Chalcogen Chemistry. Part VIII. Complexes of Arylselenium and Aryltellurium Trichlorides with Pyridine, 4-Picoline, and 4-Picoline *N*-Oxide [1]

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Arylselenium and aryltellurium trichlorides form crystalline 1 : 1 adducts with pyridine (py), 4-picoline (pic), and picoline *N*-oxide (pico). The selenium complexes are pale yellow and moderately sensitive to atmospheric moisture while the tellurium analogues are colourless and fairly stable to moist air. In contrast to *p*-$MeOC_6H_4TeCl_3$(tmtu) (tmtu = tetramethylthiourea) which is molecular in solution and a weak electrolyte, $ArTeCl_3$(py) and $ArTeCl_3$(pic) behave as 1 : 1 electrolytes in solution. The behaviour of $ArSeCl_3$(py), $ArSeCl_3$(pic), and $ArTeCl_3$(pico) in solution is intermediate to the above. It is likely that square pyramidal $ArMCl_3$(:B) molecules exist in the solid state, but available i.r. data do not allow an unambiguous conclusion in this regard.

THE recent suggestion that selenium may act as a cancer protecting agent [2] together with experimental evidence supporting this view [3] justifies intensified interest in the chemistry of this element. Thus, we have investigated the acceptor behaviour of organoselenium and organotellurium trichlorides.

The reaction of methylselenium trichloride with tetramethylthiourea(tmtu) results in reduction and demethylation as well as co-ordination, and gives dichloro(tetramethylthiourea)selenium(II).[4] In addition, the reaction of phenylselenium tribromide with tmtu also leads to a selenium(II) compound, *viz.*, octamethyl-α,α′-dithiobisformamidinium bis[phenyldibromoselenate(II)]-acetonitrile.[1] Utilization of oxidation-resistant bases, and aryl groups resistant to displacement has led to the first arylselenium trichloride–base adducts which are reported herein.

One aryltellurium trichloride adduct, *p*-$MeOC_6H_4TeCl_3$(tmtu), is known.[5] In order to examine the acceptor behaviour of organotellurium trichlorides in a more thorough manner, a number of additional aryltellurium trichloride–base adducts have been prepared.

EXPERIMENTAL

General.—Because of the hygroscopic nature of many of the compounds, all operations were carried out in dry nitrogen-filled polyethylene glove bags. Solvents were distilled and stored over Linde 4 Å molecular sieves. Pyridine and 4-picoline (pic) (Baker) were distilled shortly before use and stored over molecular sieves. 4-Picoline *N*-oxide(pico) was recrystallized from CH_3Cl–CCl_4. Phenylmercuric chloride (Alfa Inorganics) and *p*-tolylmercuric chloride (Eastman) were used without further purification.

I.r. and ^1H n.m.r. spectra and conductivity data were obtained as previously reported.[1] Conductivity data were analyzed using the method of Feltham and Hayter,[6] but compounds were also characterized by their equivalent conductance in nitromethane at 10^{-3}M.[7,8]

Elemental Analyses.—Considerable difficulty was experienced initially in obtaining reproducible analytical results on the complexes reported herein. Finally, good results were obtained by Meade Microanalytical Laboratory, Amherst, Massachusetts, on samples sealed in tin capsules.

Preparation of Arylselenium and Aryltellurium Trichlorides.—Diphenyl- and ditolyl diselenide were prepared by the method of Taboury.[9] The corresponding arylselenium trichlorides were prepared by the reaction of the aryl diselenides with chlorine in methylene chloride. The melting point of $PhSeCl_3$ (143—145°) was in agreement with the literature value.[10] Tolylselenium trichloride melts at 161—162° (Found: C, 30·6; H, 2·7; Cl, 37·25. Calc. for $C_7H_7Cl_3Se$: C, 30·4; H, 2·55; Cl, 38·45).

