Structural and Thermochemical Studies on Rb_2TeCl_6 and Comparison with Rb_2SnCl_6

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Using room temperature diffractometer intensity data the structure of Rb_2TeCl_6 has been determined by single crystal *X*-ray diffraction and refined to a final *R* of 0·050. The structure consists of regular octahedral $[TeCl_6]^{2-}$ [Te–Cl = 2·541 Å (corrected)]. Lattice energy calculations on the resulting structure (for various charge distributions within the anion) are reported and are found to be sensitive to the assumed charge distributions within the anion. The measured heats of solution of $TeCl_4$ and Rb_2TeCl_6 in hydrochloric acid allow the standard heat of formation of Rb_2TeCl_6 to be calculated as −294·4 kcal mol^{-1} at 298 K. Using the calculated lattice energy, the enthalpy of reaction (*i*) is calculated to be −21·8 ± 17 kcal mol^{-1} at 298 K where the large error in the value is a

$$2Cl^-(g) + TeCl_4(g) \longrightarrow [TeCl_6]^{2-}(g) \qquad (i)$$

reflection of the uncertainties in the charge distribution of the anion. Thermochemical measurements on the analogous tin compounds gives the standard heat of formation of Rb_2SnCl_6 as −365·5 kcal mol^{-1} at 298 K, and, together with the lattice energy calculations, allow the enthalpy change for reaction (*ii*) to be estimated. As

$$2Cl^-(g) + SnCl_4(g) \longrightarrow [SnCl_6]^{2-}(g) \qquad (ii)$$

measured by the enthalpy of the gas phase reaction, the two Lewis acids $SnCl_4$ and $TeCl_4$ have, towards the chloride ion ligand, the same acceptor strength.

SALTS containing the hexahalogenotellurate(IV) anions have been prepared with chlorine, bromine, and iodine and a variety of monovalent cations and subjected to close scrutiny by various techniques including *X*-ray diffraction, vibrational spectroscopy, nuclear quadrupole resonance spectroscopy,[1] and Mössbauer spectroscopy.[2] The evidence overwhelmingly indicates that, to a very good approximation, the $[TeX_6]^{2-}$ anion is a regular octahedron, an observation in conflict with simple Sidgwick–Powell theory and a molecular orbital approach.[3] Early work by Engel[4] established a number of compounds with the K_2PtCl_6 structure including compounds of the type $M^I_2TeCl_6$ ($M^I = NH_4$, Rb, Cs, or Tl). (See ref. 5 for a summary.) More recently Hazell has examined the structure of cubic $(NH_4)_2TeCl_6$ by single crystal *X*-ray diffraction at room temperature using photographically measured intensities[6] and found

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[3] L. S. Bartell, *J. Chem. Educ.*, 1968, **45**, 754.

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regular octahedral [TeCl$_6$]$^{2-}$ anions. K$_2$TeCl$_6$ is monoclinic at room temperature[5] and the structures of (NH$_4$)$_2$TeBr$_6$, Cs$_2$TeBr$_6$ (both cubic), and K$_2$TeBr$_6$ (monoclinic) have been examined in some detail.[5,7] Phase changes have been established for a number of compounds of this type on lowering the temperature but none apparently occurs with (NH$_4$)$_2$TeCl$_6$.[1]

I.r. and Raman spectroscopy has been extensively applied to these [TeX$_6$]$^{2-}$ compounds in the solid state and in solution.[8-16]

The number of bands and their activity are in general terms fully consistent with the group theoretical predictions for an octahedral (O_h) complex ion for the cubic compounds with sometimes additional bands observed for the non-cubic structures.[15] Some evidence has been presented that, in solution, weak bands appear in the Raman spectrum of [TeBr$_6$]$^{2-}$ inconsistent with a regular octahedral stereochemistry but the origin of these bands is far from clear.[8] It has also been noted that the half-width of the ν_3 (f_{1u}) i.r.-active fundamental of the [TeCl$_6$]$^{-2}$ anion is exceptionally large when compared with similar, and in some cases, isostructural hexachlorotin(IV) compounds M$^{\mathrm{I}}_2$SnCl$_6$.[9,11] I.r. reflectance measurements have shown that at least in part the breadth of these bands is genuine and not an artefact arising from the use of Nujol mulls to examine i.r. ' transmission ' spectra.[9,17]

