all ± 0.5°. The phenyl groups have been assumed regular hexagons with $Te-C_1 \cdots C_4$ linear. The $Te-C_1$ bonds are, within the accuracy, of normal length, about 2.10 Å.

The mean length, 2.67 Å, of the two, approximately equal Te—S bonds in III is within the accuracy the same, 2.68 Å, as found for Te—S in centrosymmetric square-planar complexes[2]. In I and II the Te—S bonds are shorter, 2.50 Å, and the Te—Cl and Te—Br bonds, in directions approximately linear to the Te—S bonds, are correspondingly longer. This is the same bond lengthening effect on Te-halogen bonds, of thiourea ligands in *trans* positions to halogen, as observed[2] in *cis*-$Te(tu)_2Cl_2$ and *cis*-$Te(tu)_2Br_2$.

The phenyl group has, however, a far more pronounced bond lengthening effect in a direction *trans* to itself than has thiourea. This effect of the phenyl group (strictly: the phenate ion when regarded as a coordinating ligand) is so large so as to virtually expel the ligand *trans* to it, and to make the complexes three-coordinated. In the crystals of III, there is a chloride ion in a direction 165° to the C—Te bond at a distance of 3.60 ± 0.02 Å from tellurium; correspondingly, in I and II there are chlorine and bromine atoms, respectively, in directions of 164° at distances $Te \cdots Cl = 3.71 \pm 0.015$ Å and $Te \cdots Br = 3.77 \pm 0.01$ Å. These may be regarded as the fourth, missing ligands of square-planar arrangements, or at any rate, as very loosely bound ligands. In terms of a bonding scheme for divalent tellurium complexes based on *p*-orbitals[2], the highly nucleophilic phenate ion engages a tellurium 5*p*-orbital in bonding so effectively, that little or no bonding power of this *p*-orbital is left for bonding in a direction *trans* to the C—Te bond.

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Structure of the Triselenocyanate Ion in the Potassium Salt

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The pseudohalogens, thiocyanogen[1,2] and selenocyanogen[3,4] add the respective pseudohalide ions to give trithiocyanate[5,6] and triselenocyanate[4,7] ions, like the halogens. Salts of the former are very unstable. In rounding off our work[8,9] on divalent tellurium complexes, we sought for a divalent selenium complex suitable for crystal structure analysis, and have succeeded in determining the structure of potassium triselenocyanate hemihydrate, $K(SeCN)_3 \cdot \frac{1}{2}H_2O$, first prepared by Verneuil[7] although by him described without crystal water.

We prepared the salt from concentrated aqueous potassium selenocyanate by oxidation at room temperature with bromine dissolved in benzene. The reddish brown crystals which separated out were recrystallized from the aqueous mother liquor, by dissolving them through gentle heating and allowing the solution to cool slowly. (Found: Se 65.07; 65.37. Calc. for $K(SeCN)_3 \cdot \frac{1}{2}H_2O$: Se 65.25).

The salt forms long monoclinic prisms elongated along the *b* axis, with $a = 17.00$ Å, $b = 4.44$ Å, $c = 13.86$ Å, $\beta = 122°$. The space group is C_2^3-C2 and there are four formula units per unit cell; density, calc. 2.72, found 2.74 g/cm³. The intensities of 206 $h0l$ and 43 $hk0$ reflections were read from zero-level Weissenberg photographs taken with Cu$K\alpha$ radiation. The approximate positions of the selenium atoms in the *b*- and *c*-axis projections were found from the Patterson maps, and the projections were refined through Fourier and difference syntheses. The reliability index R is 0.087 for the $h0l$ and 0.109 for the $hk0$ reflections. The selenium coordinates, with origin on twofold axis at $y(Se_1)$ are, Se_1: $x = 0.1553$, $y = 0$, $z = 0.1351$; Se_2: $x = 0.3035$, $y = 0.0019$,

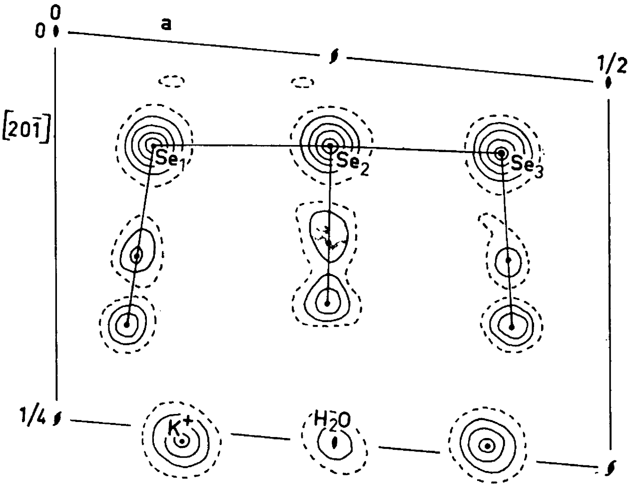

Fig. 1. Electron density projection of potassium triselenocyanate hemihydrate along the *b* axis. The 4-electron line is dashed. Contour intervals: 14 e·Å^{-2} for selenium, 7 e·Å^{-2} for potassium and 2 e·Å^{-2} for lighter atoms

$z = 0.1129$; Se$_3$: $x = 0.4540$, $y = -0.0029$, $z = 0.1021$, and the potassium coordinates, $x = 0.6303$, $y = -0.2300$, $z = 0.4855$. The water molecule lies on the twofold axis at $x = \frac{1}{2}$, $z = \frac{1}{2}$. The *h0l* Fourier map is reproduced in Fig. 1.

The Se$_1$—Se$_2$—Se$_3$ angle is 177° and the Se$_1$—Se$_2$ and Se$_2$—Se$_3$ bond lengths are 2.70 Å and 2.64 Å, respectively, with estimated standard deviations of less than 0.5° and 0.01 Å. The values for bond lengths are not far from the sum, 2.63 Å, of the single covalent radius, 1.17 Å, of selenium and a predicted[9] ''half *p*-bond'' radius of about 1.46 Å.

The selenocyanate groups have been assumed linear. The terminal selenocyanate groups of an ion lie in approximately the same plane, the middle selenocyanate group makes angle of about 60° with this plane. There are fairly close non-bonded Se—Se contacts between adjacent ions along the twofold screw axis at $x = \frac{1}{4}$, $z = 0$: 3.46 Å between Se$_2$ atoms across the screw axis, and 3.56 and 3.57 Å between Se$_1$ and Se$_3$ atoms.

A full account of the work will be published later.

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