p-Methoxyphenyltellurium trichloride was prepared by the method of Morgan [11] and recrystallized from acetonitrile as yellow needles, m.p. 194—195° (lit.,[12] 191—193°) (Found: C, 24·80; H, 2·1; Cl, 24·5. Calc. for $C_7H_7Cl_3OTe$: C, 24·65; H, 2·05; Cl, 24·5). *p*-Tolyl- and phenyltellurium trichloride were prepared by the method of Farrar.[13] *p*-Tolyltellurium trichloride recrystallized from chloroform as a white microcrystalline solid, m.p. 187—189° (lit.,[13] 181—183°) (Found: C, 25·65; H, 2·15. Calc. for $C_7H_7Cl_3Te$: C, 25·85; H, 2·15). White microcrystalline phenyltellurium trichloride (m.p. 211—213°) was recrystallized from 1,1,2,2-tetrachloroethane–acetonitrile. Further purification could be effected by vacuum sublimation (0·01 mm) which raised the melting point to 219—221°. However, considerable decomposition ensued making this purification step impractical when the compound was to be used for preparative purposes. (Found: C, 23·5; H, 1·6. Calc. for $C_6H_5Cl_3Te$: C, 23·13; H, 1·6%). Available ^1H n.m.r., molecular weight, and conductivity data for these compounds are summarized in Table 1. The i.r. spectra of the arylchalcogen trichlorides (except *p*-$MeOC_6H_5TeCl_3$[5]) in the 600—100 cm^{-1} region, together with partial assignments, are also summarized in Table 1. The assignments in the 300—350 cm^{-1} region are uncertain because of unpredictable ring vibrations.

Our i.r. data for phenyltellurium trichloride do not agree with those previously reported.[15] This discrepancy

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may be due to the use of the KBr pellet sampling technique in the previous work. Under these conditions co-ordination of Br^- to phenyltellurium trichloride in the KBr pellet or halogen exchange with the matrix can be readily envisaged. This would cause a significant disruption of the Te–Cl stretching frequencies as well as smaller shifts in the phenyl modes.

Preparation of Complexes.—The preparation of the complexes involved slow addition of a concentrated ligand solution to a saturated solution of arylchalcogen trichloride. If precipitation did not occur at this point the solution was evaporated with a stream of dry nitrogen and placed at −20°. The resulting solid was filtered off and volatiles were removed by pumping at 0·01 mm for 10—15 min. The preparation of *p*-tolyltrichloro(4-picoline)tellurium(IV) is representative of the general procedure and is outlined below. Reaction conditions, yields, m.p.s, and analytical data for the compounds prepared in this study may be found in Table 2.

p-Tolyltrichloro(4-*picoline*)*tellurium*(IV).—A solution of 4-picoline (0·63 g, 6·77 mmol) in $CHCl_3$ (25 ml) was added dropwise with stirring to a mixture of *p*-tolyltellurium trichloride (2·20 g, 6·77 mmol) in (100 ml) $CHCl_3$. After the mixture had been stirred for 0·5 h, the white solid (1·28 g) was filtered off. Evaporation of the filtrate to half its original volume gave an additional 0·29 g product. The compound may be recrystallized from MeCN as colourless plates (see Table 2 for analytical data and m.p.s). Molecular weight and conductivity data for these compounds are summarized in Table 2. Infrared spectra in the region 100—600 cm^{-1} are also summarized in Table 2.

TABLE 1

$\nu_{max.}$/cm^{-1} *	^{1}H n.m.r. spectrum [a]	Formula weight	Cryoscopic molecular weight (molality)	Λ_c,/cm^2 equiv^{-1} Ω^{-1}
$PhSeCl_3$: 468ms,[a] [365ms,[b] 327s,[b (or c?)] 300s, br[b]] br, 274m, 245m [205m, 172s,] br [d]		262·5	249 (0·20—0·011) [c,d] 371 (0·021) [e] 296 (0·0126) [e]	3·14
p-$MeC_6H_4SeCl_3$: 486ms,[a] 379ms,[b] [353s,[b] 334s,v,br,[b (or c?)] 270m] br, 249vw, [203ms, 169s, 158s, 116w] br [d]			*f*	3·31
$PhTeCl_3$: 452s,[a] [340m,[b] 325sh,[c (or b?)] 306s [b]] br, 263vw, [176s, 143s] br [d]	8.50 [g] *ortho* 7·67 *meta, para*	311·1	303 (0·018—0·048) [d,f,h]	39·2
p-$MeC_6H_4TeCl_3$: 573w, 475s,[a] [341wm,[b] 321sh,[c (or b?)] 306s [b]] br, 272vw, 226w, [178s, 139s] br [d]	8·35 [i] *ortho* 7·48 [i] *meta* 2·47 CH_3	325·1	306 (0·025—0·049) [d,f,h]	36·3
p-$MeOC_6H_4TeCl_3$	8·43 [i] *ortho* 7·22 [i] *meta* 3·90 MeO	341·1	339 (0·017—0·049) [d,f,h]	36·5 [j]

* Key: w, weak; m medium; s, strong; v, br, sh, very broad shoulder. † [a] Phenyl ' y ' or related mode.[14] [b] Se or Te–Cl stretching mode. [c] Phenyl ' t ' or related mode. [d] Se– or Te–Cl bending and/or bridging mode.

