Substitution Reactions and Luminescence Spectra of the Mixed Complexes $[ReCl_xBr_{6-x}]^{2-}$

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Reaction of $[ReBr_6]^{2-}$ with aqueous HCl followed by rapid precipitation of $Cs_2[SnCl_6]$ from the reaction medium 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 $[ReCl_5Br]^{2-}$, *cis*-$[ReCl_4Br_2]^{2-}$, and *fac*-$[ReCl_3Br_3]^{2-}$. The corresponding reaction starting from $[ReCl_6]^{2-}$ with aqueous HBr produces predominantly $[ReBr_6]^{2-}$ together with the intermediates *trans*-$[ReCl_4Br_2]^{2-}$ and *trans*-$[ReCl_2Br_4]^{2-}$ even under conditions when much of the $[ReCl_6]^{2-}$ remains unchanged. In contrast to our earlier study of the corresponding technetium(IV) complexes, a *trans* effect dominates the substitution processes in the rhenium(IV) compounds.

We have shown[1] that precipitation of $Cs_2[SnCl_6]$ from aqueous solutions containing the mixed complexes $[TcCl_xBr_{6-x}]^{2-}$ (x = 0—6) produces strongly luminescent crystalline solids in which nine of the ten possible mixed complexes can be identified by selective excitation spectroscopy. The reaction mixture obtained from either $[TcBr_6]^{2-}$ and aqueous HCl or $[TcCl_6]^{2-}$ and aqueous HBr gave solids which have luminescence spectra showing the presence of $[TcCl_5Br]^{2-}$, $[TcClBr_5]^{2-}$, *cis*-$[TcCl_2Br_4]^{2-}$, *cis*-$[TcCl_4Br_2]^{2-}$, and *mer*-$[TcCl_3Br_3]^{2-}$ in addition to the unreacted and fully reacted ions. The *trans*-disubstituted ions were present in only relatively small quantities and, so far as could be judged, the rates of the successive steps of the substitution reactions varied monotonically. This indicated that there was no marked *trans*-directing influence of the bromide substituent in these reactions.

It was of interest to study whether this result was also true for the corresponding $5d^3$ complexes $[ReCl_xBr_{6-x}]^{2-}$. We note that an understanding of the kinetics of reactions of technetium complexes is important in the design of radioscintigraphic imaging agents[2] and that comparison with rhenium compounds has been used as a guide[3] to understanding the formation of related technetium compounds. We have therefore carried out a similar study on the $[ReCl_xBr_{6-x}]^{2-}$ complex ions where the $x = 0$ and $x = 6$ ions are known to be strongly luminescent and the absorption spectra in the charge-transfer region are well resolved.

The energy levels and luminescence behaviour of $[ReX_6]^{2-}$ are[4] closely similar to those[5] of $[TcX_6]^{2-}$. Our interpretation of the selective excitation luminescence spectra uses the same methods as were derived for the technetium compounds. For the hexachloro-complex the $\Gamma_7(^2T_{2g})$ state lies *ca.* 700 cm^{-1} higher in energy than for the hexabromo-complex ion due to differences in the interelectron repulsion parameters and, as in the technetium(IV) complexes, we expected that a progressive shift to high energy of the $\Gamma_7(^2T_{2g}) \longrightarrow \Gamma_8(^4A_{2g})$ luminescence spectra of the $[ReCl_xBr_{6-x}]^{2-}$ species would occur as x is increased. We also expected that the electronic origins of the non-centrosymmetric complexes would be much stronger than their vibronic origins and that the magnitude of the splittings of the $\Gamma_8(^4A_{2g})$ ground state due to the low-symmetry field will be in the order[1] *fac*-$[ReCl_3Br_3]^{2-}$ < $[ReClBr_5]^{2-}$ ~ $[ReCl_5Br]^{2-}$ ~ *cis*-$[ReCl_2Br_4]^{2-}$ ~ *cis*-$[ReCl_4Br_2]^{2-}$ < *trans*-$[ReCl_2Br_4]^{2-}$ ~ *trans*-$[ReCl_4Br_2]^{2-}$ ~ *mer*-$[ReCl_3Br_3]^{2-}$. The most important (third-order) perturbation loops that contribute to the ground-state splitting depend on the square of the spin–orbit coupling constant. Since the $5d$ spin–orbit coupling constant of Re^{IV} is more than twice the $4d$ constant of Tc^{IV}, these ground-state splittings are expected to be much larger for the rhenium complexes than for the technetium compounds.

