X-Ray Diffraction Study of Te$_4$S$_4$(AsF$_6$)$_2$·SO$_2$; an Electron-rich S$_4$N$_4$-type Cage

Romolo Faggiani, Ronald J. Gillespie,* and John E. Vekris
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

A single crystal X-ray diffraction study has shown that the compound Te$_4$S$_4$(AsF$_6$)$_2$·SO$_2$ contains the Te$_4$S$_4{}^{2+}$ cation, which has an electron-rich S$_4$N$_4$-type cage structure.

Several cationic species of sulphur, selenium, and tellurium have been prepared from sulphur dioxide solutions by treatment of the appropriate element with a suitable oxidizing agent such as HSO$_3$F, S$_2$O$_6$F$_2$, AsF$_5$, or SbF$_5$.[1—7] Inter-chalcogen cations have been obtained by the oxidation of a mixture of two elements or by the reaction of one element and a cation of a different element, or of two cations of different elements [1,8,9] Heteropolyatomic cations of the elements of groups 5 and 6 or 6 and 7 have also been prepared.[10—12]

In an attempt to produce a group 4—6 cation, we studied the reaction of an equimolar mixture of tellurium, tin, and AsF$_5$ in sulphur dioxide solution. A crystalline by-product containing pale yellow and amber-brown crystals was isolated

from an amber-brown solution. Raman spectroscopy and preliminary crystallographic work showed that the yellow crystals were sulphur (orthorhombic modification, space group *Fddd*, No. 70 in International Tables). The plate-like amber-brown crystals were subjected to an X-ray crystal structure determination which identified the material as Te$_4$S$_4$-(AsF$_6$)$_2$·SO$_2$, the cation of which has an S$_4$N$_4$-type cage structure. The title compound was prepared in a double ampoule from a mixture of tellurium powder (3.645 mmol), tin powder (3.649 mmol), and AsF$_5$ (3.658 mmol) in anhydrous sulphur dioxide (*ca.* 30 cm^3). The mixture was stirred for 3 days. The initially red solution gave an insoluble black precipitate in a light amber-brown solution. The black precipitate has not been identified. Crystalline plates of
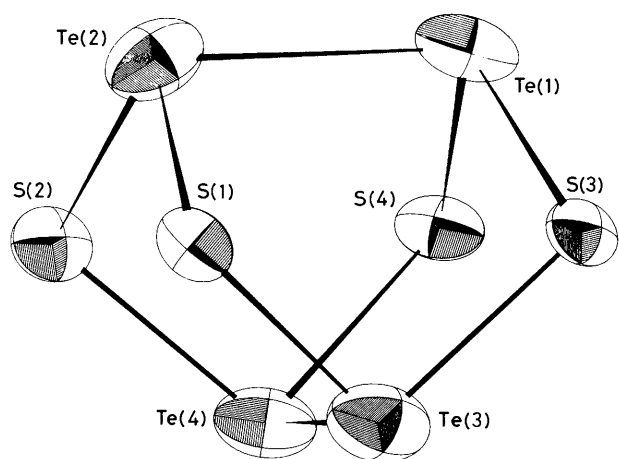
Figure 1. A view of the cation $Te_4S_4{}^{2+}$. Selected bond distances (Å) and angles (°): Te(1)–Te(2) 2.716(2), Te(3)–Te(4) 2.710(3), S(1)–Te(2) 2.303(6), S(1)–Te(3) 2.288(6), S(2)–Te(2) 2.290(8), S(2)–Te(4) 2.309(6), S(3)–Te(1) 2.315(6), S(3)–Te(3) 2.291(6), S(4)–Te(1) 2.309(7), S(4)–Te(4) 2.329(6); Te(1)–S(3)–Te(3) 102.9(2), Te(1)–S(4)–Te(4) 102.3(2), Te(2)–S(1)–Te(3) 103.4(2), Te(2)–S(2)–Te(4) 102.6(3), S(1)–Te(2)–Te(1) 97.7(1), S(2)–Te(2)–Te(1) 99.2(2), S(3)–Te(1)–Te(2) 98.5(1), S(4)–Te(1)–Te(2) 97.8(2), S(1)–Te(3)–Te(4) 98.2(2), S(2)–Te(4)–Te(3) 98.7(2), S(3)–Te(3)–Te(4) 98.8(2), S(4)–Te(4)–Te(3) 98.6(2), S(1)–Te(3)–S(3) 94.7(2), S(2)–Te(4)–S(4) 94.1(2), S(3)–Te(1)–S(4) 95.1(2), S(1)–Te(2)–S(2) 95.0(2).