[a] Chemical shift ±0·01 p.p.m. *vs.* internal tetramethylsilane in CD_3CN. [b] Concentration 10^{-3} M in nitromethane. [c] Nitrobenzene. [d] Within experimental error, *M* independent of concentration in range cited. [e] Benzene. [f] Insufficiently soluble in benzene for cryoscopic study. [g] Broad multiplet. [h] Sulpholane. [i] Doublet, splitting 9·0 Hz. [j] Obtained on a fresh solution; conductance increased slowly with time.

RESULTS

Arylchalcogen Trichlorides.—The arylchalcogen trichlorides prepared in this study appear to be substantially less soluble in non-donor solvents than certain of their previously investigated alkyl analogues.[16,17] The only arylchalcogen trichloride sufficiently soluble for cryoscopic studies in benzene was phenylselenium trichloride. This compound apparently undergoes limited association in this solvent (Table 1).

The arylchalcogen trichlorides display greater thermal stability than the alkyl derivatives and form much more stable solutions in donor solvents. Arylselenium and aryltellurium trichlorides are monomeric in donor solvents and behave, respectively, as very weak and weak electrolytes. Aryltellurium trichlorides show a particular tendency to form weak solvates. In view of their behaviour toward various donors it is likely that arylchalcogen trichlorides exist in solution as $ArMCl_3,S$ (M = Se or Te and S is a solvent molecule). In support of this view the highest frequency M–Cl absorption shifts *ca.* 40—50 cm^{-1} to low frequency relative to the solid in acetonitrile solution.

Detailed structural data are not available for any arylchalcogen trichloride. The structure of β-chloroethyltellurium trichloride is known[18] and contains square pyramidally co-ordinated tellurium achieved through a chlorine-bridged semi-ionic polymeric structure, as originally proposed for $MeTeCl_3$.[16] Except for the spectrum of *p*-$MeOC_6H_4TeCl_3$ which bears a strong resemblance to that of $MeTeCl_3$,[16] the presence of ring vibrations in the M–Cl stretching region in addition to other usual problems in the interpretation of solid-state spectra does not permit an unambiguous conclusion as to whether the structure of arylchalcogen trichlorides is similar to that found for $ClC_2H_4TeCl_3$.

Complexes of Arylchalcogen Trichlorides with Pyridine and 4-Picoline and 4-Picoline N-*Oxide*.—Arylselenium trichlorides form pale yellow 1 : 1 complexes with pyridine and 4-picoline while the analogous tellurium complexes are colourless. Excess of base must be avoided in order to obtain a pure product in all cases. These complexes are not very soluble in polar organic solvents; fair solubility was found for most in acetonitrile, but only slight solubility was found in tetramethylene sulphone, nitromethane,