Experimental

Samples of $Cs_2[SnCl_6]$ containing about 1% by weight of the mixed $[ReCl_xBr_{6-x}]^{2-}$ complexes were prepared as described for the corresponding technetium compounds[1] starting from $Cs_2[ReCl_6]$ and $Cs_2[ReBr_6]$. For the rhenium(IV) complexes the substitution of $[ReBr_6]^{2-}$ by chloride ions was markedly slower so that reaction times of 1 week at elevated temperatures were employed. In spite of these prolonged reaction times we obtained no evidence that the systems were approaching equilibrium.

Luminescence spectra were measured as previously described.[6] The emission in the $\Gamma_8(^2T_{2g}) \longrightarrow \Gamma_8(^4A_{2g})$ region was broad and weak and will not be considered further.

Results

Figure 1 shows the luminescence spectra for various exciting lines of a sample prepared from $Cs_2[ReBr_6]$ by reaction with concentrated aqueous HCl for about 1 week at elevated temperatures. Bands 16, 17, and 19 are identical in spectral position to the ν_6, ν_4, and ν_3 vibronic origins of the $[ReBr_6]^{2-}$ ion.[7,8] The relative intensity of these bands is consistent with this assignment if the contribution to band 16 from another species is considered (see below). It is noteworthy that the intensities of these bands are weak in Figure 1(*a*)—(*c*) even though this ion is strongly excited by these wavelengths. The concentration of unchanged starting material is therefore small. The luminescence of the $[ReCl_6]^{2-}$ ion is excited by both the laser lines at 454 and 457 nm and the absence of any peaks in the region of 13 700 cm^{-1} in Figure 1(*a*) and (*b*) demonstrates that this ion is essentially absent in the samples.[9]

Following the assignment procedure we used in the technetium study,[1] lines whose relative intensity is independent of the exciting line are attributed to the same species and the groups of lines can be assigned to specific $[ReCl_xBr_{6-x}]^{2-}$ ions by consideration of their relative position between the electronic and vibronic origins of the $x = 0$ and $x = 6$ ions. The splittings and intensities of electronic origins, the energy of the lowest-energy wing of the excitation spectra, and the variations in the intensities of corresponding lines from sample to sample provide additional criteria for this assignment.

Four lines 3, 4, 7, and 18 are clearly separated from overlapping features in all of the spectra. The relative intensities

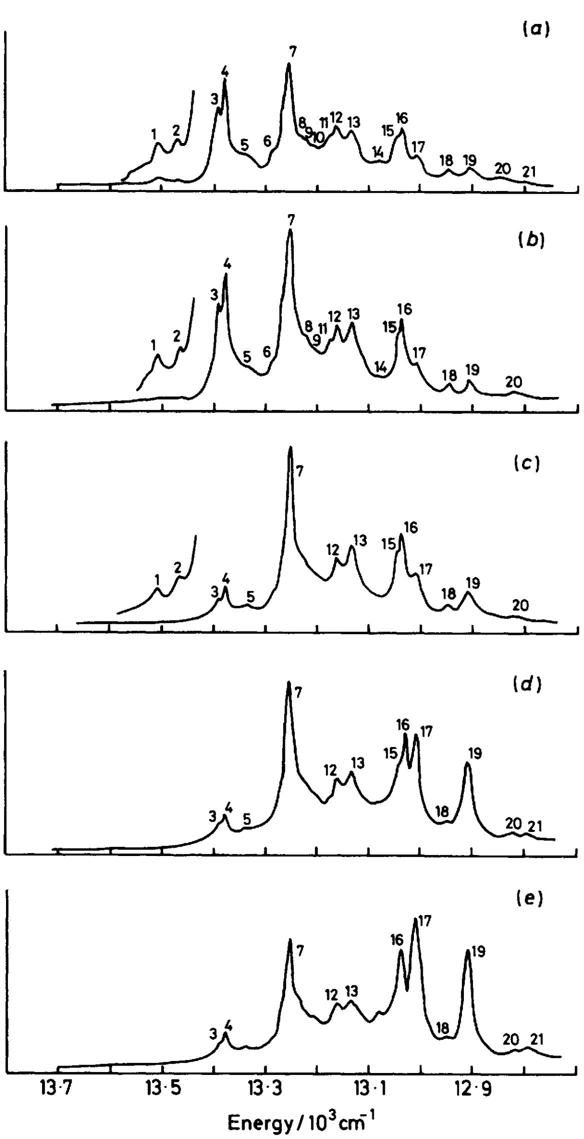

Figure 1. The luminescence spectrum of $[ReCl_xBr_{6-x}]^{2-}$ in $Cs_2[SnBr_6]$ at 80 K excited at (*a*) 454, (*b*) 457, (*c*) 465, (*d*) 472, and (*e*) 476 nm. See text for details of the preparation of the sample