The electronic spectra of the hexachloro- and hexabromo-compounds of selenium and tellurium have been measured[18-20] and a molecular orbital diagram has been produced for the regular octahedral species[18] (see also ref. 19). The two papers by Stufkens[19,20] interpret the splitting of the absorption band *ca.* 2900 Å both in the solid and solution states and the temperature dependence of the splitting in terms of a dynamic second order Jahn–Teller distortion in the excited state, and incidentally provide a useful resume of the literature.[19]

Continuing our studies on the Lewis acid behaviour of the tellurium halides we undertook a detailed examination of Rb$_2$TeCl$_6$. This compound has been prepared by a number of workers[2,4,10,21] and was chosen as being apparently cubic, for an *X*-ray study and some calorimetric experiments. The former was undertaken to establish if changing the cation (NH$_4$ and Rb) had significant effects on the anion bond lengths and to see if any peculiar features of the atomic thermal parameters were present which might suggest the presence of a distorted anion. Scanty data are available on the quantitative aspects of the Lewis acidity of the tellurium(IV) halides and in particular a comparison of Te$^{\mathrm{IV}}$ and Sn$^{\mathrm{IV}}$ is lacking. The present measurements, together with the calculated lattice energies are an attempt to remedy this situation.

The use of thermodynamic data in the study of the interaction between element halide Lewis acids and Lewis bases has been developed by a number of authors (see for example refs. 22—25 and references therein). Although one would ideally determine the enthalpy and free energy changes for the gas phase reaction, only in rare favourable cases is this possible. The problem is frequently complicated by essentially complete dissociation in the gas phase or the insolubility of the complex in a suitable solvent. Solvents themselves present problems because many are in their own right Lewis bases introducing competitive reactions or solvolysis, and the inertness of the so-called inert solvents remains at least uncertain. With the more reactive halides there are considerable experimental difficulties associated with obtaining reliable results. However, in spite of these difficulties valuable results have been obtained among groups of closely related molecules when either: (a) the Lewis acid is fixed and the ligand is changed, or (b) the ligand is fixed and the Lewis acid is changed. Within a restricted range of compounds trends in ΔH or ΔG have been discussed in terms of various electronic or steric effects. (The latter being in fact a particular form of electronic effect.)

A few thermochemical studies have been reported on tin(IV) chloride adducts of the type SnCl$_4$,2L where L is a complex organic monodentate ligand (refs. 26—28 and references therein). The second purpose of the present study was to establish, using the simple monoatomic chloride ion ligand, the enthalpy change associated with reaction (1), where M is tellurium and tin.

$$\mathrm{MCl_4(g) + 2Cl^-(g) \longrightarrow [MCl_6]^{2-}(g)} \qquad (1)$$

Rb$_2$SnCl$_6$ and Rb$_2$TeCl$_6$ are known to be isomorphous in the solid state[4] and contain the regular octahedral [MCl$_6$]$^{2-}$ anions (M = Sn or Te), and both compounds are examined in the present study.

