

## The Reaction of Main Group Polynuclear Cations with Transition Metal Carbonyls: Synthesis and Crystal Structure of $[\text{FeW}(\text{CO})_8\text{Se}_2](\text{SbF}_6)_2$

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The mixed cationic cluster  $[\text{FeW}(\text{CO})_8\text{Se}_2]^{2+}$ , prepared by reaction of  $\text{W}(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$  in a 1 : 2 molar ratio, with  $\text{Se}_4^{2+}$  in  $\text{SO}_2$ , has a tetrahedral core structure.

The reaction of cationic rings and clusters of main group elements with transition metal complexes is a novel route for the synthesis of materials incorporating cyclic moieties or fragments of the main group cluster. Planar chalcogenyl cations  $\text{Ch}_4^{2+}$  (Ch = S, Se, or Te) can lead to different types of cluster depending on the nature of the reacting species. For example, the  $\text{Se}_4$  group is retained in the diselenyl cation  $\text{Se}_4\text{W}_2(\text{CO})_{10}^{2+}$ , prepared from  $\text{Se}_4^{2+}$  and  $\text{W}(\text{CO})_6$ ,<sup>1</sup> whereas the reaction of  $\text{Te}_4^{2+}$  with  $\text{Mo}(\text{CO})_6$  gives the tetrahedrane  $[\text{Mo}(\text{CO})_4\text{Te}_3]^{2+}$  with a practically equilateral  $\text{Te}_3$  triangle as base.<sup>2</sup> On the other hand, the reaction may give neutral clusters. The major product of the reaction of  $\text{Se}_4^{2+}$  with  $\text{Fe}_3(\text{CO})_{12}$  is the known  $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ .<sup>3</sup> In the present communication, we report the preparation and structural characterisation of the tetrahedral cluster  $\text{WFeSe}_2(\text{CO})_8^{2+}$ , formed from reaction of  $\text{Se}_4^{2+}$ .

Commercial  $\text{W}(\text{CO})_6$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Se}_4(\text{Sb}_2\text{F}_{11})_2$  (prepared according to the published procedure<sup>4</sup>), were used in molar ratios of 1 : 1.8 : 1. A solution of the metal carbonyls in  $\text{SO}_2$  was allowed to react with  $\text{Se}_4(\text{Sb}_2\text{F}_{11})_2$ , similarly dissolved in  $\text{SO}_2$ , in the second branch of a two-arm vessel. A red solution was immediately formed, which afforded small crystals after three days at room temperature.  $[\text{WFeSe}_2(\text{CO})_8](\text{SbF}_6)_2$  is highly air sensitive, rapidly becoming black,

and all manipulations were carried out under an inert atmosphere. Qualitative analysis using electron dispersive spectroscopy indicated the presence of Se, Fe, W, and Sb, and the stoichiometric formula was obtained from the crystallographic results.<sup>†</sup>

The structure of the cation is shown in Figure 1. The  $\text{Se}_2\text{FeW}$  core adopts a distorted tetrahedral arrangement which is devoid of any space group-imposed symmetry. The selenium fragment in the cluster may formally be considered as an  $\text{Se}_2^{2+}$  ion stabilised by organometallic groups. Obviously the triple bond of the free  $\text{Se}_2^{2+}$  is lengthened by interaction with the carbonyl fragment and the  $\pi$  acceptor capacity of the

<sup>†</sup> Crystal data  $[\text{Se}_2\text{FeW}(\text{CO})_8](\text{SbF}_6)_2$ ,  $M = 4372.48$ , monoclinic, space group  $P2_1/c$ ;  $a = 15.251(4)$ ,  $b = 12.267(3)$ ,  $c = 12.047(3)$  Å,  $\beta = 92.81(2)^\circ$ ,  $U = 2251$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1960$ ,  $D_c = 3.23$  g cm<sup>-3</sup>;  $\mu(\text{Mo-K}\alpha) = 107.28$  cm<sup>-1</sup>. Intensity data were collected at room temperature using the  $\omega$ - $2\theta$  scan technique ( $4^\circ \leq 2\theta \leq 56^\circ$ ).

Correction was made for absorption effects. 4609 Unique reflections (internal consistency 0.036) were used for solution of the structure (SHELX76 direct methods)<sup>5</sup> and in the initial stages of refinement. The final residuals were  $R = 0.050$ ;  $R_w = 0.049$ .

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, 1986.

