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O-Ethylxanthato Halides of Tellurium(II)

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Tellurium(II) haloxanthates were obtained by reaction of tellurium(II) xanthate with chlorine, bromide or iodine; by reaction of tellurium(II) xanthate with tellurium tetrachloride or with cupric chloride or bromide as well as by reaction between tellurium tetrachloride with potassium xanthate.

The crystal structure of the bromo-complex has been determined. The unit cell is monoclinic, $P2_1/c$, a $= 10.636(1)$, b $= 6.030(1)$, c $= 13.364(1)$ Å, *and* $\beta = 103.32(1)^\circ$ *with* $Z = 4$; *R being* 0.077, R_w 0.072 *for 1396 unique reflections. The crystals are composed of left- and right-handed helices, formed from corner sharing (bromine bridges) of planar* $Te(S_2COEt)Br_2$ *units. The RO–C bond length (1.270(12) Å) is the shortest so far observed in metal xanthates.*

Introduction

Reactions of halogens with metal xanthates result in the formation of the metal halide and dixanthogen, as was observed for cobalt, chromium, and lead [1], in partial substitution (bismuth and antimony [1], and tin [2]) or in oxidative addition (copper [3], tin [2], and molybdenum [4]).

Although tellurium exhibits several stable oxidation states, only tellurium(II) xanthates are known, and these have been studied in some detail [5–7]. Haloxanthates of tellurium have so far not been reported. The synthesis, characterisation and structure of tellurium(II) haloxanthates, forms the subject of this communication. A brief account of the structure of $[Te(S_2COC_2H_5)Br]_n$ was published in a letter to this journal [8].

Results

The addition of bromine or chlorine to a dichloromethane solution of tellurium(II) xanthate, in the ratio of 1:2, resulted in the isolation of tellurium(II) haloxanthates, $Te(S_2COEt)X$, and dixanthogen. When iodine was used a black crystalline by-product was obtained, which is probably a lower iodide of tellurium. The dixanthogen was identified by its i.r. spectrum. When the ratio of bromine or chlorine was increased to 1:1, $Te(S_2COEt)X$, together with the corresponding Te(IV) halide was obtained. When the ratio was >2:1 the products were Te(IV) halides and dixanthogen.

Tellurium(II) chloroxanthate and dixanthogen were also obtained by the reaction of tellurium(II) xanthate and tellurium(IV) chloride in the ratio 3:1. When excess tellurium(IV) chloride or tellurium(II) xanthate was used the excess material remained unreacted. Similarly, the addition of potassium ethylxanthate to tellurium(IV) chloride in the ratios 1:1, 2:1, 3:1 produced tellurium(II) haloxanthate and dixanthogen. When the ratio of reagents was 4:1 tellurium(II) xanthate and dixanthogen was obtained.

The addition of copper(II) bromide or copper(II) chloride to tellurium(II) xanthate, in the ratio 1:2, gave the corresponding tellurium(II) haloxanthates. In this case copper(I) xanthate and dixanthogen were obtained, as identified by their i.r. spectra.

The reactions are summarized in equations 1–4:

$$2Te(S_2COEt)_2 + X_2 \rightarrow 2Te(S_2COEt)X + (S_2COEt)_2 \quad (1)$$

$$3Te(S_2COEt)_2 + TeCl_4 \rightarrow 4Te(S_2COEt)Cl + (S_2COEt)_2 \quad (2)$$

$$TeCl_4 + 3K(S_2COEt) \rightarrow Te(S_2COEt)Cl + (S_2COEt)_2 + 3KCl \quad (3)$$

$$4Te(S_2COEt)_2 + 2CuX_2 \rightarrow 4Te(S_2COEt)X + 2Cu(S_2COEt) + (S_2COEt)_2 \quad (4)$$

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TABLE I. Ultraviolet Absorption Spectra, nm, ϵ in brackets.

