The Preparation and Structure of [W(CO)$_4$(η^3-Te$_3$)][SbF$_6$]$_2$ containing the First Three-membered Chalcogen Ring

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The reaction of Te$_4$(SbF$_6$)$_2$ with W(CO)$_6$ in SO$_2$–AsF$_3$ produces [W(CO)$_4$(η^3-Te$_3$)][SbF$_6$]$_2$ (1), which contains a three-membered tellurium ring co-ordinated in π fashion to the tungsten carbonyl fragment.

Recently, we[1] and others[2] have begun to investigate the chemistry of cationic chalcogen clusters[3] with transition metal carbonyl fragments. We began our investigations with the square planar Se$_4^{2+}$ and Te$_4^{2+}$ cations. These compounds have been fairly well studied[4] and their bonding has been investigated by calculations at several levels of sophistication.[5—7] These molecules contain six p electrons which appear to be delocalized around the ring in π bonding orbitals, suggesting some aromatic character which is consistent with the shortness of the E–E bonds (E = chalcogen).[4] It seemed possible that these molecules might behave as 6-electron donors to metal carbonyl fragments. However, initial work with Se$_4^{2+}$ and M(CO)$_6$ (M = Mo, W) did not show this kind of behaviour. Instead, Se–Se$^+$ dimers were found to act as 2-electron donors to M(CO)$_5$ fragments, in a side-bonding fashion, while interacting with another M(CO)$_5$Se$_2^+$ fragment through a long 6-electron 4-centre bond.[1,2] We now report that Te$_4^{2+}$ reacts with W(CO)$_6$ to produce a compound

containing a tellurium ring bonded to tungsten, but it is a Te$_3$ ring rather than a Te$_4$ ring. To our knowledge, this molecule contains the first crystallographically characterized three-membered group 16 (group 6A) ring of any type.

The title compound (1) was prepared by the reaction of W(CO)$_6$ with Te$_4$(SbF$_6$)$_2$ in SO$_2$–AsF$_3$ (3 : 1 v : v) in one side of a double ampoule connected by a glass frit.[8] After stirring overnight, the red–brown solution was filtered and allowed to remain at room temperature for one week. The colour of the solution gradually diminished and dark crystals precipitated. The solution was decanted and the crystals isolated under vacuum. Several kinds of crystals were present in the product, including unchanged W(CO)$_6$. Red–orange platelets were separated by hand and investigated by single crystal X-ray diffraction.†

The structure of (1) consists of the cationic cluster [W(CO)$_4$Te$_3$]$^{2+}$ and two well separated [SbF$_6$]$^-$ counterions. The cation contains a Te$_3^{2+}$ triangle co-ordinated to a W(CO)$_4$ fragment (Figure 1). The tungsten atom and one tellurium atom lie on a crystallographic mirror plane which bisects the molecule. The W–Te distances are 2.802(1), 2.802(1), and 2.817(1) Å which are very close to the sum of the metallic radii (2.81 Å).[9] The Te–Te distances are similar but not equivalent [2.718(1) and 2.736(1) Å], and are not substantially different from those in elemental tellurium (2.74 Å)[10] or from typical Te–Te single bonds [e.g. 2.712(2) Å in
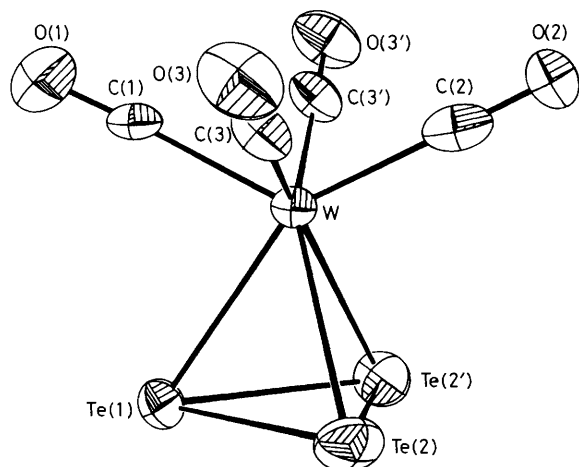

Figure 1. ORTEP view of the [W(CO)$_4$Te$_3$]$^{2+}$ molecule.

PhTe–TePh].[11] However, they are substantially longer than in Te_4^{2+} where it is probable that there is some multiple bonding.[4] Because the W–Te and Te–Te bonds coincidentally have almost the same bond lengths, the cluster forms an almost perfect tetrahedron with angles near 60° (Te–W–Te 57.9° and Te–Te–Te 60.4°).

The overall structure has 'piano stool' geometry[12] with the $W(CO)_4$ fragment possessing C_{4v} symmetry and the Te_3^{2+} ring having C_{3v} symmetry (Figure 1). The three-membered ring co-ordinated to the metal is reminiscent of compounds containing arsenic or phosphorus three-membered rings co-ordinated to a transition metal centre.[13,15] All of these complexes contain 30 electrons and are thus isoelectronic with the title compound. The E–E bonds of the co-ordinated ring in the phosphorus and arsenic compounds are considerably shorter than the parent E_4 tetrahedron. This has been attributed to a decrease in antibonding interactions within the ring due to transfer of electron density onto the metal centre.[13,14]

The bonding in the title compound can be explained using the models developed by Sacconi et al.[14] for the L_3CoP_3 system and by Shen-shu and Hoffmann[15] for hypothetical cyclic ozone complexes.[15] The cyclo-Te_3^{2+} fragment has a half-filled π^* 3e energy level as the HOMO. There is also a somewhat lower lying filled 2a orbital which is σ bonding in nature. Between these two energy levels are the filled 2e and 3a levels but these are σ bonding and not well disposed for overlap with the metal orbitals. Thus they would be expected to make only a minimal contribution to the bonding. The $W(CO)_4$ fragment in C_{4v} symmetry contains a half filled e level as its HOMO and a low lying a level as the LUMO.[16] These orbitals presumably interact with the corresponding orbitals on the Te_3^{2+} fragment generating three bonds through filling of the a and e levels. Thus Te_3^{2+} acts as a 4 π elecron donor to the metal carbonyl fragment completing its 18 electron count. This also stabilizes the Te_3 ring by removing electron density from the antibonding e orbital through donation to the metal orbitals, a situation deemed essential for the isolation of E_3 rings.[15]

Alternatively, the molecule can be viewed as being isoelectronic with tetrahedral P_4. Assuming that there is a localized lone pair on each tellurium vertex, and that $W(CO)_4$ is a 2 electron donor as in the Wade scheme,[16] the molecule contains 12 bonding electrons, which is enough for six bonds as in P_4.

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