Preparation and *X*-Ray Structure of $(Se_9Cl)(SbCl_6)$: A Seven-membered Selenium Ring

Romolo Faggiani, Ronald J. Gillespie,* Joseph W. Kolis, and Kailash C. Malhotra
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

The new compound $(Se_9Cl^+)(SbCl_6^-)$ prepared by the reaction of selenium with $NOSbCl_6$ in SO_2 contains the first example of a seven-membered selenium ring.

Although S_7 and several compounds containing seven-membered sulphur rings have been described,[1] no corresponding Se_7 rings have been reported.[2] There is evidence for the formation of Se_7 in the gas phase[3] and it appears that in CS_2 solution[4] Se_7 is in equilibrium with Se_6 and Se_8 but neither Se_7 nor any derivatives have been isolated. We report here the first example of a seven-membered selenium ring.

The cations Se_4^{2+}, Se_8^{2+}, and Se_{10}^{2+} have been prepared by oxidizing elemental selenium with oleum, $S_2O_6F_2$, AsF_5, or SbF_5.[5] However, even using excess of selenium, no cations containing a larger number of selenium atoms have been isolated. In particular, there is no evidence for the existence of Se_{19}^{2+} corresponding to S_{19}^{2+}, which is formed when excess of sulphur is oxidized by AsF_5,[6] although Se_n^{2+} cations ($n > 10$) have been postulated in molten salt systems.[7] Thus we were prompted to investigate the reaction of selenium with the mild oxidant $NOSbCl_6$ in solution in the hope of obtaining a Se_n^{2+} ($n > 10$) cation. The product of the reaction, however, was not an Se_n^{2+} cation but the novel compound $(Se_9Cl)(SbCl_6)$, which contains the Se_9Cl^+ cation.

The title compound was prepared by adding 0.491 g (0.357 mmol) of grey selenium and 0.201 g (0.714 mmol) of $NOSbCl_6$ to a double ampoule containing a frit and a Teflon stirrer bar.

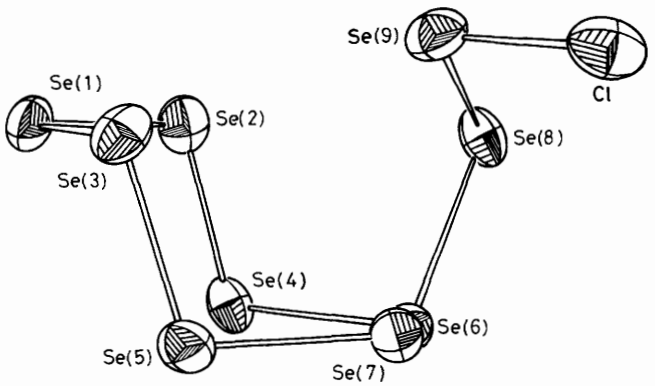

Figure 1. View of Se_9Cl^+ showing the chair conformation of the ring with the Se_2Cl in the *endo* position. Selected bond distances and angles: Se(1)–Se(2) 2.342 (4), Se(1)–Se(3) 2.324 (4), Se(2)–Se(4) 2.309 (5), Se(3)–Se(5) 2.341 (5), Se(4)–Se(6) 2.367 (4), Se(5)–Se(7) 2.270 (4), Se(6)–Se(7) 2.430 (4), Se(6)–Se(8) 2.466 (4), Se(8)–Se(9) 2.233 (5), Se(9)–Cl 2.208 (10); Se(2)–Se(1)–Se(3) 103.7(2), Se(1)–Se(3)–Se(5) 100.3(2), Se(3)–Se(5)–Se(7) 104.4(1), Se(5)–Se(7)–Se(6) 106.0(1), Se(7)–Se(6)–Se(4) 106.9(1), Se(2)–Se(4)–Se(6) 105.2, Se(1)–Se(2)–Se(4) 102.4(2), Se(7)–Se(6)–Se(8) 99.8(1), Se(6)–Se(8)–Se(9) 101.9(2), Se(8)–Se(9)–Cl 103.6(3).

Dry SO_2 (20 ml) was distilled into the flask and the mixture stirred for 1 week giving a red solution together with some unreacted selenium. The solution was filtered and placed in a freezer at −10 °C. After 1 week, large lustrous dark red crystals were formed.

The compound $(Se_9Cl)(SbCl_6)$ consists of a discrete cation $(Se_9Cl)^+$ and a well separated $(SbCl_6)^-$ counter ion. The cation has a seven-membered selenium ring with an Se_2Cl chain attached to the 6 position of the ring.† The ring is in the chair form (see Figure 1) with short and long Se–Se bonds alternating in length around the ring and varying from 2.270(4) to 2.430(4) Å. This alternation in bond length is a common phenomenon in sulphur and selenium rings and has been discussed by several authors.[6,8,9] The average Se–Se distance in the ring is 2.340(4) Å which is comparable to other Se rings [*e.g.*, 2.32(1) Å in $(Se_8)(AlCl_4)_2$].[10] The longest bond in the ring is between Se(6) and Se(7). This is also the longest bond in comparable S_7 rings. The unusual length of this bond has been attributed to the repulsion between eclipsed lone pairs on atoms 6 and 7.[8,11] The longest bonds are to the three-co-ordinated selenium atom [S(6)] as is commonly found in other cationic sulphur and selenium rings.