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TABLE 2

Compound	M.P.*	Reaction solvent ‡	Recryst. solvent ‡	% Yield	Analyses								$\nu_{max.}$/cm^{-1} §	½ Formula wt.	Cryoscopic *M* (molality)	Λ_e [a]	Slope from ($\Lambda_0 - \Lambda_e$) *vs.* $\sqrt{c}$
					C		H		N		Cl						
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found					
p-$Me_3C_6H_4SeCl_3$(pic)	190—191	A	A	73	42·25	41·95	3·8	3·7	3·8	3·75	28·75	28·65	497m, 481w, [329wm, 298s, 273s] br, [214s, 205s, 187m, 170m, 155w] br, 129w	184·7	240(0·012),[b] 200(0·0080),[b] 231 (0·050),[c] 197 (0·030) [c]	17·6	
$PhSeCl_3$(pic)	193—195	A	A	79	40·55	40·35	3·4	3·5	3·95	3·7	29·9	29·8	478m, 471m, [307m, 295m, 283m] br, 267m, 258m, 246w, 198ms,br	177·7	229·0(0·010),[b] 198·0(0·0080) [b]	18·4	
$PhSeCl_3$(py)	203	A	A	90	38·7	38·5	2·95	3·1	4·1	4·0	31·15	31·1	470m, [312m, 298m]br, [268ms, 246s, 216ms] br, 174w, (156w?)	170·7	172·5(0·0070) [b]	15·2	
p-$MeC_6H_4SeCl_3$(py)	208	A	A	83	40·55	40·5	3·4	3·4	3·95	3·9	29·9	29·95	497ms, 327m, [304m, 292m, 274s] br, (249vw,?), [217m, 193m, 171m, 157w,sh] br	184·7	220(0·010),[b] 200(0·0080)	23·37	
p-$MeC_6H_4SeCl_3$(pico)	165—168	A	A–D	86	40·5	40·45	3·65	3·65	3·65	3·65	27·6	27·6	497w, 470vw, 423m, 362w, 331w, [305sh,m, 299m, 273s] br, 240w, 206m, 160vw				
$PhSeCl_3$(pico)	125—127	A	A–D	71	38·8	38·95	3·25	3·35	3·75	3·7	28·6	28·55					
p-$MeOC_6H_4TeCl_3$(pic)	196—197	A	C–A (1:10)	53	35·95	35·9	3·25	3·25			24·5	24·5	590w, 511s, 473s, 335w, [308w, 285m, 267s, 246s, 231s, 209s] br	217·1	185(0·011),[c] 187(0·0070),[c] 285(0·032),[b] 240(0·022),[b] 217(0·017) [b]	73	229
p-$MeC_6H_4TeCl_3$(pic)	230—231	B	C	56	37·35	37·45	3·35	3·5	3·35	3·35	24·45	25·5	570w, 515w, 483s, 474s, [307m, 287ms, 269s, 244s, 213s] br, 150ms	209·1	245(0·034),[c] 241(0·019),[c] 238(0·012) [c]	77	213
$PhTeCl_3$(pic)	210—211	B–C (1:1)	C–A (1:10)	76	35·65	35·45	3·0	3·0	3·45	3·45	26·3	26·3	517m, 472s, 457s, [306w, 271s, 249s, 229s, 210ms] br, 153ms	202·1	219(0·022),[c] 207(0·018) [c]	79	241
p-$MeOC_6H_4TeCl_3$(pico)	183—184	B	†	91	34·7	34·6	3·15	3·2	3·1	3·1	23·6	22·35	590w, 512s, 481s, 464m, 410s, 399s, 335wm, [306w, 287m, 267s, 249s, 233s) br, 204w, 196w, 157w	225·1	275(0·031),[c] 258(0·025) [c]	24	
p-$MeC_6H_4TeCl_3$(pico)	209—210	B	†	85	35·95	34·6	3·25	3·25	3·25	3·0	24·5	23·8	522w, 482s, 475s, 460ms, 410s, 329w, [296m, 271s, 245s, 209s, 149m]	217·0	232(0·029,[c] 224(0·022) [c]	25	
$PhTeCl_3$(pico)	198—199	B	E	79	34·3	34·2	2·9	3·0	3·35	3·6	25·3	25·2	528m, 478m, 469m, 457s, 400s, 329w, [305m, 296m, 271ms, 256s, 232s] br, 156m	210·1	296(0·020),[c] 233(0·016) [c]	28	
p-$MeC_6H_4TeCl_3$(py)	235—237	B	B–C	81	35·65	35·65	3·0	3·05	3·45	3·4	26·3	26·25	571w, 484s, [307w, 270s, 247s, 212ms] br, 155m	202·1	225(0·023),[c] 219(0·018),[c] 211(0·012) [c]	79	178
p-$MeOC_6H_4TeCl_3$(py)	200—201	A	A–C	71	34·3	34·2	2·9	3·05	3·35	3·2	25·3	25·25	586m, 512s, 472w, 386w, 334w [306w, 289m, 268s, 247s, 233s] br, 156wm	210·1	191(0·029),[c] 183(0·020) [c]	77	205

* Uncorrected. † A suitable solvent or solvent mixture was not found from which this compound could be recrystallized. ‡ A = CH_2Cl_2, B = $CHCl_3$, C = MeCN, D = CCl_4 E = $MeNO_2$. § See Table 1 for key.