Table. Assignment of the bands in Figure 1

Band	Wavenumber/cm^{-1}	Species	Comment
1	13 508		See text
2	13 468		See text
3	13 391	*fac*-$[ReCl_3Br_3]^{2-}$	Origin
4	13 379	*fac*-$[ReCl_3Br_3]^{2-}$	Origin
5	13 338		See text
6	13 285	*fac*-$[ReCl_3Br_3]^{2-}$	Vibration
7	13 253	*cis*-$[ReCl_2Br_4]^{2-}$	Origin
8	13 235	*fac*-$[ReCl_3Br_3]^{2-}$	Vibration
9	13 225	*fac*-$[ReCl_3Br_3]^{2-}$	Vibration
10	13 208	*fac*-$[ReCl_3Br_3]^{2-}$	Vibration
11	13 175	*fac*-$[ReCl_3Br_3]^{2-}$	Vibration
12	13 163	$[ReClBr_5]^{2-}$	Origin
13	13 134	*cis*-$[ReCl_2Br_4]^{2-}$	Vibration
14	13 079	$[ReClBr_5]^{2-}$ *cis*-$[ReCl_2Br_4]^{2-}$	Vibration Vibration
15	13 043	$[ReClBr_5]^{2-}$ *cis*-$[ReCl_2Br_4]^{2-}$	Vibration Vibration
16	13 037	*cis*-$[ReCl_2Br_4]^{2-}$ $[ReBr_6]^{2-}$	Origin ν_6
17	13 009	$[ReBr_6]^{2-}$	ν_4
18	12 947	$[ReClBr_5]^{2-}$	Origin
19	12 909	$[ReBr_6]^{2-}$	ν_3
20	12 824	$[ReBr_6]^{2-}$ *cis*-$[ReCl_2Br_4]^{2-}$	$\nu_4 + \nu_2$ and $\nu_6 + \nu_1$ Vibration
21	12 798	$[ReBr_6]^{2-}$	$\nu_4 + \nu_1$

of lines 3 and 4 are independent of the exciting line and are attributed to a single species. The dependences of lines 7 and 18 on the exciting line are different from each other and from those of lines 3 and 4 and the lines due to $[ReBr_6]^{2-}$. There are therefore at least three partially substituted ions present. Although line 16 in Figure 1(*e*) is coincident with the expected position of the ν_6 vibronic origin of the $[ReBr_6]^{2-}$ ion its intensity is too high for it to be due solely to this species. Moreover the additional intensity of this line follows the intensity of line 7 as the exciting line is changed [Figure 1(*a*)—(*d*)]. It is likely therefore that lines 3, 4 and lines 7, 16 correspond to the split electronic origins of two species. These species will have a small number of chloride-ion substituents since the origins lie towards the $[ReBr_6]^{2-}$ end of the spectrum. Line 18 must be one component of a split electronic origin of a species which contains even fewer chloride ions than the species responsible for lines 3, 4 and 7, 16. The second component must lie to high energy and probably occurs in the region of lines 11—13. Whilst these lines overlap somewhat a careful study of their intensity indicates that line 11 has the same excitation dependence as lines 3, 4; line 12 follows line 18 and line 13 follows lines 7, 16. We therefore assign lines 12, 18 as the split electronic origin, whilst 11 and 13 involve vibrational intervals of *ca.* 210 and 120 cm^{-1}. Both of these vibrational wavenumbers are reasonable for mixed chloro–bromo complex ions. There remain a number of weak, mainly broad, features. All those with line numbers greater than 5 can be assigned to vibrations based on one of the previously assigned electronic origins involving reasonable vibrational intervals. The others, lines 1, 2, and 5, lie at the high-wavenumber end of the spectrum and are probably associated with trace amounts of one or more species containing more chloride ligands than the species responsible for the bands assigned so far.