$Te(S_2COEt)_2$	Cyclohexane	213 (17,000)	249 (63,000)	296 (6,400)	360 (2,800)
	Ethanol[a]	215 (20,000)	244 (65,000)	246 (8,200)	360 (2,400)
$Te(S_2COEt)Cl$	Cyclohexane	c.215 (20,000)	231 (23,500)	c.271 (3,600)	303 (2,700) 372 (1,800)
	Ethanol[a]	213 (12,000)	248 (32,000)	294 (5,300)	350 (2,500)
$Te(S_2COEt)Br$	Cyclohexane	217 (10,700)	243 (22,100)	c.270 (3,300)	c.300 (2,100) 374 (1,100)
	Ethanol[a]	215 (14,000)	249 (34,000)	297 (5,000)	360 (1,500)
$Te(S_2COEt)I$	Cyclohexane	218 (11,400)	251 (27,600)	c.294 (6,000)	c.370 (1,600)
	Ethanol[a]	216 (18,000)	249 (30,000)	297 (5,800)	c.360 (1,900)

[a] Due to instability of solutions values of ϵ are only approximate.

TABLE II. Infrared Absorptions in the 'C–O' and 'C–S' Regions (cm^{-1}).

	'C–O'		'C–S'	
	Solid	CS_2 Solution	Solid	CS_2 Solution
$Te(S_2COEt)_2$	1240, 1220	1215	1030	1035, 1005
$Te(S_2COEt)Cl$	1285(sh), 1270	1251, 1235(sh)	1020, 993	1040, 1005
$Te(S_2COEt)Br$	1285(sh), 1270	1248, 1235(sh)	1018, 990	1037, 1001
$Te(S_2COEt)I$	1270	1244, 1230(sh)	1016, 993	1034, 1001

Clearly then, in contrast to the tin haloxanthates [2], where the oxidation state IV is favoured, in tellurium haloxanthates the oxidation state II is the more stable. In this connection it is interesting to note that only one xanthate moiety in $Te(S_2COEt)_2$ is oxidized by $TeCl_4$, no further reaction taking place with excess $TeCl_4$. With excess chlorine or bromine however, both xanthate ligands are oxidized to dixanthogen.

The complexes are red brown crystalline materials, slightly soluble in aromatic and chlorinated solvents, but virtually insoluble in aliphatic hydrocarbons. The electronic spectra of the complexes in cyclohexane, shown in Table I, are attributable to transitions in the OCS_2 chromophore, and possibly to charge transfer. In ethanol solutions, which are conducting, variation of the U.V. spectra with time indicated decomposition.

The i.r. spectra of the three tellurium(II) haloxanthates are similar, but differ from that of tellurium(II) xanthate (Table II). In the low frequency region, where M–S and M–X vibrations are expected the complexes show four bands in the infrared and five bands in the Raman spectra (Table III). The lower two bands are tentatively assigned to Te–X vibrations.

In CS_2 solution of the dixanthate ($Te(S_2COEt)_2$) there are some minor shifts of the absorption bands in the 'C–O' and 'C–S' regions, probably due to rupture of the weak association which leads to the quasi dimer in the solid [5]. The haloxanthate absorptions in these regions show an even greater variation between solid and solution (Table II).

In chloroform solution $Te(S_2COEt)Br$ is monomeric (found by vapour pressure osmometry 336, calculated 328.7), so that the observed shifts in the absorbance positions may again be interpreted as a manifestation of an association in the solid. This has been confirmed by a single crystal X-ray structure determination.

X-Ray Crystallography

Only the bromo complex yielded crystals suitable for an X-ray structure determination. Dark red crystals were obtained by slow evaporation of a dichloromethane solution at room temperature. The crystals were stable in the absence of moisture.

Data collection

Oscillation and Weissenberg photographs revealed the crystals to be monoclinic, with systematic absences h0l: l = 2n + 1 and 0k0: k = 2n + 1, defining the space group as $P2_1/c$ [9(a)]. A crystal of approximate dimensions 0.18 × 0.13 × 0.45 mm was mounted so that the crystallographic b-axis was coincident with the diffractometer ϕ axis.

Accurate unit cell dimensions were obtained from the 2θ values of 12 strong, well resolved, near axial reflections, measured using Cu $K_{\alpha 1}$ radiation (wave-

TABLE III. Low Frequency IR and Raman Spectra (cm^{-1}).

			M–S		M–X	
$Te(S_2COEt)_2$	IR	440	390	310		
	Raman	N.D.*				
$Te(S_2COEt)Cl$	IR	449	403	342	287	
	Raman	450	405	346	286	fluorescence
$Te(S_2COEt)Br$	IR	451	400	344	281	
	Raman	452	403	346	283	214
$Te(S_2COEt)I$	IR	447	407	343	265	
	Raman	449	409	348	265	197

*Weak spectrum.

