The Crystal Structure of Potassium Seleniumtriselenocyanate Hemihydrate

SVERRE HAUDE

Chemical Institute, University of Bergen, Bergen, Norway

Potassium seleniumtriselenocyanate hemihydrate, KSe(SeCN)$_3$:H$_2$O, was first isolated by Verneuil, although by him described as a monohydrate.

The salt was in the present work prepared from selenium diselenocyanate, Se(SeCN)$_3$, and aqueous potassium cyanide. 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, $\alpha = 106.22(2)^\circ$, $\beta = 100.64(3)^\circ$, 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/cm$^3$.

The intensities of 3150 measurable reflections were collected by means of a Siemens AED I single-crystal diffractometer using Nb-filtered MoK$_x$ 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.

<table>
<thead>
<tr>
<th></th>
<th>$x$ (Å)</th>
<th>$y$ (Å)</th>
<th>$z$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_1$</td>
<td>0.06300(10)</td>
<td>0.138587(7)</td>
<td>−0.06314(10)</td>
</tr>
<tr>
<td>Se$_2$</td>
<td>0.07100(9)</td>
<td>0.125547(7)</td>
<td>0.19737(10)</td>
</tr>
<tr>
<td>Se$_3$</td>
<td>−0.19849(10)</td>
<td>0.104958(8)</td>
<td>0.18936(12)</td>
</tr>
<tr>
<td>Se$_4$</td>
<td>0.72016(9)</td>
<td>0.12574(7)</td>
<td>0.60281(10)</td>
</tr>
<tr>
<td>Se$_5$</td>
<td>0.46001(9)</td>
<td>0.13352(7)</td>
<td>0.60678(10)</td>
</tr>
<tr>
<td>Se$_6$</td>
<td>0.47137(10)</td>
<td>0.13623(8)</td>
<td>0.87409(10)</td>
</tr>
<tr>
<td>Se$_7$</td>
<td>0.41279(11)</td>
<td>0.12399(8)</td>
<td>0.24275(11)</td>
</tr>
<tr>
<td>Se$_8$</td>
<td>0.11005(11)</td>
<td>0.13602(8)</td>
<td>0.56510(11)</td>
</tr>
</tbody>
</table>

The anion of the salt is shown in Fig. 1. The eight selenium atoms are approximately coplanar, the largest deviation of a least squares from a square 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, Se$_4$ and Se$_5$, of the four approximately linear three-selenium systems are 170.58(6)$^\circ$ to 174.94(5)$^\circ$. 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(diselenocyanatosenenate(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, Se(SCN)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°.³ 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 Se⋯Se contacts, from 3.34 Å upwards, occur between eight-selenium units.

Details of the structure will be published later.


Received February 16, 1971.

The Diisocyanatoargentate Ion

TOR AUSTAD, JON SONGSTAD and KJELL ASE

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

The univalent silver ion, a B-subgroup ion with d¹⁰ closed-shell configuration, has a pronounced tendency to occur in linear environment, similarly to Au⁺, Hg²⁺, and Cu⁺. According to Dunlitz and Orgel,¹ this stereochemical behaviour is primarily due to the low d-s separation in these d¹⁰ 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 AgL₆⁻, with a series of inorganic and organic anions. The stability of the complex anions is considerably higher in dipolar aprotic solvents than in protonsolvants.¹,³ Furthermore, it appears that the coordination number of silver increases from protonsolvent to aprotic solvents.⁴ Several complex silver anions, as Ag(IO₃)₆⁻, Ag(NCO)₆⁻, Ag(NO₃)₆⁻, 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, Ag(SCN)₆⁻ and Ag(SeCN)₆⁻, have been prepared, and a complete crystal structure determination of NH₄Ag(SCN)₂ has shown that the substance consists of AgSCN molecules and ammonium and thiocyano and no ion of type Ag(SCN)₆⁻. The same has been found for KAg(SeCN)₆. In the salts there are therefore two different pseudo-halide groups, one ionic and one covalently bonded to the silver atom, giving rise to two separate absorptions in the C–N stretching region.⁵–⁷

Recently, Bottger and Geddes¹⁴ have shown that in salts of the general type Mo₂A₄L₆, where L is Cl or Br, there are no discrete AgL₆⁻ ions in the solids, but effectively infinite chains of tetrahedral AgL₆ units sharing common edges, making anionic units of (AgL₆)₈⁻.¹⁵ The IR spectra of the salts in dimethyl sulfoxide suggested the presence of discrete anions of type AgL₆⁻, but no definite conclusion could be reached whether these anions were bent or linear. Dallinga and Machor¹² have found that the anion AgI₆⁻ 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 Ag(NO₃)₂⁺⁺,¹⁶,¹⁷ and the anion Ag(SCN)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.¹³

We now wish to report the synthesis of salts of the Ag(NCO)₆⁻ 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-