Tetraethyldithio-oxamide Complexes of Tellurium(IV)

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The preparation, i.r., and Raman spectra of complexes of the type Te(teto)X_4 and RTe(teto)X_3 where X = Cl, Br, I; R = p-MeOC_6H_4 or p-EtOC_6H_4; and teto is *NNN'N'*-tetraethyldithio-oxamide are described. The possible structure of the complexes in the solid state is discussed.

HART and co-workers[1] suggested that fully substituted dithio-oxamides could form transition metal complexes if non-co-ordinating media were used. Using acetone or n-butanol as solvents they prepared tetraethyldithio-oxamide complexes with Mn^{II}, Fe^{II}, Ni^{II}, Cu^{II}, Pd^{II}, and Sn^{IV}. More recently further palladium(II) complexes[2] and ones with silver(I)[3] have been prepared. Apart from the report of the formation of the tin–tetraethyldithio-oxamide complex mentioned above, no further complexes of this ligand with non-transition metals have been reported. Tetraethyldithio-oxamide (teto) is thought to complex through its two sulphur atoms[1] and since a large number of tellurium(II) and (IV) compounds containing sulphur donors are known it was considered that tellurium may complex with fully substituted dithio-oxamides in non-aqueous media.

EXPERIMENTAL

Tellurium tetrachloride and tetrabromide were obtained from B.D.H. Ltd., and K and K Laboratories. Tellurium tetraiodide was prepared by the reaction of telluric acid with hydriodic acid.[4] Methanol was dried using magnesium[5] and carbon tetrachloride dried as recommended by Vogel,[6] the first ten per cent of distillate being rejected.

Preparation of NNN'N' *Tetraethyldithio-oxamide*.—Tetraethyloxamide was first prepared from diethylamine and oxalyl chloride and the product reacted with phosphorus pentasulphide to form tetraethyldithio-oxamide as described by Hart *et al.*,[1] a modification of the method first described by Hurd *et al.*[7]

Preparation of Aryltellurium Trihalides.—*p*-Methoxyphenyltellurium trichloride, and *p*-ethoxyphenyltellurium trichloride, were prepared by direct addition of tellurium tetrachloride to anisole and phenetole respectively in carbon tetrachloride.[8-11] The trichlorides were reduced with sodium sulphide to give the corresponding diarylditellurides,[12] which were then treated with iodine or bromine in carbon tetrachloride to give the tri-iodides and tribromides.[13]

Preparation of the Tetraethyldithio-oxamide Complexes.—The complexes were prepared by dissolving *NNN'N'*-tetraethyldithio-oxamide (5 mmol) in a suitable dry solvent such as n-butanol or methanol, and adding this to the tellurium compound (5 mmol) dissolved in either benzene, n-butanol, or methanol. Precipitates formed immediately in some cases but the iodides crystallised out only after cooling for two to three days.

I.r. and Raman Spectra.—The spectra of the compounds were recorded as Nujol mulls or KBr discs on a Perkin-Elmer 457 i.r. spectrophotometer over the range 4000—250 cm^{-1}; as Nujol mulls on a Perkin-Elmer 225 grating i.r. spectrophotometer, and on a Fourier spectrophotometer FS 720 (R.I.I.C.) over the range 400—80 cm^{-1}. The complete spectra have been deposited in Supplementary Publication No 20751 (4 pp.).*

Raman spectra were recorded on a Cary 81 spectrometer (laser) with an exciting line at 6328 Å. Samples were contained in glass tubes of *ca.* 1 cm diameter.

DISCUSSION

The bands at 1500 and 872 cm^{-1}, ν(CN) and ν(CS) respectively, in tetraethyldithio-oxamide are shifted to higher and to lower wavenumber respectively on complexation (see Table).[14] These shifts are to be expected if co-ordination is through the sulphur atoms of the thiocarbonyl groups. After elimination of ligand bands, new bands between 285—128 cm^{-1} are noted in the far-i.r. and Raman spectra of the complexes. Absorptions between 262—215 cm^{-1} found for all the complexes may be associated with ν(Te–S) vibrations, whilst those at 285—256 cm^{-1} can be assigned to ν(Te–Cl) and those at 189—158 cm^{-1} to ν(Te–Br). These assignments are in agreement with those reported by McWhinnie *et al.* in their studies on tetrachlorotellurates[15] and diaryltellurium dihalides.[16] It seems likely that the bands at 153—128 cm^{-1} in the iodo-complexes involve Te–I stretching.