TABLE IV. Atomic Coordinates × 10^4, Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c
Te	847(1)	3875(1)	3217(1)
Br	1963(1)	397(2)	2204(1)
S(1)	1018(2)	7095(4)	4447(2)
S(2)	3151(2)	4563(5)	4013(2)
O	3499(7)	7784(13)	5291(6)
C(1)	2637(9)	6672(18)	4680(7)
C(2)	3134(10)	9674(19)	5864(8)
C(3)	4363(12)	10664(23)	6424(10)

TABLE V. Interatomic Distances (Å) and Bond Angle (°) for $[Te(exa)Br]_n$, Standard Deviations in Parentheses.

Atoms	Separation	Atoms	Angle
Te–Br	2.895(1)	Br–Te–Br′	128.40(4)
Te–Br′	3.052(2)	Te–Br′–Te′	79.31(3)
Te–S(1)	2.524(3)	Br′–Te–S(1)	79.00(6)
Te–S(2)	2.471(2)	Br–Te–S(2)	81.39(7)
Te···Te′	3.797(1)	S(1)–Te–S(2)	71.03(8)
		Te–S(2)–C(1)	86.9(3)
Br···Br′	5.355(2)	Te–S(1)–C(1)	85.5(4)
Br′···S(1)	3.570(3)	S(2)–C(1)–S(1)	116.6(6)
Br···S(2)	3.514(3)	S(2)–C(1)–O	117.2(7)
S(1)···S(2)	2.902(3)	S(1)–C(1)–O	126.2(8)
S(1)–C(1)	1.697(10)	C(1)–O–C(2)	120.3(8)
S(2)–C(1)	1.713(11)	O–C(2)–C(3)	105.5(9)
C(1)–O	1.270(12)		
O–C(2)	1.474(14)		
C(2)–C(3)	1.475(17)		

′ –x, ½ + y, ½ – z.

length 1.54051 Å), by a least squares procedure [10]; $2\theta > 110°$.

Intensity data were collected by means of a 'five value' $\theta - 2\theta$ scan method [11] with Cu $K_{\bar{\alpha}}$ radiation (1.5418 Å) to a maximum Bragg angle of 70°. 1798 reflections were measured, a check reflection being monitored after every 20 reflections. The intensity data collected were corrected in accordance with the variation of the check reflection.

After collection of the data, the crystal had a greyish metallic lustre. This slight decomposition is in contrast to that observed for $[Et_4N][Te(S_2COEt)_3]$ [7], where decomposition was so great that 3 crystals were needed for the data collection.

Reflections for which $I < 3\sigma(I)$ were regarded as unobserved. This left 1466 observed reflections, the structure amplitudes of which were then corrected for Lorentz, polarization and absorption factors [9(b), 12]. Of these, 1396 reflections were unique.

The crystal was well formed, the indices of the crystal faces were: (100), ($\bar{1}$00), (010), 0$\bar{1}$0), ($\bar{1}$10), (1$\bar{1}$0), (001), (00$\bar{1}$).

Crystal data: $C_3H_5BrOS_2Te$, M = 328.7, dark red needles, monoclinic, a = 10.636(1) Å, b = 6.030(1) Å, c = 13.364(1) Å, β = 103.32(1)°, U = 834.04, D_m = (by flotation) 2.66 Mg m^{-3}, Z = 4, D_c = 2.617 Mg m^{-3}, F(000) = 600.00, space group $P2_1/c$ (C^5_{2h}, No. 14), Cu $K_{\bar{\alpha}}$ (nickel filtered) 1.5418 Å, μ = 38.01 mm^{-1} absorption correction applied, Siemens automatic diffractometer.

Structure determination

A three-dimensional Patterson synthesis revealed the position of the tellurium atom. The positions of the other non-hydrogen atoms were found from subsequent difference maps. Full matrix least squares refinement, and individual anisotropic temperature factors assigned to each atom gave R 0.085 where $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$.