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Structure Determination of Rb_2TeCl_6

Yellow crystals of Rb_2TeCl_6 were prepared from an aqueous hydrochloric acid solution following the method of Brauer[29] and pumped dry under vacuum. Weissenberg and precession photographs confirmed the cubic symmetry and the systematic absences for hkl; $h + k$, $k + l$, $l + h = 2n + 1$; agreed with the space group $Fm3m$ (No. 225). Cell dimensions measured from the photographs and from diffractometer 2θ values agreed well with Engel's value of 10·233 Å.[4]

Crystal Data.—Cubic, $a = 10{\cdot}233$ Å, $M = 511{\cdot}24$, $U = 1075{\cdot}5$ Å^3, $Z = 4$, $D(X\text{-ray}) = 3{\cdot}16$. D(found) (flotation in CH_2I_2/CCl_4 mixtures) = 3·08. μ Cu-K_α ($\lambda = 1{\cdot}5418$) = 474·0 cm^{-1}; μ Mo-K_α ($\lambda = 0{\cdot}7107$) = 134·4 cm^{-1}.

Data Collection.—A suitable crystal was mounted on a glass fibre and aligned on the G.E. XRD-6 manual diffractometer. 87 Reflections were measured from a unique part of reciprocal space up to a 2θ max. of 54·6° using zirconium filtered Mo-K_α radiation (45 kV, 11·0 mA). Using a take-off angle of 1°, reflections were scanned in the $2\theta/\omega$ mode over a range of *ca.* 1·5° at 2° per min with increasing 2θ. A stationary background count for 10 s was recorded at the start and finish of the scan. Two standard reflections were monitored during the data collection and used to provide a scale factor to allow for deterioration in the crystal and long term fluctuations in the X-ray source intensity.

Calculation of Intensities.—For each reflection the measured intensity $I(hkl)$ was calculated as:

$$I(hkl) = \left(C_S - (C_1 + C_2)\frac{t_S}{t_B}\right) \times \text{(reference reflection factor)}$$

where C_S = total counts during scan, C_1, C_2 = background counts at start and end of scan, t_S = scan time (s), t_B = total background counting time (s). For reflections that were measured more than once the average value of $I(hkl)$ was taken. The crystal chosen for this data was a nearly perfect octahedron with one vertex incomplete and with a diagonal measured as 0·40 mm. The absorption correction was applied assuming a regular octahedral shaped crystal by the method of de Meulenaer and Tompa.†

Structure Determination and Refinement.—The atomic coordinates given by Wyckoff[30] were used as the starting point for the structure refinement (Te 0,0,0; Rb $\frac{1}{4},\frac{1}{4},\frac{1}{4}$; Cl 0·245, 0, 0). The atomic form factors for Rb^+, and neutral Cl and Te, together with the dispersion correction $\Delta f'$ and $\Delta f''$ for all three atom types were taken from International Tables for X-ray Crystallography.[31] After correction for the Lorentz and polarisation factors, a set of observed structure factors was obtained and used in the subsequent analysis. One cycle of full matrix least squares refinement using unit weights reduced R to 0·160 (see Table 1). Two principal approaches are available for deriving weighting schemes for a least squares analysis. (i) The weights (w) may reflect trends in $|\Delta F|$ and are chosen in such a way that $w\Delta^2$ is a constant. A plot of $|\Delta F|$ versus F_o for various ranges of F_o was fitted approximately by the equation $\Delta F = A + BF_o$ and this was used in the empirical weighting scheme (Scheme 1). (ii) The weight may reflect the precision of F_{obs} [$w = 1/(\text{variance of } F_{obs})$], and for diffractometer experiments this can be related to the number of counts at the detector. Such schemes often include an additional parameter to allow for other random sources of error[32] and Grant *et al.*[33] have suggested a method of optimising this parameter (Scheme 2). It is known that thermal parameters are sensitive to changes in the weighting scheme and it was felt worthwhile to explore both approaches. The results are shown in Table 1. The point group symmetries of Rb and Te are such that for the atom thermal parameter $U_{11} = U_{22} = U_{33}$ and U_{ij} $(i \neq j) = 0$ while for Cl the restrictions are $U_{22} = U_{33}$, U_{ij} $(i \neq j) = 0$.[34] The thermal parameters derived from the two schemes for isotropic atoms are within one standard deviation of each other and this gives some confidence in their values. Weighting scheme 1 gave a slightly lower R index and was used for the anisotropic atom refinement to give a final R of 0·050. In the Figure we present the 50% probability ellipsoids. It seems reasonable to treat the $[TeCl_6]^{2-}$ ion as a rigid body following the method of Cruickshank[35] which is valid for this particular site symmetry.[36,37] For the tellurium atom the elements of the translation tensor (T_{ij}) are equal to the elements of U. For the chlorine atom U_{22} ($= U_{33}$) allows us to calculate the ω_{33} ($= \omega_{22}$) element of the libration tensor (ω) and hence a root mean square amplitude of libration of $4\frac{1}{2}$°. The Te–Cl bond length (uncorrected) is 2·525 (0·005) Å and when corrected for rigid body motion we obtain a value of 2·541 (0·005) Å. [The correction was calculated from Cruickshank's treatment[38] assuming a width parameter (q^2) large compared with s^2 and t^2 and using Johnson's treatment (ref. 37 p. 223 equation 15).] Attempts to refine scattering factors were inconclusive.

