The Crystal Structures of the Methylxanthates of Divalent Sulphur, Selenium, and Tellurium

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A study of compounds of bidentate dithio- and related ligands with divalent group VI central atoms [1] has been extended to the following three compounds: Sulphur di(methylxanthate), $S(MeOCS_2)_2$ (I), selenium di(methylxanthate), $Se(MeOCS_2)_2$ (II), and tellurium di(methylxanthate), $Te(MeOCS_2)_2$ (III). Crystals of compounds II and III were obtained by a procedure similar to that used to prepare tellurium bis(dimethyldithiophosphate),[2,3] while I was prepared by nucleophilic substitution on the central sulphur atom in the pentathionate ion. Their structures have been solved by means of three-dimensional X-ray crystallographic methods. Data relevant to the solution of the structures are found in Table 1, while the structures of the molecules are shown in Fig. 1.

The configuration around the central atoms in the three compounds is trapezoid planar, as can be seen from Fig. 1. This is the characteristic configuration found earlier for compounds of divalent selenium and tellurium with bidentate dithio ligands.[1] The four-coordination in tellurium di(methylxanthate) is obtained through the formation of four intramolecular Te–S bonds, with average length 2.687 Å (sum cov. radii = 2.41 Å). This configuration is quite similar to that found in tellurium di(ethylxanthate) [4] and in divalent selenium and tellurium dithiocarbamates.[5–8] In addition, there is a tendency towards five-coordination in this type of tellurium compound, as can be seen from Fig. 1c. In the selenium and sulphur methylxanthates, the four-coordination arises through the formation of two strong intramolecular, and two extremely weak intermolecular, central atom to sulphur bonds, similar to the situation found in selenium bis(diethyldiselenophosphinate).[9] These weak bonds

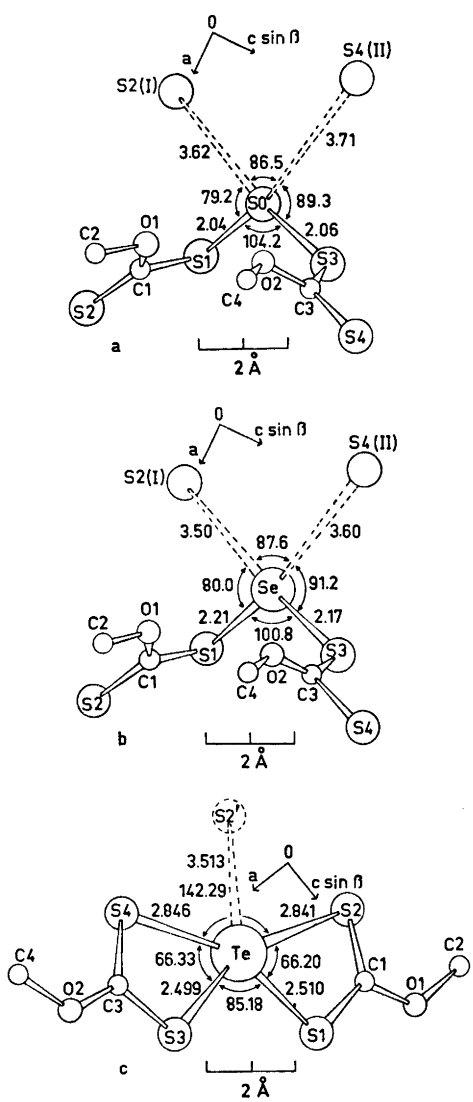

Fig. 1. a. The structure of $S(MeOCS_2)_2$ as seen along *a*. (E.s.d.: S–S = 0.007 Å, ∠S–S–S = 0.2°). b. The structure of $Se(MeOCS_2)_2$ as seen along *a*. (E.s.d.: Se–S = 0.008 Å, ∠S–Se–S = 0.2°). c. The structure of $Te(MeOCS_2)_2$ as seen along *a*. (E.s.d.: Te–S = 0.001 Å, ∠S–Te–S = 0.04°). Atom S2′ lies 1.10 Å above the TeS_4 plane and belongs to a neighbour molecule across a center of symmetry.

The standard deviations quoted above, are average values.

Table 1. a. Unit cell and space group data.