Refinement was continued, using a weighting scheme of $w = (\sigma^2(F) + 0.05013)^{-1}$, until the shift of any parameter over its e.s.d. was less than 0.01. This gave R 0.077 and R_w 0.072, where

TABLE VI. Equations of Mean Planes in the Form lX + mY + nZ − d = 0 and Distances (Å) of the Atoms from the Planes. X, Y and Z are orthogonal coordinates related to the fractional coordinates given in Table IV by X = x + z cos β, Y = y and Z = z sin β. ^{I}(−x, ½ + y, ½ − z); ^{II}(−x, 1½ + y, ½ − z); ^{III}(x, 1 + y, z)

Atoms	Coeff	Plane 1 Te_n	Plane 2 Br_n	Plane 3 $Br_2TeS_2COC_2$
Te		0.000(1)	−1.037(1)*	−0.070(1)
Br		1.987(1)*	0.000(1)	0.038(1)
Br^{I}		−1.987(1)*	0.000(1)	0.102(1)
S(1)		−1.102(2)*	−2.577(3)*	−0.121(3)
S(2)		1.172(2)*	−2.440(3)*	0.030(3)
C(1)				−0.043(10)
O				−0.018(8)
C(2)				−0.030(11)
C(3)				−0.112(13)
Te^{I}		0.000(1)	1.037(1)*	
Te^{II}		0.000(1)		
Te^{III}		0.000(1)		
Br^{III}			0.000(1)	
Br^{II}			0.000(1)	
	l	0.808	−0.174	0.278
	m	0.000	0.000	0.612
	n	−0.589	−0.985	−0.740
	d	−2.538	−3.068	−1.622

*Atom not included in plane definition.

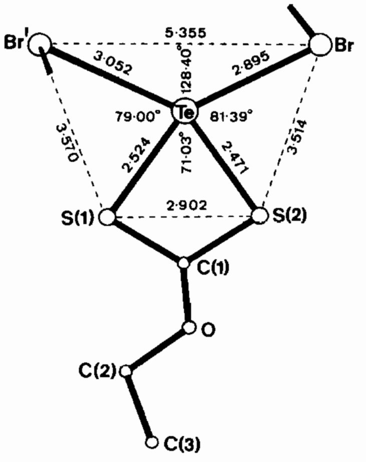


Fig. 1. $[Te(S_2COEt)Br]_n$ viewed in a direction perpendicular to the $Br_2TeS_2COC_2$ plane, showing the numbering scheme and some dimensions.

TABLE VII. Interatomic Contacts Distances (Å). Separations involving tellurium atoms < 4.5 Å, separations not involving tellurium atoms < 4.0 Å.

Contact	Separation	Contact	Separation
Atom contacts within the helix			
$Te\cdots S(1^{I})$	3.809(3)	$Br\cdots C(1^{II})$	3.926(10)
$Te\cdots S(1^{II})$	4.395(3)	$S(2)\cdots C(2^{II})$	3.851(11)
$Te\cdots Br^{III}$	4.410(1)	$S(2)\cdots C(3^{II})$	3.957(14)
$Br\cdots S(1^{II})$	3.918(3)		
Atom contacts between adjacent helices			
$Te\cdots S(1^{IV})$	4.108(3)	$Br^{VI}\cdots C(2)$	3.891(11)
$Te\cdots C(2^{V})$	4.483(11)	$Br\cdots C(3^{VII})$	3.967(13)
$Br\cdots C(3^{V})$	3.804(13)	$S(1)\cdots S(1^{IV})$	3.838(3)
$Br^{VI}\cdots C(1)$	3.816(9)	$S(2)\cdots O^{VII}$	3.747(8)
$Br\cdots C(2^{V})$	3.824(11)	$S(2)\cdots C(3^{V})$	3.963(13)
$Br^{VI}\cdots O$	3.848(8)	$O\cdots C(3^{VIII})$	3.702(15)
$Br^{VI}\cdots S(1)$	3.891(3)		

^{I}−x, −½ + y, ½ − z. ^{II}x, −1 + y, z. ^{III}x, 1 + y, z. ^{IV}x, 1 − y, 1 − z. ^{V}x, 1½ − y, −½ + z. ^{VI}−x, ½ − y, ½ + z. ^{VII}1 − x, 1 − y, 1 − z. ^{VIII}1 − x, 2 − y, 1 − z.

