

## Stable Salts of the Tellurocyanate Ion

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Recently, Downs<sup>1</sup> has shown that it is possible to isolate a salt of the tellurocyanate anion, provided the cation employed is very weakly polarizing. Attempts to isolate salts of this anion with small alkali cations have failed.<sup>1,2</sup>

The salt synthesized by Downs,<sup>1</sup> tetraethylammonium tellurocyanate, made from the corresponding cyanide and tellurium in dimethylformamide, formed pale yellow crystals, probably containing one mole of dimethylformamide per mole of salt. Its highly deliquescent nature, and its sensitivity to oxygen, precluded further studies.

Previously we have shown that protic solvents, and small alkali ions and other hard Lewis acids, associate to the nitrogen end of the thiocyanate ion and selenocyanate ion, and thereby markedly affect the electronic distribution in these ions.<sup>3</sup> In the case of the selenocyanate ion, this association causes a weakening of the carbon-selenium bond sufficient to make the selenium atom electrophilic. Similarly, in the case of the tellurocyanate ion, hard Lewis acids are anticipated to facilitate the breaking of the even weaker carbon-tellurium bond.

As water will decompose salts of the tellurocyanate ion immediately,<sup>1</sup> a synthesis of non-deliquescent salts of this ion would simplify further studies of the ion. As tetramethylammonium and tetraphenylarsonium salts of the thiocyanate and selenocyanate ions, contrary to the tetraethylammonium salts, are very stable and non-hygroscopic salts,<sup>3</sup> we attempted to make salts of the tellurocyanate ion with these two cations. As solvent for the reaction of tetramethylammonium cyanide and tetraphenylarsonium cyanide with black tellurium powder, acetonitrile was used. This solvent, when purified according to Coetzee,<sup>4</sup> has previously been found not to polarize the selenocyanate ion sufficiently to weaken the carbon-selenium bond.<sup>3</sup> Furthermore, the lower dielectric constant of this solvent,<sup>5</sup> compared with that of

dimethylformamide, might lead to products that do not retain solvent molecules.

The reaction between the cyanides and excess tellurium, in acetonitrile at room temperature, was found to be fairly rapid and close to quantitative. Due to the high solubility of the tetramethylammonium salt in acetonitrile, only modest yields, 10–20 %, of this salt could be obtained by direct crystallization from the filtered reaction mixture, even from very concentrated solutions, after several hours at  $-30^{\circ}\text{C}$ . As this salt was found to be far less soluble in acetone, the reaction mixture was evaporated to dryness in vacuum, and the product recrystallized from a minimum amount of acetone. In this way the yield of pure tetramethylammonium tellurocyanate was usually more than 50 %. The use of acetone offered an additional advantage, as traces of unreacted tetramethylammonium cyanide, due to its very low solubility in this solvent, was easily separated from the tellurocyanate.

Tetraphenylarsonium tellurocyanate, on the other hand, was far less soluble in acetonitrile than the corresponding cyanide, and the product separated as a feebly yellow precipitate during the reaction between the cyanide and tellurium. Upon crystallization from acetonitrile, a yield of more than 60 % of pure tetraphenylarsonium tellurocyanate was obtained. Acetone was found to be a convenient crystallization agent for this salt as well.

Additional crops of impure salts could be obtained by adding diethyl ether to the mother liquors. As both salts decomposed in warm solvents, crystallization could only be performed from luke-warm solutions. Elemental analysis, UV and IR spectra of the two salts of the tellurocyanate ion, crystallized from acetonitrile or acetone, did not suggest any retention of solvent molecules in the crystals.

Tetraphenylarsonium tellurocyanate, when properly dried, decomposed only slowly in humid air. This salt, when kept in a closed bottle, may be stored for months, even in direct sunlight, without any visible signs of decomposition. If, however, traces of solvent are left on the crystals, the decomposition in humid air is rapid. Tetramethylammonium tellurocyanate is less stable, and slowly darkens on prolonged storage. This salt decomposes rather rapidly in humid air and appears

Table 1. IR and UV data of some pseudohalide ions in acetonitrile.

	IR			UV	
	$\nu_{\max}$ $\text{cm}^{-1}$	$\Delta\nu_{\frac{1}{2}}$ $\text{cm}^{-1}$	$A \times 10^{-4} \text{ M}^{-1}\text{cm}^{-2}$	$\lambda_{\max}$ $\text{m}\mu$	$\epsilon \times 10^{-3} \text{ M}^{-1}\text{cm}^{-2}$
$\text{TeCN}^-$	2081	12	1.8	247	14.05
$\text{SeCN}^-$	2068	10	2.2	273	5.00
$\text{SCN}^-$	2059	12	4.1	252	4.52
$\text{OCN}^-$	2140	9	5.2	231	3.62
$\text{CN}^-$	2058	14	0.059		
$\text{NNN}^-$	2005	10	7.2		

deliquescent, but this may be due to the presence of traces of tetramethylammonium cyanide, either co-precipitated or formed through already started decomposition. The very hygroscopic cyanide will then absorb water, increase the amount of cyanide and thus rapidly accelerate the decomposition.

As noted by Downs,<sup>1</sup> a solution of a salt of the tellurocyanate ion reacts readily with oxygen. Tellurium dioxide is precipitated. The reaction is studied further. The dry salts, on the other hand, were found to be unaffected by oxygen.

