

The Isolation of a Salt of the Tellurocyanate Anion

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A RECENT study¹ has shown that potassium tellurocyanate cannot be prepared by the obvious methods, and so probably does not exist at room temperature. It is known² that a solution of potassium cyanide in liquid ammonia will dissolve tellurium, giving a solution which on evaporation leaves only potassium cyanide and tellurium. This suggests that tellurocyanate ion may exist in solution, but that it cannot exist adjacent to a cation, even as big as that formed by potassium, without an interposed solvent molecule. I report the preparation of a salt containing tellurocyanate as its only anion.

The first fundamental vibration of the tellurocyanate group has been calculated to occur at 2083—2086 cm.^{-1} and has been observed¹ in the previously known tellurium dicyanide.³ Acetone is relatively transparent in this region and is a powerful solvent for potassium selenocyanate and thiocyanate but not for potassium cyanide, so it seemed a reasonable medium in which to investigate the reaction of potassium cyanide and tellurium. These two, when warmed with acetone, give no obvious signs of reaction after half an hour. However, the filtrate from the foregoing mixture, when added to water, precipitated tellurium.

The i.r. spectrum of this filtrate showed in addition to bands due to the solvent a strong band at 2079 cm^{-1} . A solution of potassium cyanide only, in acetone, prepared in the same way, showed only the solvent bands. The tellurium-containing solution after being boiled with selenium in the absence of oxygen was found to be free of tellurium, and its i.r. spectrum now lacked the band at 2079 cm^{-1} , but had instead a band at 2067 cm^{-1} ; this band also appeared in a solution of potassium selenocyanate in acetone. Substitution of sulphur for selenium gave an analogous result. Evaporation of a solution of potassium cyanide and tellurium in acetone left a mixture of potassium cyanide and tellurium together with a little oily material, probably produced by attack on the acetone by the potassium cyanide. Caesium cyanide and tellurium in liquid ammonia behaved similarly. Such a mixture was much more soluble in acetone than in liquid ammonia and gave a yellow-orange solution. Attempted concentration of this solution to crystallisation resulted in the liberation of tellurium.

As even the caesium ion was too strongly polarising to permit the isolation of an unsolvated tellurocyanate, the much larger, and hence more feebly polarising, tetra-alkylammonium cations were employed in further attempts to prepare a

solid tellurocyanate. Tetraethylammonium cyanide and tellurium react in the presence of dimethylformamide to give a solution from which pale yellow crystals were obtained on evaporation. They had a tellurium content of 34.5% which compared with the calculated value of 35.8% for $\text{C}_{12}\text{H}_{27}\text{N}_3\text{OTe}$, corresponding to the retention of one mol. of dimethylformamide per mol. of tetraethylammonium tellurocyanate. Its highly deliquescent nature and sensitivity to oxygen has so far precluded the obtaining of satisfactory figures for elemental analysis. This compound, which is rapidly, and exothermically, oxidised by air is soluble in acetone, and dimethylformamide. It is decomposed by addition to water and tellurium is liberated. Non-aqueous solutions, of the salts of the first row transition metals and also silver, lead, and mercury decompose the compound at once. Its Raman spectrum in dimethylformamide solution shows a band at 2080 cm^{-1} , absent in the parent solvent, and its conductivity in dimethylformamide is comparable to those of the corresponding selenocyanate, thiocyanate, and iodide, showing it to be a 1:1 electrolyte.

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¹ N. N. Greenwood, R. Little, and M. J. Sprague, *J. Chem. Soc.*, 1964, 1292.

² F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1926, **48**, 2319.

³ H. E. Cocksedge, *J. Chem. Soc.*, 1908, **23**, 2175.