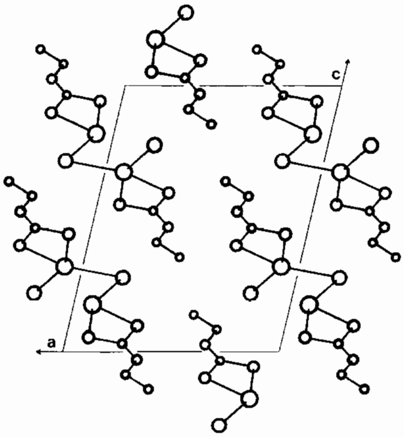


Fig. 2. The unit cell of $[Te(S_2COEt)Br]_n$ viewed down the [010] direction.

$$R_w = [\Sigma w \| F_o | - | F_c \|^2 / \Sigma w | F_o |^2]^{1/2}.$$

The final difference map showed peaks whose heights were less than or equal to 1.2 $eÅ^{-3}$, mainly in the vicinity of the heavy atoms. None of these peaks could be assigned to hydrogen atoms, and indeed, hydrogen atom positions could not be established from the difference map.

The scattering factors used for atomic C, O, S and Br were those collected by Sheldrick [13], while the scattering factors for atomic Te were those given in 'International Tables for X-ray Crystallography', [9(c)], the value being corrected for both the real and imaginary anomalous dispersion terms,

TABLE VIII. Bond Lengths, Angles, Absorption Frequencies and Resonance Contributions in Tellurium Xanthates.

Parameter	This work $[Te(S_2COEt)Br]_n$		Ref. 5 $Te(S_2COEt)_2$		Ref. 7 $[Et_4N][Te(S_2COEt)_3]$	
(a) *Bond lengths* (Å)						
Te–S	2.524(3)	2.471(2)	2.486(11)	2.897(17)	2.679(4)	3.059(4)
			2.480(13)	2.857(14)	3.051(4)	2.647(4)
					2.503(3)*	
C–S	1.697(10)	1.713(11)	1.67(5)	1.69(3)	1.688(14)	1.676(14)
			1.79(4)	1.63(4)	1.642(16)	1.715(15)
					1.708(12)*	(1.655(12))
C–O	1.270(12)		1.30(5)		1.320(17)	
			1.30(6)		1.330(14)	
					1.312(14)*	
(b) *Angles* (°)						
S–Te–S	71.03(8)		65.5(4)		61.7(1)	
			66.4(3)		62.1(1)	
S–C–S	116.6(6)		121.7(3.0)		123.3(8)	
			118.4(3.3)		125.5(9)	
					121.0(7)*	
(c) *I.r. absorption frequencies* (cm^{-1})						
'C–O'	1285(sh), 1270		1240, 1220		1210, 1185	
'C–S'	1018, 990		1030		1040, 1030	
(d) *Contribution by form III* (%)						
	40		28, 28		23, 19	

*Monodentate xanthate ligand.

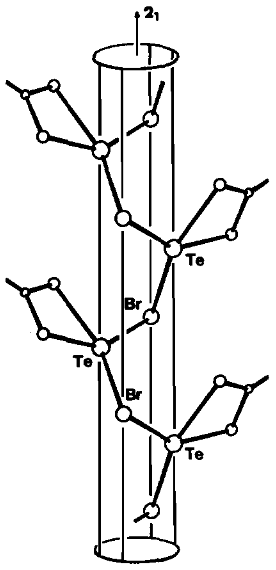


Fig. 3. A portion of the crystal structure of $[Te(S_2COEt)Br]_n$ viewed along the $[\bar{3}01]$ direction showing the nature of one of the helices adopted by the Br and Te atoms which extends in the *b*-direction with the periodicity b.

$\Delta f'$ and $\Delta f''$ [9(d)]. Structure determination and refinement were performed using the SHELX-76 program system [13].

The final atomic coordinates together with their e.s.d. values, are given in Table IV. Listings of the temperature factors and of the final observed and calculated structure factors have been deposited with the editors.

Description of structure

The atomic labelling scheme is shown in Fig. 1, while Fig. 2 shows the unit cell when viewed along the [010] direction. Bond lengths and angles are given in Table V.

Each tellurium atom is bonded to the two sulphur atoms of the xanthate moiety and two bromine atoms. The tellurium and bromine atoms are arranged in a helix, with two pairs of tellurium and bromine atoms forming the repeat unit. The helices are situated around a twofold screw axis, (0, y, ¼; 0, y, ¾), and extend along the y axis, the period *b* [6.030(1) Å]. Part of the helix is shown in Fig. 3, viewed along the $[\bar{3}01]$ direction. In the helix all the tellurium atoms and all the bromine atoms are coplanar (Table VI). The dihedral angle between these planes is 64°.

