

Synthesis and X-Ray Crystal Structure of the Hexafluoroantimonate Salt of the Dimeric Tungsten Pentacarbonyl Diselenyl Cation $W_2(CO)_{10}Se_4^{2+}$

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Reaction of $W(CO)_6$ with $Se_4(Sb_2F_{11})_2$ in SO_2 results in the formation of a compound formulated as $W_2(CO)_{10}Se_4^{2+}(SbF_6^-)_2$ the dimeric cation geometry of which has been established by X-ray crystal structure determination.

Great interest has arisen recently in the study of naked metal clusters.¹ A new development in this field of chemistry has been achieved by combining clusters of main group elements with transition metals.^{2–4} A recent investigation of the insertion of a transition metal into naked polyanionic metal clusters has shown the existence of mixed $(PPh_3)_2PtSn_9^{4-}$ species in a polar basic solvent (ethylenediamine).⁵ Another synthetic route to mixed clusters is the reaction of transition metal complexes with polycationic clusters of main group elements in a strongly acidic medium.

The title compound was prepared by reaction of $Se_4(Sb_2F_{11})_2$ prepared as previously described⁶ with tungsten hexacarbonyl in sulphur dioxide. The solution, which was red at the early stages, rapidly turned dark brown on stirring at room temperature. It was left to stand for two days. The slow evaporation of SO_2 led to the formation of shiny black flat crystals. The crystals were qualitatively analysed using electron dispersive spectroscopy to establish the presence of W, Se, and Sb. The complete formula was obtained from the crystallographic results.

Crystal data: $W_2(CO)_{10}Se_4(SbF_6)_2$, $M = 1435$, monoclinic, space group $P2_1/c$; $a = 8.806(3)$, $b = 7.098(2)$, $c = 22.145(8)$ Å, $\beta = 95.47(2)^\circ$, $Z = 2$, $F(000) = 1267.83$, $D_c = 3.46$ g cm⁻³, $\mu(Mo-K\alpha) = 150.47$ cm⁻¹. Intensity data were collected by the ω - 2θ scan technique on a Nonius CAD 4 diffractometer ($4 < 2\theta < 50^\circ$): 1902 unique reflexions were obtained with $I > 3\sigma(I)$.

The structure was solved and refined by full-matrix least-squares to a final R of 0.028 ($R_w = 0.029$) with anisotropic thermal parameters. Computer programs were those of the SHELX-76 system.⁷

The atomic scattering factors (corrected for the anomalous dispersion of W, Se, and Sb) were taken from ref. 8. The structure of the cation is shown in Figure 1.[†]

The dimeric cation is composed of two cationic $W(CO)_5Se_2^+$ units related through the inversion centre at (0,0,0). The heavy-atom framework consists of a six-membered ring in a chair conformation (W_2Se_4) in which two short diselenide bonds [2.208(1) Å] correspond to an approximate valence bond order of 1.7 according to the bond order–distance correlation proposed by Dahl *et al.*⁹ The $W(CO)_5$ group is bonded to this Se_2^+ fragment with W–Se distances of 2.626(1) and 2.631(1) Å. The $W(CO)_5Se_2^+$ units interact through long Se–Se bonds [3.017(1) Å].

Similar interactions between radical centres to give loose dimers have been described by Gillespie *et al.*¹⁰ Each long bond could be considered as having a formal valence bond order of 0.5; however, such a description implies that there should not be odd electron density remaining at the selenium atoms. According to Gillespie, an alternative description could be given in terms of three-electron bonds.¹⁰ The Sb–F distances in the hexafluoroantimonate anion range from 1.842 to 1.874 Å and are close to the accepted values. None of these bonds shows any lengthening due to bridging interactions with the selenium atoms as, for instance, in $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)$.¹¹

[†] The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

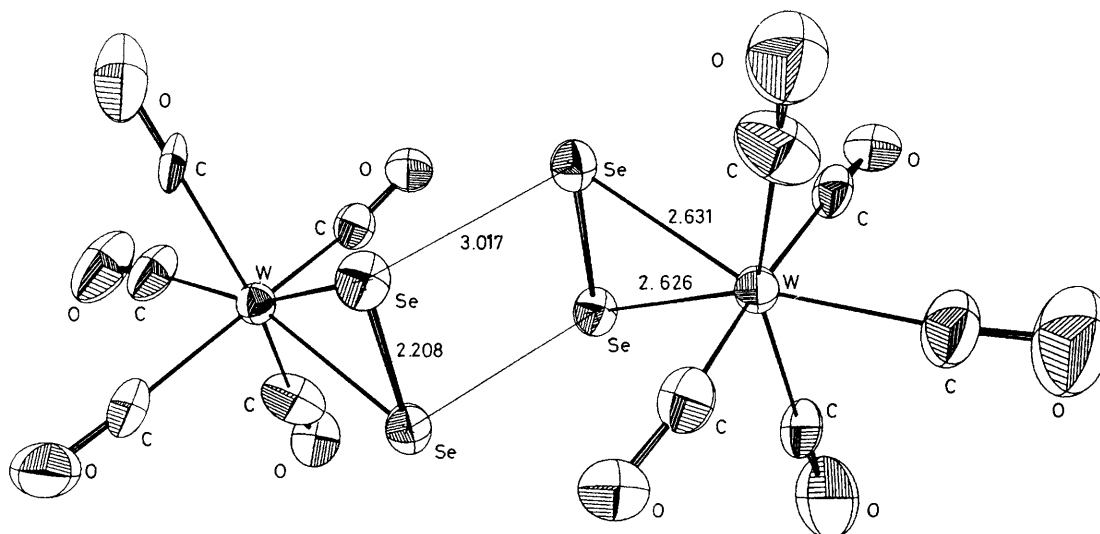


Figure 1. Crystal structure of $\text{W}_2(\text{CO})_{10}\text{Se}_4^{2+}(\text{SbF}_6^-)_2$, with distances in Å.

There is no Se-F distances shorter than 3.5 Å. The FSbF angles, which are within *ca.* 2° of 90 and 180°, confirm the absence of any significant distortion from the regular octahedral geometry.

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