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Trichlorosulphonium Tetrachloroiodate and the Constitution of Jaillard's Compound

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Between 1860 and 1904 an orange crystalline compound variously prepared (i) from I_2, S, and Cl_2 [1], (ii) *via* chlorination of I_2 in CS_2 [2], and (iii) by allowing a dilute solution of ICl_3 in SCl_2 to crystallise [3] was formulated, respectively, as $SICl_4$, $(SCl_2)_2$-ICl_3 and $SCl_4(ICl_3)_2$. In 1975 Tavares-Forneris and Forneris [4] repeated the elemental preparation (i) and interpreted the Raman spectrum on the basis of Jaillard's analysis in terms of a mixed crystal of SCl_3^+-ICl_2^{-1} and a novel compound $SICl_3$. However, preparation (ii) had been previously shown by Weber [2] to give a product identical to that of Jaillard, but with an analysis corresponding to S_2ICl_7 (apparently based on S = 16), *i.e.* $SICl_7$ (based on S = 32).

In the course of a study of various complexes involving square-planar ICl_4^- and $AuCl_4^-$ ions we have re-investigated Jaillard's compound and propose a radically different interpretation, formulating it as $SCl_3^+ICl_4^-$. Preparations using Jaillard's method yield an orange crystalline material (Form I), existing at room temperature only under its own vapour pressure or under an atmosphere of chlorine, and for which a halogen analysis (Found: Cl, 60.97; I, 30.99%. Calc. for $SICl_7$: Cl, 60.96; I, 31.17%) corresponds to $SICl_7$, in agreement with Weber. The Raman spectrum of this product is identical to that reported by Tavares-Forneris and Forneris [4]. The product obtained by passing chlorine into a solution of ICl_3 in SCl_2 (Form II) is analytically identical to Form I but differs in some respects in its Raman spectrum. Form II slowly changes to Form I on standing at room temperature, but may be reformed by dissolution in SCl_2 with passage of chlorine. In no preparations do our analytical results support the $S_2I_2Cl_8$ stoichiometry assumed by Tavares-Forneris and Forneris as the basis of their spectroscopic interpretation.

TABLE. Raman Wavenumbers (cm^{-1})[a] and Tentative Assignments for $KICl_4 \cdot H_2O$ and Forms I and II of $SCl_3^+ICl_4^-$.

Form I	Form II	$KICl_4H_2O$	Assignment[b]
130(w)	125(w)	120(vw)	ICl_4^- deformations
142(m)	143(mw)	142(w,sh)	
150(w,sh)	154(mw)	151(w)	
212(m)	205(w)		$\nu_4(e), SCl_3^+$
220(w,sh)		219(w)	
244(m)	218(vw)	247(m)	$\nu(ICl)$
256(mw)	228(w)		
279(vs)[c]	260(s)	271(s)	
298(vs)	282(vs)[c]	291(s)	
485(s)	482(ms)		$\nu_1(a_1), SCl_3^+$
498(mw)	496(mw)		$\nu_3(e)SCl_3^+$
512(w)	510(mw)		

[a] Spectra recorded on a Coderg PHO Raman spectrometer with 647.1 nm excitation. [b] Bands below 100 cm^{-1} assigned to lattice modes. [c] Also $\nu_2(a_1), SCl_3^+$.

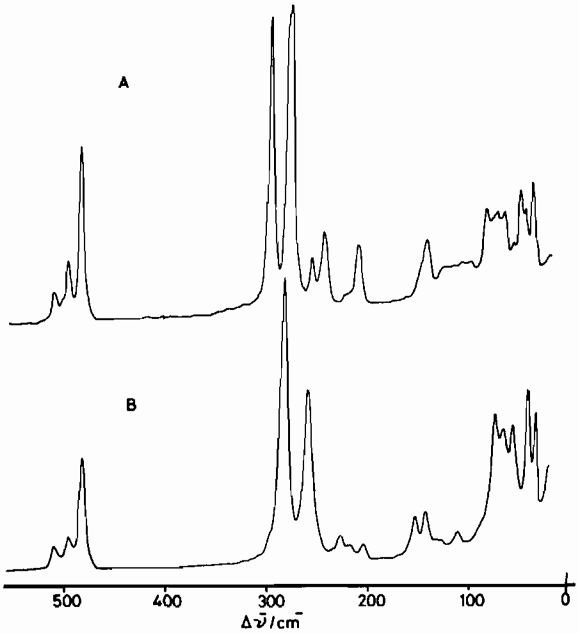

Figure. Raman spectra of two modifications of $SCl_3^+ICl_4^-$; A, Form I, B, Form II.

Details of the Raman spectra of both modifications are shown in the Table and Figure from which the presence of SCl_3^+ bands [5] is clear. However, there are significant differences between the remaining bands in the two forms which can be satisfactorily assigned to two types of distorted ICl_4^- ions. Selection rules for a square planar $(D_{4h})ICl_4^-$ species predict three Raman-active bands (typically, in $KICl_4$, at 286(a_{1g}), 260(b_{2g}), and 128(b_{1g}) cm^{-1}) [6]. However, the pattern of the spectrum in $KICl_4 \cdot H_2O$, in which X-ray diffraction has shown distortion of the ICl_4^- ion [7] clearly indicates the appearance of formally-inactive Raman modes and also shows a close correspondence to the pattern in Form I. The Raman bands at 298, 279, 256 and 244 cm^{-1} in Form I all have coincident bands in the infrared, indicating removal of the centre of symmetry. The spectrum of Form II shows some significant differences, with the ICl_4^- stretching modes at 298 and 279 cm^{-1} shifted to 282 and 260 cm^{-1} respectively, suggesting an ICl_4^- ion but with a different distortion. The possibility that Form I has the constitution $SICl_7 \cdot H_2O$ may be confidently discounted on the basis of (a) elemental analysis and (b) preparation and manipulation under stringently anhydrous conditions. Further spectroscopic studies are in progress on these and related systems and a more detailed treatment will be given elsewhere.

In summary, the spectra can be convincingly assigned on the basis of two crystal modifications of $SCl_3^+ICl_4^-$, both of which involve a distorted ICl_4^- ion, and without the necessity of invoking the existence of $SICl_3$, for which there is no antecedent or analytical evidence.

Acknowledgment

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