Tellurocyanate: *X*-Ray Crystal Structure of the Bis(triphenylphosphoranylidene)ammonium Salt

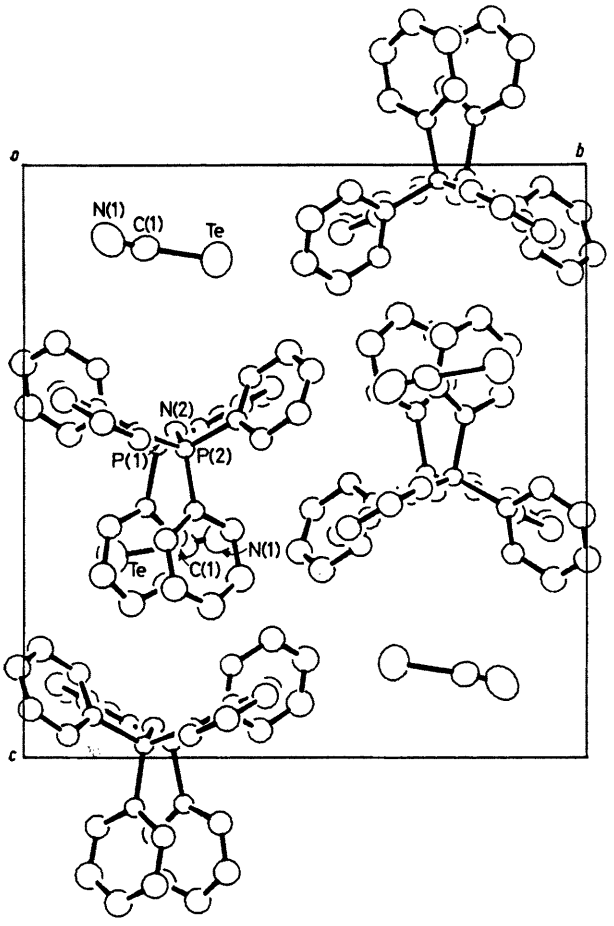
By ALAN S. FOUST

(*Chemistry Department, University of Bergen, N-5014 Bergen, Norway*)

Summary The bis(triphenylphosphoranylidene)ammonium salt of tellurocyanate has been shown by single-crystal *X*-ray crystallography to contain monomeric essentially linear $TeCN^-$.

THE tellurocyanate ion, $TeCN^-$, was probably first made in 1926[1] although it was claimed in 1925 and retracted in 1930 by another group of workers.[2,3] It has been stated[4] that $TeCN^-$ does not exist at room temperature. In 1968,[5] the sensitive NEt_4^+ salt of $TeCN^-$ was isolated, chemically analysed, and the CN stretching frequency measured by i.r. and Raman spectroscopy. The absence of 'mutual exclusion' was taken to prove the monomeric nature of the tellurocyanate.

The NMe_4^+ and $AsPh_4^+$ salts of $TeCN^-$ were reported[6] in 1971 and shown to be more stable. However, structural confirmation by *X*-ray methods was hindered by disorder



and incomplete i.r.,[7] Raman,[7] and ESCA[8] data were presented.

The stable bis(triphenylphosphoranylidene)ammonium salt of tellurocyanate has been reported[9] recently with complete i.r. and Raman data and force constants have been analysed.[10] In this communication we report the *X*-ray structure determination of this salt which confirms that tellurocyanate is monomeric and essentially linear.

Crystal data: pale yellow needles, space group $P2_1/n$, $a = 12{\cdot}034(1)$, $b = 15{\cdot}672(1)$, $c = 16{\cdot}779(1)$ Å, $\beta = 92{\cdot}44(2)°$, D_m (flotation) = 1·44, $D_c = 1{\cdot}454$ g cm^{-3} for $Z = 4$. Data were collected with Nb-filtered Mo-K_α radiation to $\theta = 25°$ in one independent unit and yielded 3032 observations [$I > 3\sigma(I)$] for the 6228 measurements. The test crystal was small ($\mu R = 0{\cdot}06$), so no absorption correction was performed. The current stage of refinement with phenyl hydrogens in assumed positions and only the tellurocyanate and P and N atoms anisotropic has converged with conventional weighted and unweighted *R* values of 4·6 and 6·3%, respectively.†

The anion is essentially linear [∠Te–C–N, 175(1)°] and the distances Te–C and C–N are 2·02(1) and 1·07(1) Å, respectively. The cation is characteristically bent [∠P(1)–N–P(2), 143·2(3)°] with P–N distances of 1·563(5) and 1·578(5) Å. The cyanide nitrogen has two short contacts with phenyl hydrogens [2·61(1) and 2·77(1) Å].

The Te–C and C–N distances are shorter than predicted.[11] These distances may be increased to 2·03 and 1·09 Å with thermal riding motion corrections but we have not succeeded in deriving a satisfactory rigid-body model for the thermal motion. Temperature factors and standard deviations are high within the tellurocyanate ion and the tellurium population drops to 93% if this parameter is allowed to vary.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as a Supplementary Publication from the British Library, Lending Division, No. SUP. 22535 (31 pp.). For details of obtaining this material, see *J.C.S. Dalton* or *Perkin I* and *II*, 1978, Index Issues.

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