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An Unexpected Double Salt Structure in Pyridinium Enneachlorodithallate(III)

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The confacial bioctahedron structure of the $Tl_2Cl_9^{3-}$ anion in its cesium salt is a classic one, having been determined early in the era of X-ray crystallography in a search for thallium(III) compounds having relatively simple structures (*1*). Since then, other $M_2X_9^{3-}$ salts have been shown to contain ions of similar structure, sometimes with variable degrees of interaction between the two metal atoms in the anion (*2*, *3*). The pyridinium salt, $(C_5H_6N)_3Tl_2Cl_9$, is almost as ancient as the cesium one, being first prepared by Renz in 1898. More recently, this compound has been resurrected by us (*4*), since it occurs as the product of the reaction of pyridine on the solution obtained by saturating an aqueous thallic oxide suspension with HCl gas—this reaction having been incorrectly reported originally as yielding $(C_5H_6N)_2TlCl_5$ (*5*).

$(C_5H_6N)_3Tl_2Cl_9$ is a thermally stable, white crystalline solid which recrystallizes unchanged from ethanol or dilute HCl, but converts to $(C_5H_6N)TlCl_4$ on crystallizing from water or THF (*4*). The recent availability of reliable preparations for $(C_5H_6N)_2TlCl_5$ has now made it possible to compare the tetrachloro-, pentachloro-, and enneachloro derivatives of Tl(III) in the pyridinium salts. These three compounds appear to have relatively complex solution behavior, apparently acting as 1 : 1 (for $TlCl_4^-$) or mixtures of 1 : 1 electrolytes in ethanol. The Raman spectra of these solutions are characteristic of the $TlCl_4^-$ ion only and thus do not necessarily reflect the solid state structures.

On the other hand, Raman spectra on polycrystalline samples yield distinctly different Tl–Cl stretching frequencies, with that of the enneachloride displaying *two* strong peaks in this region. This is a spec-

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trum which is markedly different from that reported by Beattie *et al.* for the D_{3h} $Tl_2Cl_9^{3-}$ ion in the cesium salt (*6*).

The enneachloride occurs in two distinct crystalline forms (mp 120 and 130°C) (*4*). Since both forms display virtually identical Raman spectra, the thallium-containing species are constant in the two cases. This eliminates the possibility that one form contains the binuclear $Tl_2Cl_9^{3-}$ ion while the other does not.

A general rule in vibrational spectroscopy is that the metal–chloride stretching frequency decreases as the coordination number about the metal increases. Thus, for example, $FeCl_4^-$: ν(Fe–Cl) = 370 cm^{-1}; $FeCl_5^{2-}$: ν(Fe–Cl) = 336 cm^{-1}, and $FeCl_6^{3-}$: ν(Fe–Cl) = 251 cm^{-1} (*7*). For the chlorothallate(III) salts, the $TlCl_4^-$ ion has ν(Tl–Cl) = 305 cm^{-1} and for $TlCl_5^{2-}$, ν(Tl–Cl) = 280 cm^{-1}, these being by far the strongest peaks in the spectra. The two most intense peaks in the spectrum of the enneachloride (302 and 277 cm^{-1}) match these frequencies very closely. The Raman spectra suggest that the enneachloride—far from containing the expected $Tl_2Cl_9^{3-}$ ion—actually contains both $TlCl_4^-$ and $TlCl_5^{2-}$ ions (with pyridinium counterions).

This unexpected result is corroborated by the ^{205}Tl NMR spectra of the solids. ^{205}Tl ($I = \frac{1}{2}$, natural abundance 70.48%) yields anomalously large chemical shifts which enable Tl(I) and Tl(III) compounds to be distinguished quite readily (*8*). Furthermore, it is possible to differentiate between Tl(III) compounds of different coordination number (*8, 9*). While $(C_5H_6N)TlCl_4$ yields a narrow line of relatively high S/N ratio, $(C_5H_6N)_2TlCl_5$ is characterized by a weak, broad line. In a 10-kG (1T) field, the peaks are in the following positions: $TlCl_4^-$, 24.633 MHz and $TlCl_5^{2}$, 24.610 MHz. The peak associated with the $Tl_2Cl_9^{3-}$ ion in the cesium salt (24.609 MHz) is of considerably higher S/N ratio and readily distinguished from the $TlCl_5^{2-}$ signal. The high sensitivity obtained for the $TlCl_4^-$ signal is illustrated by the fact that brief exposure to $(C_5H_6N)_2TlCl_5$ to moist air will cause a $TlCl_4^-$ peak to become visible. The NMR spectrum of $(C_5H_6N)_3Tl_2Cl_9$ contains a strong, sharp peak in the $TlCl_4^-$ position adjacent to a broad, weaker peak close to the $TlCl_5^{2-}$ position. A physical mixture of authentic $(C_5H_6N)TlCl_4$ and $(C_5H_6N)_2TlCl_5$ (ca. 1 : 1) yielded an almost identical spectrum.

Two variations observed in the structures of other $A_3M_2X_9$ compounds are illustrated by $Cs_3Sb_2Cl_9$, which is considered to consist of discrete $SbCl_3$ molecules in a lattice of cesium and chloride ions (*10*) and by $(C_5H_6N)_3Fe_2Cl_9$ which is a double salt of $FeCl_4^-$ and pyridinium chloride (*11*). The Raman and NMR evidence here suggests another variation: that of an array of $TlCl_4^-$ and $TlCl_5^{2-}$ ions with $C_5H_6N^+$ counterions. While the pyridinium ion has been shown to have the ability to distort metal–chlorine bonds in other chlorometallate systems (notably $SnCl_6^{2-}$) (*12*), there is no evidence yet which links the $(C_5H_6N)_3Tl_2Cl_9$ structure with that of $Cs_3Tl_2Cl_9$. Indeed, there is yet no evidence of the $Tl_2Cl_9^{3-}$ ion existing in the solutions from which these salts crystallize. An X-ray structural investigation on the pyridinium salt is in progress to discover any relationship between the structures.

Experimental

The compounds $(C_5H_6N)TlCl_4$ (*4*), $(C_5H_6N)_3Tl_2Cl_9$ (*4*), $Cs_3Tl_2Cl_9$ (*13*), and $(C_5H_6N)_2TlCl_5$ (*14*) were prepared according to published procedures.

Raman spectra were obtained on polycrystalline samples (sealed in glass capillaries using the 514.5-nm line of the Ar ion laser of the Spex Ramalog instrument at the University of Melbourne.

The NMR spectra were taken at a field of 10 kG with a conventional pulsed Fourier transform spectrometer assembled essentially from Matec components.

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