The shortest cross-ring interaction is 3.769(5) Å which is much longer than other transannular Se–Se bonds (*e.g.*, 2.789 Å in Se_8^{2+}),[10] so there appears to be little, if any, cross-ring interaction. The average of the angles in the ring is 104.2° which is typical for seven membered rings (*e.g.*, 104.7° in S_7I^+).[12]

The only previously reported examples of functionalized selenium rings are Se_6I^+, $Ph_2Se_6^{2+}$, and $Se_6I_2^{2+}$ which contain six-membered selenium rings.[13—15] But functionalized S_7 rings have been found in S_7O,[11] $(S_7I)(AsF_6)$,[12] $(S_{19})(AsF_6)_2$,[2] and $[(S_7I)_2I](SbF_6)_3$.[16] The ions S_{19}^{2+} and $(S_7I)_2I^{3+}$ contain S_7 rings bridged by S_5 and I respectively. In both cases, the bridging group is in the 6 position and it is *endo* as is the Se_2Cl group in the title compound.

The Se_9Cl^+ ions are well separated but there is a fairly close contact between the Se(1) atom and the Se(8) atom of a neighbouring cation [Se–Se 3.357(4) Å]. The $SbCl_6^-$ group is normal [average Sb–Cl distance 2.363(10) Å]. There are several long Se · · · Cl–Sb contacts, the shortest being 3.358(9) Å for Se(3)—Cl(4).

The Se_9Cl^+ ion is strikingly similar to a fragment of S_{19}^{2+}.[6] It is possible that Se_{19}^{2+} is formed initially, as in the oxidation of sulphur to S_{19}^{2+}, then an Se–Se bond of the bridging chain is oxidatively cleaved to form Se_9Cl^+. The active oxidant may be trace $SbCl_5$ resulting from an equilibrium such as $NOSbCl_6 \rightleftarrows NOCl + SbCl_5$. This is supported by the observation that selenium metal and $NOSbF_6$ do not appear to react under the same conditions.

We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

Received, 28th July 1986; Com. 1066

† *Crystal data:* crystals were sealed in Lindemann capillaries under dry nitrogen. M = 1080.6, Se_9Cl_7Sb, monoclinic, space group $P2_1/n$ (nonstandard setting of No. 14), a = 12.042(1), b = 12.44(1), c = 14.497(1) Å, β = 115.03(1)°, U = 1968(1) Å, Z = 4, $F(000)$ = 1903, $\mu(\text{Mo-}K_\alpha)$ = 201.8 cm^{-1}, D_c = 3.64 g cm^{-3}. Accurate cell parameters were obtained from 15 well centred reflections $20° < 2\theta < 30°$ using a Syntex $P2_1$ monochromatized diffractometer [$\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å]. Data were collected to 2θ = 50° for a total of 3860 reflections. Lorentz and polarization corrections and averaging (R_{int} = 0.025) gave 3091 unique reflections. The structure was solved by direct methods using the SHELX 76 package. After anisotropic displacement parameters were applied the structure refined to R = 11.7% for all reflections and R = 0.0708 (ωR = 0.0755) for 1849 reflections with $F > 3\,\sigma(F)$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

References

1 R. Steudel, R. Reinhardt, and F. Schuster, *Angew. Chem., Int. Ed. Engl.*, 1977, **10**, 715.
2 R. Steudel and E. M. Strauss, *Adv. Inorg. Radiochem.*, 1984, **28**, 135.
3 H. Fujisaki, J. B. Westmore, and A. W. Tickner, *Can. J. Chem.*, 1966, **44**, 3063.
4 R. Steudel and E. M. Strauss, *Z. Naturforsch., Teil B*, 1981, **36**, 1085.
5 R. J. Gillespie, *Chem. Soc. Rev.*, 1979, **8**, 315.
6 R. C. Burns, R. J. Gillespie, and J. F. Sawyer, *Inorg. Chem.*, 1980, **19**, 1423.
7 R. Fehrmann and N. J. Bjerrum, *Inorg. Chem.*, 1977, **16**, 2089.
8 J. Passmore, G. Sutherland, P. Taylor, T. K. Whidden, and P. S. White, *Inorg. Chem.*, 1981, **20**, 3839.
9 R. Steudel and F. Schuster, *J. Mol. Struct.*, 1978, **44**, 143.
10 R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, 1971, **10**, 1749.
11 R. Steudel, R. Reinhardt, and T. Sandow, *Angew. Chem., Int. Ed. Engl.*, 1977, **10**, 716.
12 J. Passmore, P. Taylor, T. K. Whidden, and P. White, *J. Chem. Soc., Chem. Commun.*, 1976, 689.
13 W. A. Shantha Nandana, J. Passmore, and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1983, 526.
14 R. Faggiani, R. J. Gillespie, and J. W. Kolis, *J. Chem. Soc., Chem. Commun.*, 1987, following communication.
15 J. Passmore, P. S. White, and C. M. Wong, *J. Chem. Soc., Chem. Commun.*, 1985, 1178.
16 J. Passmore, G. Sutherland, and P. S. White, *Inorg. Chem.*, 1982, **21**, 2717.