The crystals of tetramethylammonium tellurocyanate were irregularly shaped. Tetraphenylarsonium tellurocyanate formed slightly yellow, tetragonal prisms from acetone, suitable for single-crystal X-ray work. The prisms were bounded by {110} and {011}. The external symmetry corresponds to a fourfold inversion axis. Using  $\text{MoK}\alpha_1$  radiation ( $\lambda = 0.70926 \text{ \AA}$ ), the unit cell dimensions, with standard deviations in parentheses, were found to be,  $a = 12.347(10) \text{ \AA}$ , and  $c = 7.317(7) \text{ \AA}$ . Density, found by flotation, 1.56, calc. for  $Z = 2$ , 1.55  $\text{g/cm}^3$ . Systematic absences are for  $hkl$  when  $h + k + l = 2n + 1$ . The space group is assumed to be  $I\bar{4}$  (No. 82). Since the general positions of this space group are eightfold, both cation and anion must possess fourfold symmetry. This can only be the fourfold inversion axis. As the tellurocyanate ion cannot reasonably possess a fourfold inversion centre, the apparent symmetry of the ion may be explained by systematic disorder in the crystals.

In Table 1 are collected some UV and IR data for the tellurocyanate ion and other pseudohalide ions, in acetonitrile

at room temperature. The measurements were performed on tetraphenylarsonium salts, free from hydrated water. The UV spectra of the tellurocyanate ion in the tetraphenylarsonium salt and in the tetramethylammonium salt were identical in the 230–350  $\text{m}\mu$  range. IR measurements were performed on a Perkin-Elmer 225 Grating Infrared Spectrophotometer, using a 0.1 cm liquid cell. UV measurements were performed on a Beckmann DB Spectrophotometer, using 0.1 cm quartz cells.

Further studies on the tellurocyanate ion are in progress in this laboratory.

*Experimental.* Acetonitrile and methanol were purified as reported previously.<sup>3</sup> The solvents were carefully flushed with dry nitrogen prior to use. All operations with solutions of the tellurocyanate salts were performed under dry nitrogen.

*Tetraphenylarsonium cyanide.* The salt, made according to Andreades and Zahnow,<sup>6</sup> was repeatedly dissolved in acetonitrile, some benzene was added, and the solvent mixture was removed in vacuum to ensure a complete removal of hydrated water in order thereby to cause precipitation of the last traces of the potassium salts. Finally, the salt was recrystallized from a minimum amount of acetonitrile, the crystals were powdered in a mortar, and dried to constant weight in a pre-weighed bottle, in which the product was dissolved in acetonitrile and diluted to desired volume.

*Tetraphenylarsonium tellurocyanate.* To 0.663 g tetraphenylarsonium cyanide in 50 ml acetonitrile was added 0.4704 g black tellurium powder. The reaction mixture was stirred at room temperature for 3 h, where-

upon excess tellurium was filtered off. Weight of unreacted tellurium, 0.2770 g, calc. 0.2642 g.

To 11.5 g tetraphenylarsonium cyanide, dissolved in 200 ml acetonitrile, was added 3.58 g tellurium powder. The reaction mixture was stirred for 6 h, and the slightly yellow product precipitated slowly. The reaction mixture was finally slowly heated to 40°C to dissolve the product, the solution was set aside for some minutes, and the clear solution was decanted from traces of unreacted tellurium. The residue was washed with 20 ml acetonitrile, making the total volume 220 ml. After 2 h at -7°C, the clear solution was decanted from the precipitated product, and the crystals were washed with cold acetonitrile and finally with ether, yielding 5.5 g pure tetraphenylarsonium tellurocyanate. Removal of the mother liquor from the product by filtration was found to cause severe decomposition, as the crystals, when wet by acetonitrile, were rapidly attacked by moisture.

The volume of the mother liquor was reduced in vacuum to 50 ml, and an additional amount of 4.5 g pure tetraphenylarsonium tellurocyanate thereby precipitated, making the total yield 10 g, or 66 % based on consumed tellurium. By addition of diethyl ether to the mother liquor, unreacted tetraphenylarsonium cyanide and the rest of the tellurocyanate could be precipitated.

In a similar experiment, but where the reaction mixture was evaporated to dryness after completed reaction and the product recrystallized from acetone after filtration, the yield of pure tetraphenylarsonium tellurocyanate, from 7.95 g tetraphenylarsonium cyanide and excess tellurium, was 5.5 g, or 53 %. (Found: C 56.62; H 3.98; N 2.57. Calc. for  $C_{24}H_{20}AsN_2Te$ : C 55.92; H 3.75; N 2.61.)

*Tetramethylammonium tellurocyanate.* To tetramethylammonium cyanide in 250 ml acetonitrile, made *in situ* from 26.4 g tetramethylammonium chloride and 31.0 g potassium cyanide,<sup>6</sup> and filtered, was added 12.76 g tellurium powder, and the mixture was stirred for 3 h at room temperature. Traces of unreacted reactants were filtered off, and the solvent was removed in vacuum, yielding 21.6 g raw product, 95 % based on added tellurium, of rather high purity. Pure samples could be obtained in more than 50 % yield through one crystallization from acetone. (Found: C 26.43; H 5.45; N 11.32; Calc. for  $C_8H_{12}N_2Te$ : C 26.33; H 5.30; N 12.29.)

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### Fluorimetric Determination of Homovanillic Acid in Tissues, Using Anion Exchange Separation and Mixed Solvent Elution

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Several methods have been employed for the quantitative determination of homovanillic acid (HVA, 3-methoxy-4-hydroxyphenylacetic acid) in biological material such as brain tissue, cerebrospinal fluid and urine. The final assay procedures for this important metabolite of dopamine include, *e.g.*, gas-liquid chromatography, spectrophotometry and spectrofluorimetry, after suitable chemical rearrangement of the HVA.

A spectrofluorimetric method commonly used is that of Andén *et al.*,<sup>1</sup> which with minor modifications has been adopted by other workers.<sup>2-4</sup> The method involves oxidation of the sample, using potassium ferricyanide in ammonia. This results in the formation of a highly fluorescent