Selenourea Oxidation Products: the Structure of αα′-Diselenobisformamidinium Cation

By A. CHIESI, G. GROSSONI, M. NARDELLI,* and M. E. VIDONI

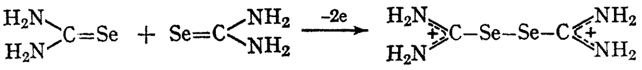
(*Istituti dei Chimica Generale ed Inorganica e di Strutturistica Chimica, Università degli Studi, Parma, Italy*)

Summary Aqueous solutions of silver(I) chloride–selenourea complexes decompose giving α,α′-diselenobisformamidinium dichloride.

SILVER chloride dissolves in aqueous concentrated selenourea solutions to give yellow liquids which slowly decompose at room temperature, even in the dark. An attempt to isolate crystals of selenourea–Ag^I complexes after several days gave a few pale-yellow stable crystals and a black-red powder which was not analysed but probably consisted of elemental selenium and silver. There were not enough crystals for a conventional chemical analysis, but they were sufficiently well developed for a successful *X*-ray study. This was started assuming the product to be a silver chloride–selenourea complex, but it was soon evident that no silver was present in the crystals which were then shown to be α,α′-diselenobisformamidinium dichloride, formed by oxidation of selenourea to give a stable diselenium-bridged cation. In some respects this oxidation is similar to that of diselenomalonamide which gives the diselenolylium cation.[1]

Oxidation of selenourea in a cooled HCl–EtOH solution with hydrogen peroxide, gave a pale yellow crystalline substance melting at 195° and decomposing at >210—212°, This product was the same *X*-ray powder diffraction pattern as the crystals described above and i.r. (KBr) (tentative assignments are given in parentheses): 3180—3220s,br, 3057s,br (NH_2-stretch); 1716sh, 1675sh, 1662s (NH_2-bending); 1402s, 1300sh,br (N–C–N–stretch, NH_2-rocking, C–Se-stretch); 1131w, 1122sh, 1080w, 1068sh (N–C–N stretch, NH_2-rocking); 645s, 632sh, 562w (C–Se-stretch, N–C–N deformation); 376m (N–C–Se-deformation).

The X-ray structural analysis shows that each selenourea part of the cation has a conformation similar to that expected for selenourea itself, so the mechanism of the oxidation probably involves the joining of two selenourea molecules, with a charge rearrangement and no proton transfer:



$$(H_2N)_2C{=}Se + Se{=}C(NH_2)_2 \xrightarrow{-2e} (H_2N)_2\overset{+}{C}{-}Se{-}Se{-}\overset{+}{C}(NH_2)_2$$

the oxidising agent, in the case of the Ag complex, being selenourea itself (which decomposes), atmospheric oxygen, or the Ag^+ ion.

Crystal data from rotation and Weissenberg photographs (Ni-filtered Cu-radiation) are as follows: $[SeC(NH_2)_2Cl_2$, $M = 316{\cdot}9$, $a = 12{\cdot}82(2)$, $b = 6{\cdot}01(1)$, $c = 12{\cdot}22(1)$ Å, $\beta = 108{\cdot}1°$ $(0{\cdot}1°)$, $Z = 4$, $U = 895{\cdot}6$ Å^3, $D_c = 2{\cdot}35$, $\mu = 167$ cm.$^{-1}$ (Cu-K_α), $F(000) = 600$; space group Cc or $C\,2/c$, the latter being used in the structural analysis. 865 independent reflexions were measured photometrically from equi-inclination Weissenberg photographs taken around (100) and (010). The structure was solved and refined by standard three-dimensional Patterson and Fourier methods; after three isotropic and four anisotropic cycles of Booth's differential synthesis the R was 9·2%.

The molecular conformation with distances and angles is shown in the Figure. The two selenourea parts of the molecule are strictly planar and nearly parallel to (100) with their terminal NH_2 groups hydrogen-bonded to the chloride ions which lie in the same plane.

No isostructurality with the similar α,α′-dithiobisformamidinium dichloride is observed from powder diffraction patterns, and from rotation and Weissenberg single-crystal data: $a = 8{\cdot}83(1)$, $b = 10{\cdot}54(1)$, $c = 19{\cdot}78(1)$ Å, $Z = 8$, $D_c = 1{\cdot}61$, $U = 1840$ Å^3, space group $Pbca$.

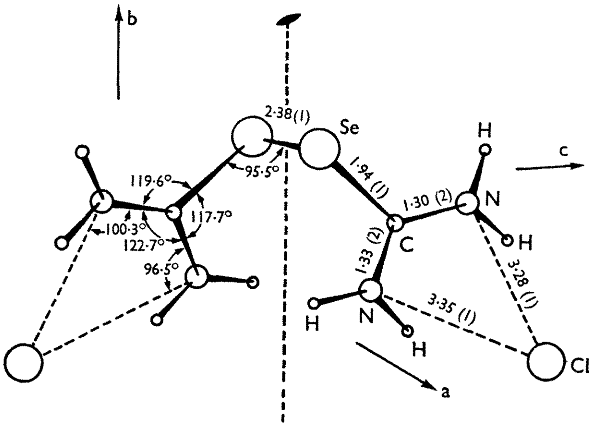


FIGURE. *Clinographic projection of a formula unit* $[SeC(NH_2)_2]_2Cl_2$. *Standard deviations for bond lengths are given in parentheses, those for angles range from* 0·5° *to* 1·4°.

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[1] K. A. Jensen and U. Henriksen, *Acta Chem. Scand.*, 1967, **21**, 1991.