

The Crystal Structure of Potassium Seleniumtriselenocyanate Hemihydrate

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Potassium seleniumtriselenocyanate hemihydrate, $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was first isolated by Verneuil,¹ although by him described as a monohydrate.

The salt was in the present work prepared from selenium diselenocyanate, $\text{Se}(\text{SeCN})_2$, and aqueous potassium cyanide.² The salt forms reddish-brown prisms extended along the short a - c diagonal, with $a=9.170(2)$ Å, $b=13.377(3)$ Å, $c=9.057(2)$ Å, $\alpha=106.22(2)^\circ$, $\beta=100.64(2)^\circ$, and $\gamma=99.07(2)^\circ$. The space group, from structure analysis, is $P\bar{1}$ (No. 2), and there are four formula units per unit cell; density, calc. 2.87, found 2.89 g/cm³.

The intensities of 3150 measurable reflections were collected by means of a Siemens AED 1 single-crystal diffractometer using Nb-filtered $\text{MoK}\alpha$ radiation. The intensities were corrected for absorption.

The structure was solved by three-dimensional Patterson and Fourier methods, and refined by full-matrix least squares with anisotropic temperature factors. Altogether 208 parameters were refined. The final reliability index, R , was 0.042. The coordinates of the selenium atoms are listed in Table 1.

Table 1. Coordinates of the selenium atoms, in fractions of triclinic cell edges. Origin at a centre of symmetry. Standard deviations from least squares are given in parentheses.

	x	y	z
Se ₁	0.06300(10)	0.13858(7)	-0.06314(10)
Se ₂	0.07100(9)	0.12554(7)	0.19737(10)
Se ₃	-0.19849(10)	0.10495(8)	0.18396(12)
Se ₄	0.72016(9)	0.12574(7)	0.60281(10)
Se ₅	0.46001(9)	0.13382(7)	0.60678(10)
Se ₆	0.47137(10)	0.13623(8)	0.87409(10)
Se ₇	0.41279(11)	0.12399(8)	0.24275(11)
Se ₈	0.11003(11)	0.13602(8)	0.56510(11)

The anion of the salt is shown in Fig. 1. The eight selenium atoms are approximately coplanar, the largest deviation of a selenium atom from the least squares plane of the eight atoms being 0.21 Å. The six cyano groups of the unit are all located on the same side of the least squares plane.

There are four rather short Se-Se bonds, and four rather long, bridging Se-Se bonds within the unit. The short ones are 2.395(2) to 2.419(2) Å, and thus definitely longer than the Se-Se single-bond distance, 2.34 Å. The long ones are 3.089(2) to 3.244(2) Å, and thus shorter than van der Waals approaches. Each long Se-Se bond occurs *trans* to a short Se-Se bond, the Se-Se...Se angles at the middle selenium atoms, Se₂ and Se₅, of the four approximately linear three-selenium systems are 170.58(6)° to 174.94(5)°. The total lengths of these rather unsymmetrical systems (the sum of the lengths of the two Se-Se

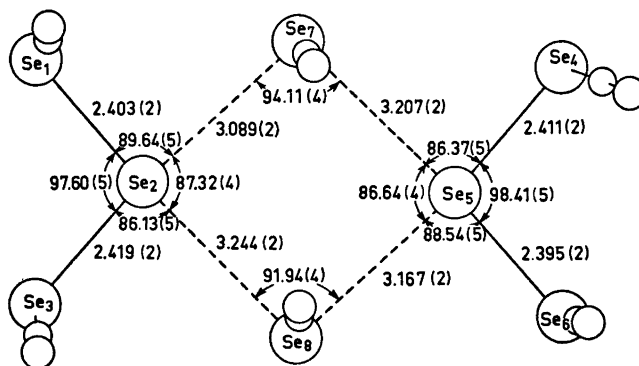


Fig. 1. The di- μ -selenocyanato-bis(diselenocyanatoselenate(II)) anion, as seen normal to the least squares plane of the selenium atoms.

bonds) are 5.508 to 5.647 Å, and thus 0.19 to 0.33 Å longer than the more symmetrical linear three-selenium systems of the triselenocyanate and triselenourea ions.³

