

Concerning the Nature of Solid Tellurium Tetrachloride

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RECENT nuclear quadrupole observation¹ of a total of six ³⁵Cl resonances for TeCl₄ was treated as two groups of three frequencies each, and interpreted as indicative of the presence of trigonal bipyramidal molecules as the major species in the substance. Since this conclusion is at odds with the ionic formulation, TeCl₃⁺ Cl⁻, proposed from the Raman study² of both liquid and solid TeCl₄, we felt the infrared spectrum of the solid would be of interest.

The only absorption by TeCl₄ in a mineral oil mull above 250 cm.⁻¹ is a broad, intense envelope with peaks at 348 and 361 cm.⁻¹ The symmetry of pentachlorotellurate(IV) ion,³ or that of the TeCl₄ molecule, should result in a much richer infrared spectrum if these species were present in any significant amount. Also, our infrared data for potassium hexachlorotellurate(IV) show only a rather broad absorption below 300 cm.⁻¹, and our failure to find any corresponding frequency in the TeCl₄ spectrum leads us to reject the TeCl₆²⁻ ion as a major constituent of crystalline TeCl₄. While instrumental limitations prevented us from examining the region below 250 cm.⁻¹ the vibrational data, coupled with the observation that molten TeCl₄ displays electrical conductivity,⁴ are

in accord with the proposal of ionic species for the solid material.

TABLE			
Absorption Frequencies, cm ⁻¹ , for TeCl ₄			
	Raman ^a		Infrared ^b
Liquid		Solid	Solid
		87 (6)	
148 ± 5 (1-2), dp?		143 (3)	
[176] (0-1)			
195 (0+)		191 (2-)	
231 (1-2)			
		[246] (0+)	
		[290] (0-1)	
330 (0-1)			
342 (16), dp		342 (20)	248 } vs.
377 (20), p		374 (18)	
		415 (0+)	361 }
[458] (1-2)			
[499] (1-)		[492] (0)	

^a Data from reference 2. Figures given in brackets are uncertain. Relative intensity estimates are given in parentheses. p = polarized; dp = depolarized.

^b This work.

While final decision regarding the nature of crystalline TeCl₄ must await the results of X-ray crystallographic analysis, preliminary reports of which have been given,⁵ it would seem that the

¹ A. Schmitt and W. Zeil, *Z. Naturforsch.* 1963, **18a**, 428.

² H. Gerding and H. Houtgraaf, *Rec. Trav. chim.*, 1954, **73**, 737.

³ G. F. Bell and K. Lott, "Modern Approach to Inorganic Chemistry", Butterworths, London, 1963, p. 237.

⁴ A. Voigt and W. Biltz, *Z. anorg. Chem.*, 1924, **133**, 298.

⁵ (a) P. Khodadad, P. Laruelle, and J. Flahaut, *Compt. rend.*, 1964, **259**, 794; (b) C. B. Shoemaker and S. C. Abrahams, *Acta Cryst.*, 1965, **18**, 296; (c) A. W. Cordes *et al.*, *Acta Cryst.*, 1964, **17**, 17.

bulk of the presently available information favours the $\text{TeCl}_3^+ \text{Cl}^-$ formulation. The quadrupole resonance findings are perhaps better explained as resulting from crystal packing effects.

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