It is of interest to note that strong Te–Cl absorptions in the region 330—300 cm^{-1} are reported by McWhinnie and Thavornyutikarn[17] for *para*-substituted aryltel-

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* For details of the Supplementary Publications scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue. Items less than 10 pp. are sent as full-sized copies.

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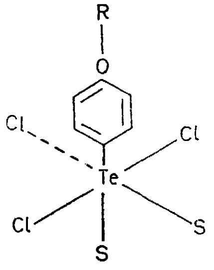
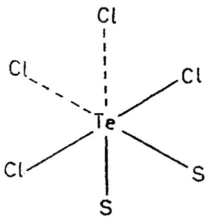
	Analyses [a]							I.r. and Raman spectra [b]			
								ν(TeX)		ν(TeS)	
	C	H	N	S	Te	ν(CN)	ν(CS)	I.r.	Raman	I.r.	Raman
Tetraethyldithio-oxamide	52·05		12·05	27·85		1500	872				
	(51·7)		(12·05)	(27·6)							
Tellurium(IV) chloride complex	23·95	4·0	5·55	13·0	25·0	1560	858	285msh	289ssh	236sbr	230wsh
	(23·95)	(4·0)	(5·6)	(12·75)	(25·45)			268sbr	268vs	224s	
Tellurium(IV) bromide complex	17·7	2·95	4·1	9·45	18·85	1545	858	184s	180msh	249s	249wsh
	(17·65)	(2·95)	(4·1)	(9·4)	(18·8)			164sh	158s	229w	
Tellurium(IV) iodide complex		2·25	3·35	7·35	14·9	1545	858	153s		252s	
	(13·85)	(2·3)	(3·25)	(7·4)	(14·7)					236ssh	
p-Methoxyphenyltellurium trichloride complex	35·35	4·8	5·0	10·7	22·5	1535	861	275ssh	272s	240sbr	
	(35·6)	(4·7)	(4·9)	(11·15)	(22·25)			256ssh	253s	216ms	
p-Methoxyphenyltellurium tribromide complex	29·75	4·0	4·05	8·95	17·6	1545	862	189s	186m	242m	250sh
	(28·9)	(3·8)	(3·95)	(9·05)	(18·05)			159s	158s	223s	
p-Methoxyphenyltellurium tri-iodide complex		3·5	3·35	7·95	14·8	1538	863	143s		238sh	
	(24·05)	(3·2)	(3·3)	(7·55)	(15·05)			130s		215s	
p-Ethoxyphenyltellurium trichloride complex	36·8	4·9	4·7	11·0	21·7	1540	861		276s	235s	
	(36·8)	(4·95)	(4·75)	(10·9)	(21·75)			260mbr	258s	214s	
p-Ethoxyphenyltellurium tribromide complex	30·1	4·3	3·95	9·0	17·4	1540	862	192m	185s	262ssh	
	(30·05)	(4·05)	(3·9)	(8·9)	(17·7)			162w	158s	249s	
p-Ethoxyphenyltellurium tri-iodide complex	25·7	3·55	3·35	7·55	14·8	1530	865	139sh	142m	242s	
	(25·1)	(3·35)	(3·25)	(7·45)	(14·8)			128sh	128sh	233sh	

[a] Required values in parentheses. [b] The more important bands, in cm^{-1}

lurium trichlorides and that high Te–Cl frequencies at 338 and 315 cm^{-1} (said to be due to *cis*-$TeCl_2$ groups) are also noted for $MeTeCl_3$.[18] However, in the tetramethylthiourea adduct of $MeTeCl_3$ the bands at 338 and 315 cm^{-1} are absent and a new band appears at 251 cm^{-1} which is said to involve *trans*-$TeCl_2$ groups. It is possible that in the teto complexes the absorptions at 285—256 cm^{-1} are also due to *trans*-Cl–Te–Cl stretching rather than to *cis*-$TeCl_2$ groups. A structure involving six-co-ordinate tellurium with one long Te–Cl bond could be envisaged for the $ROC_6H_4TeCl_3$(teto) complexes whilst a similar *trans* bond lengthening effect of the sulphur atoms in the $TeCl_4$(teto) complexes would result in a similar structure with two long Te–Cl bonds.



$ROC_6H_4TeCl_3$(teto)



$TeCl_4$(teto)

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