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LETTER

The Luminescence of $[\text{SbCl}_6]^{3-}$ in Crystals and in Solution

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Recently Vogler and Paukner [1] discussed the photoredox chemistry of chloro complexes of Sb(III) and Sb(V). In that paper they also reported the room-temperature luminescence of the complex $[\text{SbCl}_6]^{3-}$ in chloroform. Emission from the Sb(III) ion at 300 K has seldom been observed in solution. As remarked in ref. 1, the photochemistry of such a complex has also not been much studied. Here we compare the photophysics results of ref. 1 with those reported for crystalline solids [2]. In the latter work the efficient luminescence of Sb(III) in the elpasolites $\text{Cs}_2\text{NaLnCl}_6$ (Ln = Sc, Y, La) is reported. In view of the cubic crystal structure and Ln-site symmetry, these systems are very suitable model systems to investigate Sb(III) electronic spectroscopy. It is a pity that solid-state physicists and coordination chemists do not have closer contacts, since comparison of their work is instructive, as we hope to show in this Letter.

The $[\text{SbCl}_6]^{3-}$ complex in chloroform solution shows luminescence with an emission band peaking at 520 nm, a quantum efficiency Φ of 2.4×10^{-3} and a decay time $\tau \leq 50$ ns [1]. The absorption spectrum shows three bands assigned to the well-known A, B and C transitions, viz. $^1\text{S}_0 \rightarrow ^3\text{P}_1$, $^3\text{P}_2$ and $^1\text{P}_1$ [1, 2]. The maxima of these bands are given in Table 1, where the corresponding data for $\text{Cs}_2\text{NaYCl}_6\text{-Sb(III)}$ are also given. Furthermore, the Stokes shift is tabulated. In order to make the Stokes shift of $\text{Cs}_2\text{NaYCl}_6\text{-Sb(III)}$ comparable to that of $[\text{SbCl}_6]^{3-}$ in chloroform, it is necessary to increase the former value by 500 cm^{-1} , because in ref. 1 the Stokes shift is taken relative to the

TABLE 1. A comparison of the luminescence of the $[\text{SbCl}_6]^{3-}$ complex at 300 K in a chloroform solution [1] and in a $\text{Cs}_2\text{NaYCl}_6$ crystal [2]

	Solution	Crystal
Maximum A band (cm^{-1})	33000	30900
Maximum B band (cm^{-1})	38020	35700
Maximum C band (cm^{-1})	40800	39300
Maximum emission band (cm^{-1})	19200	21400
Stokes shift (cm^{-1})	13800	9400
Lifetime (μs)	≤ 0.05	~ 0.2

$^1\text{S}_0 \rightarrow ^3\text{P}_1$ absorption maximum and in ref. 2 to the lower component of this absorption band. In the solid the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition is split by about 1000 cm^{-1} because of the dynamic Jahn–Teller effect.

Table 1 shows several interesting aspects.

(a) The positions of the absorption bands do not appear to be consistent. This, however, is misleading. The values for the crystal $\text{Cs}_2\text{NaYCl}_6\text{:Sb(III)}$ are undoubtedly correct in view of the conspicuous Jahn–Teller splittings [2]. The values for the $[\text{SbCl}_6]^{3-}$ group in solution are situated at somewhat more than 2000 cm^{-1} higher energy. The C band should be at about $41\,500 \text{ cm}^{-1}$. From the Figure in ref. 1 it is clear that the C band is at the limit of the instrumental response. It is probable that the experimental value is at some 5 nm shorter wavelengths, so in fact there is good agreement between the two sets of data.

(b) Although the absorption bands in solution are at higher energy, the emission is clearly at lower energy than in the crystal. This is due to the much larger Stokes shift for the solution. In ref. 2 the Stokes shift was found to depend on the nature of Ln in the host lattice $\text{Cs}_2\text{NaLnCl}_6$ (Ln = Sc, 8000 cm^{-1} ; Ln = Y, 9400 cm^{-1} ; Ln = La, $10\,500 \text{ cm}^{-1}$). The Stokes shift in solution is therefore very large.

(c) The lifetime of the crystal ($\sim 0.2 \mu\text{s}$) is for the greater part radiative [2]. In view of the quantum efficiency of the solution reported in ref. 1, the lifetime of the $[\text{SbCl}_6]^{3-}$ complex in solution is estimated to be 0.1 ns, in agreement with, but less than, that suggested by the limit given in ref. 1.

Let us now try to find a general explanation for these differences. This is, in fact, simple in view of earlier work in our laboratory [3]. There we studied the charge-transfer excitation of the Eu^{3+} luminescence in GdB_3O_6 glass and crystals. The former modification yields a much lower quantum efficiency of the luminescence in combination with a shift of the charge-transfer absorption transition to higher energy. This was explained in a single-configurational coordinate diagram by increasing

the parabolae offset going from the crystalline to the glassy modification. The energy of the absorption transition increases, but so does the non-radiative rate [4].

For $[\text{SbCl}_6]^{3-}$ we cannot use a configurational-coordinate diagram based on the totally-symmetrical breathing mode. There is circumstantial evidence that the Jahn–Teller active e_g mode must be used. This follows not only from the obvious dynamic Jahn–Teller effects in the absorption spectra of $\text{Cs}_2\text{NaLnCl}_6:\text{Sb(III)}$ [2], but also from the clear progression in e_g in the emission spectrum of the isoelectronic $[\text{TeCl}_6]^{2-}$ in Cs_2ZrCl_6 which is, for our purpose, isoelectronic with the elpasolites [5].

Nevertheless, the higher energies of the absorption bands, the larger Stokes shifts and the lower quantum efficiencies of the $[\text{SbCl}_6]^{3-}$ complex in chloroform relative to the $[\text{SbCl}_6]^{3-}$ complex in the elpasolite crystals show clearly that the parabolae offset Δr in the former is larger than in the latter, in agreement with our earlier results that Δr is always larger in disordered phases [3, 6].

Finally, we note that Vogler and Paukner [1] did not observe any luminescence for the $[\text{SbCl}_6]^-$ complex in solution. This is in good agreement with early solid-state results that highly charged d^{10} ions do not show luminescence [7]. Of course, the monovalent ions are an exception to this rule [8].

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