$Te_4S_4(AsF_6)_2 \cdot SO_2$ were formed from the solution. Suitable crystals for X-ray structural determination were sealed in Lindemann capillaries.†

The structure consists of discrete cations of $Te_4S_4{}^{2+}$ (Figure 1), distorted octahedral anions of $AsF_6{}^-$, and SO_2 molecules. The cation has the S_4N_4 structure, resembling that of α-As_4S_4,[14] β-As_4S_4,[15] and α-P_4S_4.[16] The four sulphur atoms are almost coplanar, with deviations from the mean plane of 0.0072, −0.0092, −0.0093, and 0.0082 Å. This plane cuts in half the tetrahedron formed by the four tellurium atoms. The intramolecular bond lengths and angles are given in the Figure caption. The Te–Te distances of 2.716(2) and 2.710(3) Å (average 2.713 Å) are, within the standard deviations, equivalent and slightly shorter than twice the accepted radius of Te (2.74 Å),[17] and are almost equal to that of the Te–Te single bond in PhTe–TePh [2.712(2) Å].[18] The S–Te distances vary from 2.290 to 2.329 Å, with an average of 2.304 Å. This distance is a little less than the mean (2.36 Å) of the normal single S–S bond length (2.02 Å) and the Te–Te distance (2.71 Å) in the present cation, and is significantly less than the mean S–Te distance of 2.45 Å in $Te_3S_3(AsF_6)_2$.[19] The four coplanar sulphur atoms are separated from each other by an

(1)

$Te_4S_4{}^{2+}$

(3)

cuneane

(2)

(4)

$Te_6{}^{4+}$

(5)

(6)
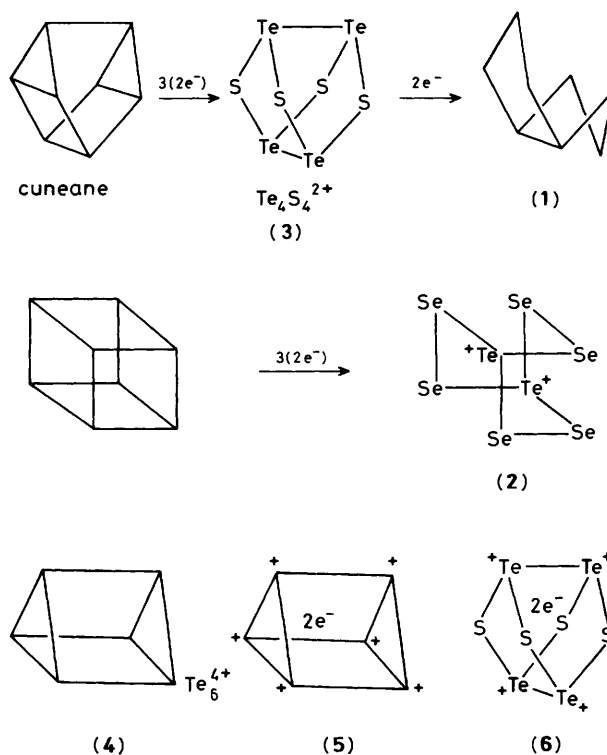
average of 3.39 Å. The Te–S–Te, S–Te–Te, and S–Te–S bond angles have mean values of 102.8, 98.5, and 94.5°, respectively, similar to the corresponding As–S–As, S–As–As, and S–As–S angles (101.2, 99.1, and 94.4°) of β-As_4S_4.[15]

The very slight distortion and deviation of the shape of $Te_4S_4{}^{2+}$ from D_{2d} symmetry may be attributed, at least in part, to the non-bonding (charge-transfer) interactions of the cation with the accompanying anions. Bond distances (average 1.679 and 1.693 Å) and bond angles in the $AsF_6{}^-$ anions are similar to the values found in other structures. The lengthening of some As–F bonds and the deviation of $AsF_6{}^-$ from O_h symmetry may be attributed to secondary bonding interactions between anions and cation.

The present structure represents the third type found for chalcogen and interchalcogen cations $M_8{}^{2+}$. The homoatomic ions $S_8{}^{2+}$ (ref. 20) and $Se_8{}^{2+}$ (ref. 21) both have the bicyclo-octane structure (1) with a long cross-ring bond. The heteroatomic cation $Te_2Se_6{}^{2+}$ (ref. 22), however, has the cage structure (2) that can be considered to be derived from a cube by breaking three bonds by the addition of three pairs of electrons. The more electropositive tellurium atoms are expected to carry the majority of the positive charge and they are in the two unique three-co-ordinate positions. The structure of $Te_4S_4{}^{2+}$ (3) can be similarly considered to be derived from the cuneane structure by breaking just two bonds, even though three pairs of electrons must be added. Thus $Te_4S_4{}^{2+}$ has two more electrons than are needed to describe the structure in terms of single bonds. The observed structure seems to indicate that there is a strong tendency for the four tellurium atoms to become equivalent, even though this leads to an excess of two electrons over that expected for a singly-bonded cage. The structure could be described in terms of several no-bond and/or double-bond resonance structures. However, this does not seem very satisfactory, particularly as there is no evidence that any of the bonds is either longer or shorter than expected for a single bond. Essentially the same problem arises in trying to describe the structure of $Te_6{}^{4+}$ (4),[3] which also has two electrons in excess of that required for the

fully singly-bonded triangular prism structure. It is tempting to suggest that Te_6^{4+} and $Te_4S_4^{2+}$ are examples of a class of electron-rich clusters (6) in which a pair of delocalised electrons is 'trapped' inside the cluster (5). A similar suggestion has recently been made in connection with a localised electron-pair model for the boranes.[23]

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