A noteworthy feature of the structure is that each tellurium atom is in close proximity to two other tellurium atoms within the helix, the separation being 3.797(1) Å, compared to 4.12 Å, for the sum of the van der Waals radii [14]. This suggests a substantial interaction between the tellurium atoms, which occurs throughout the helix. Other atom separations within the helix are greater than this (Table VII).

Within the crystal the helices are alternately left- and right-handed. The shortest separation between atoms in different helixes is 3.7 Å (Table VII).

The tellurium atom, the two bromine atoms, and the xanthate moiety are essentially planar, the greatest deviation of any atom being 0.121(3) Å, as seen in Table VI. The four atoms surrounding the tellurium atom form a trapezoid similar to that observed for $Te(S_2COEt)_2$ [5]. There are significant differences in the two Te–Br distances [3.052(2) Å and 2.895(1) Å] as well as in the two Te–S distances [2.471(2) Å and 2.524(3) Å], with the shorter Te–S bond being opposite the long Te–Br bond, and *vice versa*. However, the difference in the Te–S distances of 0.05 Å is very much smaller than that found in $Te(S_2COEt)_2$ [5] and $[Et_4N][Te(S_2COEt)_3]$ [7], where differences of about 0.5 Å appear in the chelating moiety (Table VIII).

Discussion

The most interesting part of the structure is the helical arrangement adopted by the tellurium and bromine atoms. Few inorganic materials are known to possess this type of structure in the solid state. These include modifications of elemental sulphur [15], selenium [16] and tellurium [17] and the mercury(II), 1,1-dithiolates $Hg[(i\text{-}C_3H_7)_2PS_2]_2$ [18] and $Hg(i\text{-}C_3H_7OCS_2)_2$ [19], where the helix comprises the mercury atoms and the bridging bidentate ligands.

In the dinuclear $[Te_2(ethylenethiourea)_4Br_2]^{2+}$ cation [20], the structure is such that each tellurium atom is also surrounded by two sulphur atoms (from two monodentate ethylenethiourea ligands) and two bridging bromine atoms in an almost regular square planar arrangement. The two Te–Br and two Te–S bond lengths of $[Te(S_2COEt)Br]_n$ are remarkably similar to those of $[Te_2(etu)_4Br_2]^{2+}$. The bond angle around the bromine atoms is 79.31(3)° in $[Te(S_2COEt)Br]_n$, compared to approximately 95° in the cation; indicating that there is considerable strain in the Te–Br bonds of the helical structure.

It can be seen from Table IX that, although the Te–Te separation is greater than that observed for Te–Te double bonds (Te_2) [21] and single bonds (Te metal) [17], it is close to the secondary, metallic interactions found in the normal [17] and high pressure form of elemental tellurium [22].

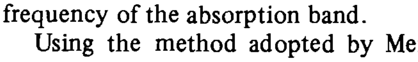
TABLE IX. Tellurium–Tellurium Bond Distances (Å).

Substance	Separation	Reference
$[Te(xan)Br]_n$	3.797(1)	this work
Te_2	2.61	21
Te metal	2.835(x2), 3.495(x4)	17
H.P. Te metal	3.00(x6), 3.72(x6), 3.82(x2)	22
Van der Waals	4.12	14

The similarities between the two Te–Br distances and between the two Te–S distances, suggest that the lone pairs of electrons, contained in the valence shell of the tellurium atom, lie approximately perpendicular to the $Br_2Te(S_2COEt)$ plane. One of the lone pairs seems to point in the direction of a bromine atom in the same helix 4.410(1) Å away, while the other seems to occupy a cavity between the helices.

The variation in C–O bond length and the S–C–S angle of the xanthate moiety in the three tellurium ethylxanthate complexes (Table VIII) correlates with the shifts of the 'C–O' and 'C–S' bands in the i.r. spectra of the complexes. As the C–O bond length and S–C–S angle decreases, the frequency of the 'C–O' band increases while the frequency of the 'C–S' band falls slightly. This is in agreement with Hunt *et al.* [23], who have suggested that variation in 'C–O' frequencies of metal xanthate complexes was due to variations in the S–C–S angle of the xanthate moiety; the smaller the S–C–S angle the higher the frequency of the 'C–O' band.