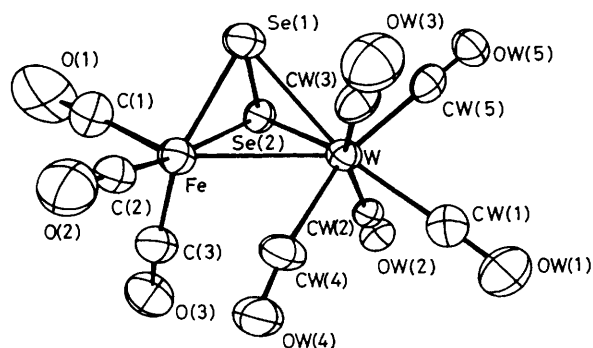


Figure 1. Crystal structure of  $[\text{FeW}(\text{CO})_8\text{Se}_2](\text{SbF}_6)_2$ .

$\text{Se}_2$  moiety. The Se-Se bond length, 2.281(3) Å, corresponds to an approximate Se-Se bond order of 1.5,<sup>6</sup> showing the presence of extensive delocalisation. This distance is significantly longer than that found in the diselenyl cation,  $[\text{W}_2(\text{CO})_{10}\text{Se}_4]^{2+}$ , 2.208 Å, and closely approaches that in the mixed iron-selenium cluster,  $[\text{Se}_2\text{Fe}_2(\text{CO})_6]$ , 2.293 Å (a neutral analogue, isoelectronic in the broad sense). Se-W distances, 2.601(2) and 2.606(2) Å, are also shorter than those in  $[\text{W}_2(\text{CO})_{10}\text{Se}_4]^{2+}$ , 2.626(1) and 2.631(1) Å. The Fe-W bond length is 2.857(3) Å. Angles at Fe, Se(1), and Se(2) are in the range 58–64°, those at tungsten 50–52°.

As a result of steric crowding around tungsten, the carbonyl group CW(4)-OW(4) is semi-bridging to iron [CW(4)-Fe 2.543(18) Å;  $\angle\text{OW}(4)\text{-CW}(4)\text{-Fe}$  117(1)°]. Furthermore, this interaction probably serves to mitigate the charge separation brought about by the 'dative' covalent bond from the 16 electron fragment  $\text{W}(\text{CO})_5$  to  $\text{Fe}(\text{CO})_3\text{W}^+ \rightarrow \text{Fe}^-$ .<sup>7</sup>

Other short non-bonded interactions occur between selenium and fluorine. Although the network of Se-F interactions is not as extensive as that found in  $(\text{Se}_4)(\text{Sb}_2\text{F}_4)(\text{Sb}_2\text{F}_5)(\text{SbF}_6)_5$ ,<sup>8</sup> there are four Se-F distances less than 3.2 Å. These contacts appear to distort the geometry of the hexafluoroantimonate anion. The longest Sb-F distance, 1.899(12) Å, involves the fluorine atom in strongest interaction with Se [2.876(16) Å]. The average Sb-F bond length is 1.86(2) Å. Similarly, four short (~3.2 Å) non-bonded Se-F interactions were found in  $[\text{W}_2(\text{CO})_{10}\text{Se}_4](\text{SbF}_6)_2$ .

Further studies of the reactivity of  $\text{Se}_4^{2+}$  and  $\text{Te}_4^{2+}$  for the synthesis of mixed di- and tri-metal clusters are in progress.

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## References

- 1 C. Belin, T. Makani, and J. Rozière, *J. Chem. Soc., Chem. Commun.*, 1985, 118.
- 2 A. Seigneurin and J. Rozière, unpublished results. Crystallographic work on this compound with a restricted data set ( $R$  0.13) has allowed identification of only the cluster arrangement  $\text{Te}_3\text{Mo}$  with certainty; further  $X$ -ray studies are underway.
- 3 L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.
- 4 R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, 1979, **20**, 4053.
- 5 G. M. Sheldrick, SHELX76, Program System for Crystal Structure Determination, University of Cambridge, 1976.
- 6 C. F. Campana, F. Y.-K. Lo, and L. F. Dahl, *Inorg. Chem.*, 1979, **18**, 3060.
- 7 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley Interscience, New York, 1980, ch. 25.
- 8 G. Cardinal, R. J. Gillespie, J. F. Sawyer, and J. E. Vekris, *J. Chem. Soc., Dalton Trans.*, 1982, 765.