were weak in the 472-nm spectrum are the most intense features in the spectrum. The former doublet becomes weaker compared with the latter as the excitation wavelength is further increased, but the relative intensity of the components of each remains constant. Following our general method of assignment we attribute these to the split electronic origins of $[TcCl_3Br_3]^{2-}$ and *cis*-$[TcCl_2Br_4]^{2-}$. The 514-nm excited spectrum shows just one strong unassigned band at 13 354 cm^{-1} which decreases in intensity with shorter-wavelength excitation. It is assigned as the electronic origin of $[TcClBr_5]^{2-}$. There remain a number of weak, usually broad bands. By monitoring the relative intensity of these features with excitation wavelength it is generally possible to assign them as vibronic origins based on one or other of the electronic origins considered above (Table 2). Whilst these assignments are somewhat tentative, all the vibrational intervals are reasonable for the species involved. Three weak bands at 13 326, 13 307, and 13 265 cm^{-1} do not have the same exciting-line dependence as any of the electronic origins and two distinct species are responsible. We presume that they are due to mixed compounds other than the species so far identified (see next section).

Replacement of a third chloride ion in *cis*-$[TcCl_4Br_2]^{2-}$ by a bromide ion will lead predominantly to the meridional isomer if the *trans* substitution is the faster or to the facial isomer if *cis* substitution dominates. The ground-state splitting in the facial isomer is expected to be smaller than that in the *cis*-disubstituted compounds and much smaller than for the meridional trisubstituted compounds. Since the doublet at 13 577, 13 588 cm^{-1} is clearly the split electronic origin of a single trisubstituted species this can only be the meridional isomer. It seems probable therefore that the facial isomer is not readily formed starting from either the hexachloride or hexabromide ion. Steric considerations may be significant in this step.

Conclusions

Perhaps the most unexpected result from this study is the ease with which plausible assignments of the individual spectral features to specific isomers have been made. It is probable that the use of a continuously tunable source would have enabled an even better separation of the spectra to be achieved. In principle the method should be applicable to the other luminescent Nd^n (N = 4 or 5, n = 3—5) hexahalogeno complex ions and we are currently investigating this possibility. Estimation of the relative amounts of each isomer present in the solution before precipitation cannot be quantitative because of uncertainties concerning the absorption spectra, the quantum efficiencies, and the details of the precipitation process. Nevertheless it seems certain that the replacement of a second chloride or bromide ion in the monosubstituted species does not lead in either case to predominantly the *trans*-disubstituted product.[8,9]

References

1 P. B. Dorain and R. G. Wheeler, *J. Chem. Phys.*, 1966, **45**, 4.
2 C. D. Flint and P. F. Lang, *J. Chem. Soc., Faraday Trans. 2*, 1986, 465.
3 C. D. Flint and A. G. Paulusz, *Mol. Phys.*, 1980, **41**, 907.
4 A. M. Black and C. D. Flint, *J. Mol. Spectrosc.*, 1978, **70**, 481.
5 See for example, C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw-Hill, New York, 1962.
6 C. K. Jorgensen, 'Modern Aspects of Ligand Field Theory,' North-Holland, Amsterdam, 1971.
7 R. M. MacFarlane, *J. Chem. Phys.*, 1967, **47**, 2066.
8 W. Preetz and H. D. Zerbe, *Z. Anorg. Allg. Chem.*, 1981, **479**, 7.
9 H. D. Zerbe and W. Preetz, *Z. Anorg. Allg. Chem.*, 1982, **484**, 33.

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