Compound	Crystal colour	Space group	a (Å)	b (Å)	c (Å)	β (°)	Z	Density (g/cm³): Calc	Found
I $S(MeOCS_2)_2$	Col. less	$I2/c$	13.580(5)	8.243(3)	18.429(4)	92.80(4)	8	1.59	1.57
II $Se(MeOCS_2)_2$	Yellow	$I2/c$	13.640(6)	8.299(3)	18.409(14)	93.56(6)	8	1.87	1.86
III $Te(MeOCS_2)_2$	Red	$P2_1/c$	4.2341(5)	14.202(2)	17.299(2)	92.99(2)	4	2.19	2.18

b. Intensity data *etc.*

	Compound I	Compound II	Compound III
No. of intensities collected above background	712 [a]	386 [a]	2124
Type of intensity data	Film	Diffractometer	Diffractometer
Radiation used	CuKα	MoKα	MoKα
Absorption correction undertaken	No	Yes	Yes
Anisotropic temp. factors used (atom type)	S	Se and S	Te, S, O and C
R-value	0.109	0.052	0.029
Method used to solve structure	Isomorphism with II	Direct methods	Patterson
Types of atoms included in full-matrix, least squares refinement	S, O, and C	Se, S, O, and C	Te, S, O and C[b]

[a] Relatively poor data due to instability of crystals.
[b] H atoms included in structure factor calculation, but their parameters were not refined.

are for I of the order of magnitude of a van der Waals contact, 3.70 Å, being 3.62 and 3.71 Å respectively. In II they are 3.51 and 3.60 Å, respectively, as compared to a Se···S van der Waals distance of 4.00 Å. However, the direction of the bonds and their coplanarity in the trapezoid planar configuration, indicate a secondary bonding interaction.[10] The structure of a dithiocarbamate of divalent sulphur shows no tendency towards planar four-coordination.[11]

The C–S–S–S–C and C–S–Se–S–C sequences of I and II have the *cis* configuration, while the *trans* configuration is found for the corresponding sequence in selenium bis(diethyldiselenophosphinate) [9] and related compounds. In the three xanthates studied here, the bonding in the S–M···S sequence, where M···S represents the weaker sulphur to central atom bond, *trans* to the stronger S–M bond, probably is of the three-center four-electron type.[1,12]

Divalent tellurium in such four-coordinate complexes is a better acceptor than selenium. It therefore has a greater tendency to form trapezoid planar complexes with the shortest average bonds, *i.e.* the type based on four intramolecular Te–S bonds. Thus with excellent donors as dithiocarbamates, both tellurium and selenium give this type complex. With the slightly poorer donor, the methylxanthate ion, only tellurium yields this type complex, while selenium gives a complex where the four-coordination is based on two intra- and two intermolecular Se–S bonds. For tellurium, this change in complex type occurs at the dimethyldithiophosphate ion,[3] which with divalent tellurium gives a complex similar to that of selenium di(methylxanthate). In tellurium bis(dimethyldithiophosphate) the intermolecular Te···S bonds are relatively strong, both being 3.31 Å.

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β-Lactones in the Perkin Reaction*

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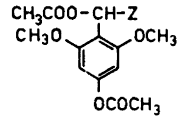
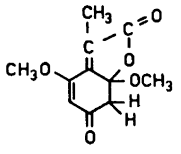
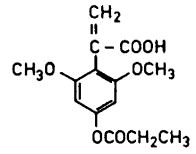
It is now well established that the Perkin reaction, which is generally applied for aromatic aldehydes,[1] readily takes place, utilizing a great variety of quinones.[2-10] Due to the instability of the products formed, the reaction generally goes further, leading mostly to aromatic compounds. In the case of 2,6-dimethoxy-*p*-benzoquinone it has been shown [4,6,8,10] that with acetic, propionic, and isobutyric acid anhydrides the products (*1a*), (*1b*), (*2a*), (*2b*) and (*3a*),** respectively, are formed. Moreover, small amounts of corresponding diesters of 2,6-dimethoxy-hydroquinone are produced.



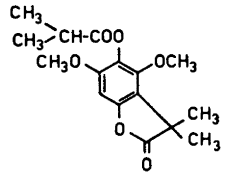
(1a) Z = H
(1b) Z = COOH



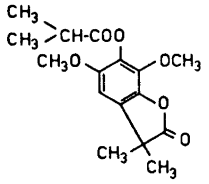
(2a)



(2b)



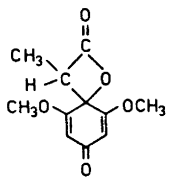
(3a)



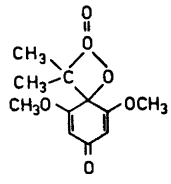
(3b)

By analogy with commonly accepted schemes, the mechanisms outlined in Refs. 2 to 8 can be presented for the formation of these compounds. However, as has been pointed out recently,[9,10] at least some of these compounds may be formed through a β-lactone.

When the standard reaction procedure [2-8] is modified by utilizing shorter reaction times and lower temperatures, it is possible in the cases of propionic and isobutyric acid anhydrides to isolate β-lactones from the reaction mixtures. For



(2c)



(3c)

* Part X. Sur les Réactions des Quinones. For Part IX, see Ref. 10.

** Analytical data presented for product (*3a*)[8] do not exclude the structure (*3b*).