[a] At 10^{-3} molar in nitromethane. [b] Nitrobenzene. [c] Sulpholan.

chloroform, and methylene chloride. The tellurium compounds were not appreciably sensitive to atmospheric moisture; their melting points were unchanged after exposure to moist air for 24 h. The selenium compounds were more moisture sensitive with substantial depressions in melting points being noted after exposure to the atmosphere for 2—4 h.

Solution Studies: Pyridine and 4-*Picoline Complexes*.—The molecular-weight data on the adducts in nitrobenzene and sulpholane indicate that dissociation occurs in solution and that the extent of dissociation is to a small degree dependent on concentration (Table 2). Conductivity data on the aryltellurium trichloride–pyridine and –4-picoline adducts clearly indicate that these behave as 1 : 1 electrolytes in nitromethane. A substantial downfield shift of 0·48 p.p.m. is observed for the 4-picoline 4-methyl resonance [*] in CD_3CN clearly indicating that 4-picoline is co-ordinated.[19,20] An upfield shift of *ca.* 0·13 p.p.m. was observed for the methyl group in the p-MeC$_6$H$_5$Te moiety in py and pic p-tolyltellurium trichloride complexes. In addition to the above, solution i.r. spectra showed shifts in co-ordinately sensitive 4-picoline peaks indicating co-ordination.

The arylselenium trichloride–pyridine and –4-picoline complexes behave in a generally similar fashion in solution, but there are certain consistent differences. Molecular-weight data for p-MeC$_6$H$_4$SeCl$_3$(pic) and p-MeOC$_6$H$_4$TeCl$_3$(pic) in nitrobenzene show that in the concentration range *ca.* 0·01 *m* the selenium complex is more associated than that of tellurium. Presuming this trend holds in nitromethane, we can rationalize the much lower conductivities of the selenium complexes. The latter, nevertheless, display substantially higher conductivities than the parent trichloride.

It is clear from our ^{1}H n.m.r. and solution i.r. data that, as for the tellurium adducts, no measureable amount of free ligand is present in CD_3CN solutions of the ArSeCl$_3$ adducts. The shift of co-ordination-sensitive 4-picoline peaks [†] for PhSeCl$_3$(pic) as well as the observation of separate peaks due to bound and free ligand in solutions of complex and ligand provide additional evidence in this regard.

4-*Picoline* N-*Oxide Complexes*.—The very low solubility of the arylselenium trichloride–4-pico complexes prevented solution studies. Molecular-weight data on aryltellurium trichloride–4-picoline *N*-oxide complexes reveal that (depending on concentration) these compounds are rather extensively dissociated in solution. However, in contrast to the py and pic complexes the pico adducts display *lower* conductivities than the parent trichlorides. In saturated nitrobenzene solution the 4-methyl resonance is shifted downfield substantially relative to the free base resonance indicating co-ordination.[‡][§]

Solid-state Studies.—The very strong absorption envelopes (see Experimental section) centred at 270 (Se) and 240 cm^{-1} (Te) for the respective complexes are no doubt due mainly to chalcogen–chlorine stretching modes. As expected, these absorptions occur at substantially lower frequencies than in the parent trichlorides. Ring modes for both acceptor and donor are superposed on the chalcogen–chlorine absorptions and make a detailed assignment of the peaks in this region difficult. It is important to note, however, the relative constancy of a strong pair of absorptions at *ca.* 295 and 270 cm^{-1}, and at *ca.* 270 and 246 cm^{-1} for the selenium and tellurium complexes, respectively. These frequencies are close to those expected for linear Cl–Se–Cl [4] and Cl–Te–Cl [22] groupings.

Shifts in co-ordination-sensitive py and pic peaks were observed in accord with previous findings.[23] For example peaks at 1605, 1226, and 997 cm^{-1} in the free ligand are found at 1622, 1245, and 1038 cm^{-1} in PhTeCl$_3$(pic). A peak occurring at 336 cm^{-1} in pico shifted to 400 cm^{-1} when complexed.