These results are quite different from those obtained from similar experiments on the technetium complexes. In that case (Figure 1 of ref. 1) the substitution reaction resulted in the formation of nine of ten possible complex ions. In particular, ions with four to six chloride ligands were present in considerable quantity even when the reaction mixture contained a large amount of the unreacted $[TcBr_6]^{2-}$ ion. The emission spectra of these species occurred at the high-energy end of the spectrum as expected. Following our general methods we assign lines 12, 18 as the split electronic origin of $[ReClBr_5]^{2-}$. The splitting of 216 cm^{-1} is reasonable in comparison to the splitting of 167 cm^{-1} of the ground state of the trigonal crystal $K_2[ReF_6]$. Similarly, lines 7, 16 are assigned as the split electronic origin of *cis*-$[ReCl_2Br_4]^{2-}$. The splitting is again (presumably fortuitously, but see below) 216 cm^{-1}. First-order crystal-field theory predicts that the splittings in these two compounds would be equal in magnitude but of opposite sign. Lines 3, 4 are then assigned as the split origin of *fac*-$[ReCl_3Br_3]^{2-}$, first-order crystal-field theory predicting that the splitting in this case will be zero if the ligands lie on orthogonal axes. Wavenumbers and assignments of all the observed lines are collected in the Table.

We attribute the difference in behaviour of $[ReBr_6]^{2-}$ and $[TcBr_6]^{2-}$ towards substitution by chloride ions to the much stronger *trans*-directing influence of the bromide ion in the $5d^3$ ion. Substitution of a bromide ion *trans* to another bromide ion

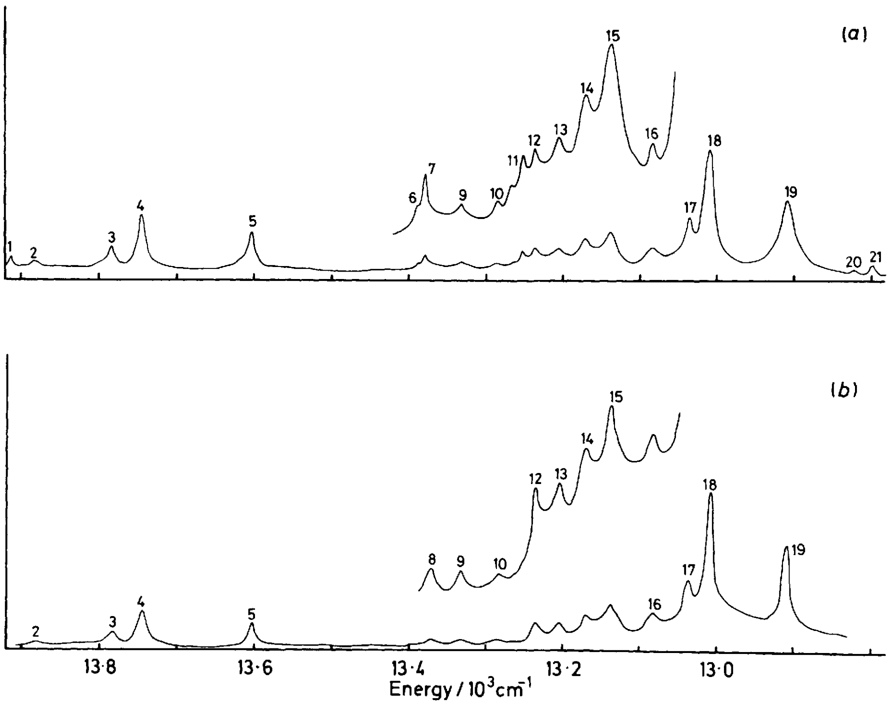

Figure 2. The luminescence spectrum of $[ReCl_xBr_{6-x}]^{2-}$ in $Cs_2[SnBr_6]$ at 80 K excited at (*a*) 454 and (*b*) 457 nm. See text for details of the preparation of the sample

proceeds much more rapidly than substitution *trans* to a chloride ion. The reaction pathway is then $[ReClBr_5]^{2-} \longrightarrow$ *cis*-$[ReCl_2Br_4]^{2-} \longrightarrow$ *fac*-$[ReCl_3Br_3]^{2-}$. Further substitution is then very slow. If this is correct the reaction pathway starting from $[ReCl_6]^{2-}$ will have different intermediate ions. In particular the two *trans*-disubstituted ions will be the most important species before the formation of $[ReBr_6]^{2-}$. The electronic origins in these complexes will be weak and the luminescence spectra dominated by vibronic origins based on the split electronic origins. The number of medium to strong bands associated with a particular species will be large and the luminescence spectrum will be quite different from that obtained above or in ref. 1.