The change in the i.r. spectra may also be interpreted in terms of the relative contributions by three resonance forms of the xanthate ligand suggested by Chatt, Duncanson and Venanzi [24]:



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Thus variations in the contributions by form (III) will be expected to affect the C–O bond order. An increase in the contribution would result in shortening of the C–O distance and a higher frequency of the absorption band.

Using the method adopted by Merlino [25–27] the contribution by form (III) to the three tellurium ethylxanthates were calculated, as shown in Table VIII. For $[Te(S_2COEt)_3]^-$ there is a relatively small contribution of form (III) to the structure. In $Te(S_2COEt)_2$ with only two ligands, each ligand can delocalize more electron density onto the tellurium atom, resulting in an increased contribution by form (III). $[Te(S_2COEt)Br]_n$ has only one xanthate ligand and the electron density can be delocalized not only onto the tellurium atom, but also onto the electronegative bromine atoms. Thus the contribution of form (III) to the structure of the xanthate ligand becomes even greater. The C–O bond length of 1.270(12) found in $[Te(S_2COEt)Br]_n$ is in fact the shortest known for metal xanthates.

For the chloride and iodide the position of the 'C–O' absorption band is similar, so that a similarly short C–O distance is likely.

Experimental

Bis(O-ethylxanthato)tellurium(II)

A modification of the method used by Husebye [5] was adopted.

To tellurium(IV) chloride (1 g) in 70 ml dichloromethane was added potassium xanthate (2.4 g). After stirring for two hours the mixture was filtered and the filtrate evaporated under reduced pressure to give a red solid, which was recrystallized from chloroform/light petroleum. The i.r. spectrum of the material was identical to that obtained by the method of Husebye [5].

(O-ethylxanthato)halogenotellurium(II)

Method 1

To tellurium(II) ethylxanthate (2 g) in 50 ml dichloromethane was added 0.5 mole equivalent of chlorine, bromine, or iodine dissolved in carbon tetrachloride. After stirring for one hour (followed by filtering for the iodo complex), the solution was evaporated under reduced pressure. The resulting solid was then washed with boiling light petroleum to remove dixanthogen and recrystallized from chloroform/light petroleum.

Analyses for the chloro-, bromo-, and iodo-complexes, $[Te(S_2COEt)X]$, with calculated values in parentheses were: C 13.0 (12.7), 10.8 (11.0), 9.9 (9.6); H 1.8 (1.8), 1.5 (1.5), 1.4 (1.3); S 22.7 (22.7), 19.2 (19.5), 17.4 (17.1); X 12.0 (12.5), 24.9* (24.3), 33.6% (33.8%).

Method 2

To tellurium tetrachloride (1 g) in 70 ml dichloromethane was added potassium ethylxanthate (1.8 g). After stirring for two hours the solution was filtered and the filtrate evaporated under reduced pressure. The solid was then washed with boiling light petroleum to remove dixanthogen and recrystallized from chloroform/light petroleum. The i.r. spectrum was identical to the product obtained by method 1.

Method 3

To tellurium tetrachloride (1 g) in 70 ml dichloromethane was added tellurium(II) ethylxanthate (4.1 g). After stirring for two hours the solution was evaporated under reduced pressure. The solid was then washed with boiling light petroleum to remove dixanthogen and recrystallized from chloroform/light petroleum. The i.r. spectrum was identical to the product obtained by method 1.

Method 4

To tellurium(II) xanthate (2 g) in 70 ml dichloromethane was added copper(II) bromide (1.2 g) or copper(II) chloride (0.7 g). After stirring for three days the mixture was filtered and the filtrate evaporated under reduced pressure. The solid was washed with boiling light petroleum to remove dixanthogen and recrystallized from chloroform/light petroleum. The i.r. spectra were identical to the analogous products obtained by method 1.

Instrumentation

Infrared spectra were obtained from KBr discs on a Perkin-Elmer 457 spectrophotometer. For U.V. spectra a Varian Techtron 635D spectrophotometer was used. Raman spectra were collected on a SPEX Ramalog 14018 spectrophotometer by M. E. Beyer of this department.

Analyses

Analyses were performed by the Australian Microanalytical Service.

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*Figure variable – some analytical interference was observed.

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