The N–O stretching frequency in pico (1233 cm^{-1} [27,28]) is lowered on co-ordination through oxygen.[24–27] Assignment of this band in the pico complexes is difficult because of the many strong donor and acceptor phenyl modes in this region. Assuming the constancy of certain peaks in the donor and acceptor, the peaks at 1198 [p-MeOC$_6$H$_4$TeCl$_3$(pico)], 1199 [PhTeCl$_3$(pico)], and 1190 (p-MeC$_6$H$_4$TeCl$_3$(4pico)) were assigned to the N–O mode.

DISCUSSION

Solution Studies.—N.m.r. and i.r. spectroscopic data suggest that the pyridine, 4-picoline (in CD_3CN), and 4-picoline *N*-oxide (in $PhNO_2$) ligands are mainly co-ordinated in saturated solutions. One starting point for discussion concerning the species present in solution would then concern whether the compounds are ionic [ArMCl$_2$,B]Cl (I) or molecular ArMCl$_3$,B (II) in solution (M = Se, Te; B = Lewis base). The possibility that these adducts might exist in the alternative ionic form $[\mathrm{ArMCl_2,B_2}]^+[\mathrm{ArMCl_4}]^-$, a formulation similar to that proposed for TeF$_5$,B adducts,[27] seems to be ruled out by molecular weight, n.m.r. and, in some cases, conductivity studies.

Conductivity studies suggest that the adducts of py and pic with aryltellurium trichloride are best represented by formulation (I) in solution, since these compounds behave as 1 : 1 electrolytes in nitromethane. In contrast the previously prepared p-MeOC$_6$H$_4$TeCl$_3$(tmtu) appears to be undissociated (in $PhNO_2$) and a weak electrolyte.[28]

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[*] Pic, δ-2·17; PhTeCl$_3$(pic), δ-2·63; p-MeC$_6$H$_4$TeCl$_3$(pic), δ-2·67; p-MeOC$_6$H$_4$TeCl$_3$(pic), δ-2·65.

[†] In MeCN: 4-Picoline, 484 ms, 513 s; corresponding peaks in PhSeCl$_3$(pic), 470 s, 518 m.

[‡] In $PhNO_2$: pico, δ-2·20; PhTeCl$_3$(pico), δ-2·62; p-MeC$_6$H$_4$-TeCl$_3$(pico), δ-2·50; p-MeOC$_6$H$_4$TeCl$_3$(pico), δ-2·60.

[§] Compare with a downfield shift of 0·16 p.p.m. for pico in (C_2H_4)PtCl$_2$(pico).[21]

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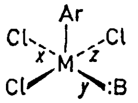
[28] A conductivity measurement on p-MeOC$_6$H$_4$TeCl$_3$(tmtu) at 10^{-3}M in CH_3NO_2 gave Λ_e, 31·0 cm^2 eq^{-1} Ω^{-1}.

Arylselenium trichloride–pyridine and –4-methylpyridine and aryltellurium trichloride 4-picoline *N*-oxide complexes are best represented in solution by formulation (II), as they behave as weak electrolytes. Whether the latter behaviour is observed because these complexes are close knit ion-pairs or true molecular complexes cannot be ascertained with the data presently available. The molecular-weight data indicate that these complexes undergo dissociation in sulpholan and nitrobenzene, but to a lesser extent than the aryltellurium–py and–pic adducts. In view of the ease of ionization of the latter and the firmness with which the ligand is apparently bound it is likely that the dissociation is an ionic rather than molecular process.

The complexes prepared in this work were studied in acetonitrile (i.r., n.m.r.), nitrobenzene (m.w., n.m.r.), sulpholan (m.w.), and nitromethane (cond.). These represent a class of solvents similar in dielectric constant and solvating ability.[29] Despite the similarity of these solvents there appears to be a systematic trend toward more dissociation of the complexes in sulpholan than in the other solvents.

Solid-state Studies.—Considering the tendency of selenium and tellurium to achieve maximum co-ordination in the solid state[18] and the strong *trans* bond-lengthening effect of an aryl group[30] it is likely that all the complexes reported herein contain five-co-ordinate central atoms. Unfortunately our i.r. data are rather complex in the critical chalcogen–chlorine stretching region. The general shift of the M–Cl stretching modes to low frequency in the complexes relative to the parent trichloride does support the above model in a general way, as does the observation of peaks which suggest the presence of a linear Cl–M–Cl group. However, these features would be rather insensitive to variations in the distance x (Figure) if x were substantially greater than z.[4] Information concerning the critical distances x and y in the model proposed above must await more detailed studies.



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