Inorganic Optical Activity

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Summary The tris(pentasulphido)platinate(IV) compound $(NH_4)_2[Pt(S_5)_3]$ has been crystallised in both a racemic and an optically active form.

Most known optically active molecules contain carbon atoms and resolved chelated inorganic species are no exception. The only optically active molecular species which are carbon-free are Werner's 'hexol',[1] $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, and *cis*-bisaquobis-sulphamatorhodate(III) resolved by Mann.[2] These examples contain a first and a second row transition metal, respectively.

We now add a third example, $[Pt(S_5)_3]^{2-}$, which contains atoms of only two elements, platinum (from the third transition series) and sulphur. Ammonium tris(pentasulphido)platinate(IV) dihydrate was originally prepared by Hofmann and Höchtlen.[3] Wickenden and Krause[4] have recently reported improved methods for the preparation of this complex which they found to be anhydrous. The tris-chelated octahedral structure has been confirmed by Jones and Katz,[5] and we have obtained optically active $[Pt(S_5)_3]^{2-}$ by classical resolution using (+)-$[Ru(phen)_3]^{2+}$. The preparation and crystal structure of the analogous potassium salt, K_2PtS_{15}, have also been reported.[6]

We prepared $(NH_4)_2PtS_{15}$ using method B of Wickenden and Krause. Under these highly alkaline conditions (pH *ca.* 10·8) the product usually crystallised slowly (several days), forming large deep-red (brick-red when powdered) crystals of the racemate (*ca.* 50% yield). The complex is fairly soluble in water and the spectroscopic properties agree with those reported by Wickenden and Krause.

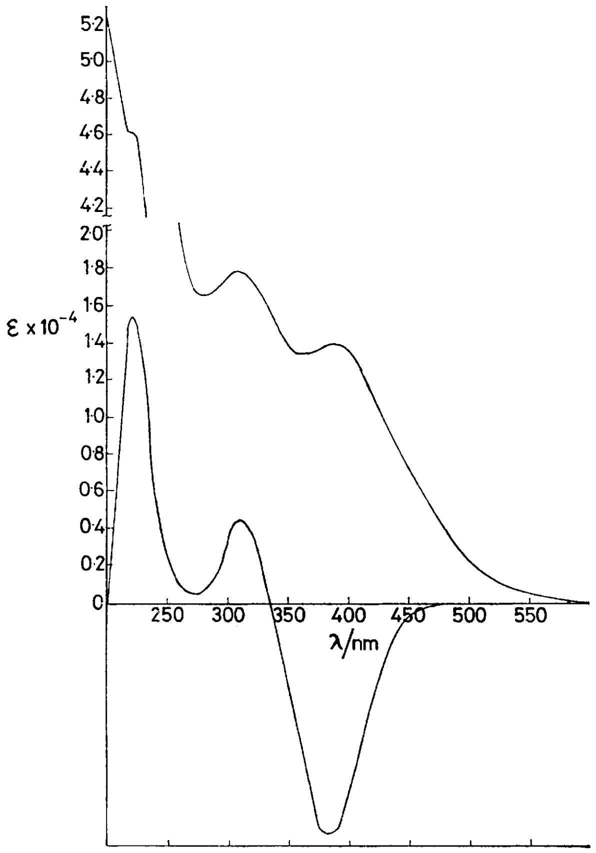

FIGURE. Absorption spectrum (upper curve) and circular dichroism (lower curve) of (−)-$[Pt(S_5)_3]^{2-}$.

When the complex was rapidly crystallised (*i.e.* over a period of either minutes or hours depending on the conditions), maroon microcrystals were obtained in significantly higher yield (*ca.* 75%). This process was sometimes observed in the reaction mixture itself, but usually required the addition of concentrated hydrochloric acid to lower the pH. Under these conditions it appears that the product crystallises as the dihydrate. This form of the complex is less soluble in water than the racemate.

Circular dichroic and polarimetric measurements show that this solid contains an excess of one enantiomer. The maximum optical rotation in aqueous solution that has been observed at 546·1 nm is 1910° and we believe that this value is due to complete resolution. Typical values are usually of the order of 600—800°. So far we have only isolated the *laevo*-enantiomer. The circular dichroic and the u.v.–visible spectra of the complex are shown in the Figure. This is, to our knowledge, the first inorganic example of a spontaneous second-order asymmetric transformation.[7]

$(NH_4)_2PtS_{15}$ is reasonably stable in neutral aqueous solution. Turbidity develops over a period of several hours and this is accompanied by partial reduction to the known[4] species $[PtS_{10}]^{2-}$. Complete decomposition takes several days. The reduction is more rapid in alkaline solutions such as concentrated ammonia.

The mechanism for the racemisation (and hence resolution) of the complex probably involves reduction to platinum(II) since (a) treatment of $[PtS_{15}]^{2-}$ with aqueous sodium sulphide results in rapid reduction to $[PtS_{10}]^{2-}$; (b) the optical activity of the complex disappears immediately upon dissolution in an ammonium polysulphide solution (which must contain a small proportion of free sulphide); and (c) $[PtS_{10}]^{2-}$ is known to react with ammonium polysulphide to give $[PtS_{15}]^{2-}$.[4]

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