Figure 2 shows the luminescence spectra of a sample prepared by treating $Cs_2[ReCl_6]$ with concentrated aqueous HBr for about 1 min. Lines 1—5 are identical to the luminescence spectrum of $[ReCl_6]^{2-}$ in $Cs_2[SnCl_6]$ and lines 17—21 are identical to the luminescence spectrum of $[ReBr_6]^{2-}$. Lines 6, 7 appear to be identical to lines 3, 4 of Figure 1 although a slight difference in relative intensity suggests there may be another underlying transition. The remaining lines do not all have the same dependence on the exciting line and at least two further species are present. No electronic origins have been identified and the spectrum is consistent with the presence of a large number of vibronic origins. This is precisely what would be expected if lines 8—15 are due to a mixture of *trans*-$[ReCl_2Br_4]^{2-}$ and *trans*-$[ReCl_4Br_2]^{2-}$. In this case a total of 24 vibronic bands might be expected but spectral congestion will prevent many of these being resolved. We therefore do not attempt to give a detailed analysis.

Discussion

Several conclusions are immediately apparent even without considering the detailed assignments of individual bands. Figure 1 shows that little of the $[ReCl_6]^{2-}$ or $[ReBr_6]^{2-}$ ions are present in the reaction mixture although both species are excited by 454- and 457-nm radiation (Figure 2). Comparison of Figures 1 and 2 shows that the ions present do control subsequent substitution reactions. The ion *fac*-$[ReCl_3Br_3]^{2-}$ is almost inert towards further substitution by chloride ions. We have previously commented on the uncertainties of using the spectra obtained by this technique as a quantitative estimate of the concentration of the various species in the reaction medium. Nevertheless it seems from the intensities of lines 12 and 18 that the concentration of $[ReCl_5Br]^{2-}$ is small in the reaction pathway. We noted above the apparent identity of the separation of lines 7, 16 and 12, 18. In practice, because of the overlap of line 15 and the two contributions to line 16, this identity of wavenumber is only to within 5 cm⁻¹. Whilst on the assignments given above the separations would be expected to be comparable, changes in the bond lengths and bond angles in the complexes, and higher-order contributions, would probably lead to differences of up to some tens of wavenumbers. It is possible that lines 7, 16 represent the split components of an electronic origin and lines 12 and 18 are vibrations of 90 cm⁻¹ based on these origins. Since both lines 12 and 16 are overlapped by other transitions we are unable to exclude this possibility by following the intensities of the lines as a function of excitation wavelength. However it seems unlikely that only a single vibronic origin would be observed with high intensity and that $[ReCl_5Br]^{2-}$ would be entirely absent from all spectra. We assume that the identity of the separations is fortuitous.

Figure 2 demonstrates that starting from $[ReCl_6]^{2-}$ there is little evidence for the non-centrosymmetric intermediates that occur in the technetium(IV) system and in Figure 1. Indeed the concentration of even the *trans* intermediates is small. Whilst a small quantity of $[ReCl_5Br]^{2-}$ or *mer*-$[ReCl_3Br_3]^{2-}$ would not easily be observed, it appears that these ions rapidly react with bromide ions to generate the two *trans* products. The small amount of *fac*-$[ReCl_3Br_3]^{2-}$ is probably formed by a competing side reaction. This species is observed only because its emission intensity is concentrated in two electronic origins with a characteristic separation which occur in a region where there is no other emission. All of these observations can be understood if the substitution reaction *trans* to bromide is favoured over the reaction *trans* to chloride. One factor operating here will be the greater steric effect of the bromide, but the difference in reaction rates compared to the technetium(IV) complexes indicates that an electronic effect is also significant.

Conclusions

As in our previous study, assignments of most of the spectral features in the luminescence spectra were straightforward. Even if a few of the assignments are incorrect, the difference between the reaction products starting from the hexachloro- and hexabromo-complex ions in the case of the rhenium(IV) complexes but not for the technetium(IV) complexes is sufficient to indicate that the stereochemical path of substitution reactions of Tc^{IV} and Re^{IV} must be different so that studies on rhenium complexes may not be a reliable guide to the formation of technetium radioscintigraphic imaging agents.

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