The eight-selenium unit can be looked upon as built up of two selenium diselenocyanate molecules, $\text{Se}(\text{SeCN})_2$, bridged together through the selenium atoms of two selenocyanate ions. In the crystals of selenium diselenocyanate, the molecules lie across a crystallographic mirror plane, with the middle selenium atom in the plane; the Se-Se bond lengths are 2.33 Å and the Se-Se-Se angle is 101°. In the present adduct with potassium selenocyanate, the selenium diselenocyanate molecules retain their approximate shape. The Se-Se bonds, on being approached at approximately 180° by selenocyanate ions, become a little longer.

Several rather short $\text{Se}\cdots\text{Se}$ contacts, from 3.34 Å upwards, occur between eight-selenium units.

Details of the structure will be published later.

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The Diisocyanatoargentate Ion

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The univalent silver ion, a B-subgroup ion with d^{10} closed-shell configuration, has a pronounced tendency to occur in linear environment, similarly to Au^+ , Hg^{2+} , and Cu^+ . According to Dunitz and Orgel,¹ this stereochemical behaviour is primarily due to the low d - s separation in these d^{10} ions.

With regard to Ag^+ , which is known to form octahedral, tetrahedral, and linear complexes, the coordination number generally decreases with increasing electron-donor ability of the attached ligands.¹ The Ag^+ ion is known to form complex anions, generally formulated as AgL_2^- , with a series of inorganic and organic anions. The stability of the complex anions is considerably higher in dipolar aprotic solvents than in protic solvents.^{2,3} Furthermore, it appears that the coordination number of silver increases from protic to aprotic solvents.⁴ Several complex silver anions, as $\text{Ag}(\text{IO}_3)_2^-$,⁵ $\text{Ag}(\text{NCO})_2^-$,⁶ $\text{Ag}(\text{NO}_2)_2^-$,⁷ $\text{Ag}(\text{NO}_3)_2^-$,⁸ *etc.*, have been suggested from studies of solubilities and from potentiometric measurements, but no actual salts of these anions have been isolated so far. Salts of the assumed anions, $\text{Ag}(\text{SCN})_2^-$ and $\text{Ag}(\text{SeCN})_2^-$, have been prepared, and a complete crystal structure determination of $\text{NH}_4\text{Ag}(\text{SCN})_2$ ⁹ has shown that the substance consists of AgSCN molecules and ammonium and thiocyanate ions and no ion of type $\text{Ag}(\text{SCN})_2^-$. The same has been found for $\text{KAg}(\text{SeCN})_2$.¹⁰ In these salts there are therefore two different pseudohalide groups, one ionic and one covalently bonded to the silver atom, giving rise to two separate absorptions in the C-N stretching region.¹¹⁻¹³

Recently, Bottger and Geddes¹⁴ have shown that in salts of the general type Me_nNAgL_2 , where L is Cl or Br, there are no discrete AgL_2^- ions in the solids, but effectively infinite chains of tetrahedral AgL_4 units sharing common edges, making anionic units of $(\text{Ag}_2\text{L}_4)_n^{2n-}$. The IR spectra of the salts in dimethyl sulfoxide suggested the presence of discrete anions of type AgL_2^- , but no definite conclusion could be reached whether these anions were bent or linear. Dallinga and Machor¹⁵ have found that the anion AgI_2^- is bent in solution, with the I-Ag-I angle 111°, that is, rather close to the tetrahedral angle. The well-known linear silver complexes, the cation $\text{Ag}(\text{NH}_3)_2^+$ ^{16,17} and the anion $\text{Ag}(\text{CN})_2^-$,^{18,19} are therefore examples more of exceptional than of general coordination behaviour of the univalent silver ion, confirming that only very electron-donating ligands will form linear di-coordinated complexes with the silver ion.¹

We now wish to report the synthesis of salts of the $\text{Ag}(\text{NCO})_2^-$ ion. As pointed out by Norbury,²⁰ the cyanate ion has received relatively little attention as a ligand, probably due to the rather rapid decom-