TABLE 1

Structure refinement and weighting scheme *

	Isotropic atoms		Anisotropic Cl atom
Parameter	Weight scheme 1	Weight scheme 2	Weight scheme 1
x/a co-ordinate of Cl x/a, 0,0	0·247(1)	0·250(1)	0·2468(5)
U_{11} or U (Cl)	3·87(30)	4·05(29)	2·32(24)
U_{22} (Cl)			6·09(40)
U (Te)	1·70(21)	1·78(32)	2·17(08)
U (Rb^+)	4·42(24)	4·05(29)	4·82(12)

Weight scheme 1. Weight = $1{\cdot}0/(A + BF_o)$; $A = 15{\cdot}25$, B = 0·0365

Weight scheme 2. $1/\text{Weight} = \dfrac{K}{4Lp}\dfrac{(I + B)}{(I - B)} + C^2|F(h)|^2$ where K is obtained from a Wilson plot and C^2 from calculated σ_1 and G^2, ref. 33. $G^2 = \sum_h|\Delta(h)|^2|\sum_h|F(h)|^2$

* All U values × 10^2. Least squares standard deviation in parentheses.

Discussion of the Structure.—The Te–Cl bond length in

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† Using the program ABSCOR from the X-RAY '63 suite of programs.

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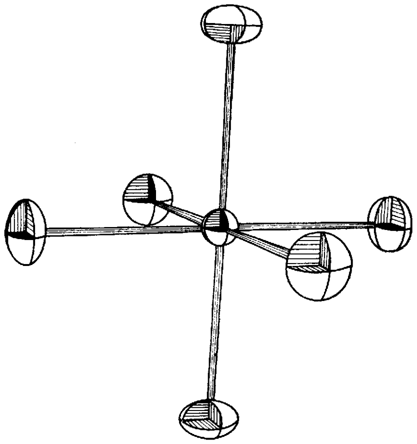
[37] C. K. Johnson in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, 1970, pp. 209, 223.

[38] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

Rb_2TeCl_6 [2·541 Å (corrected)] is in good agreement with Hazell's value for $(NH_4)_2TeCl_6$ [2·541 Å (corrected)] [6] and thus it seems that the Te–Cl bond length is not sensitive to the gegen ion in these two compounds. Similarly we conclude from the normal magnitude of the vibrational amplitudes that there is no crystallographic evidence to support a distorted octahedral stereochemistry in the ground state which acquires the observed regular (O_h) configuration by time or lattice averaging.



All calculations were performed at the Atlas Computer Laboratory, Chilton, using J. M. Stewart's *X*-ray suite of crystallographic programmes. The Figure was drawn using Johnson's ORTEP programme [39] implemented at the above installation.

Lattice Energy Calculations on Rb_2TeCl_6 *and* Rb_2SnCl_6

The structural parameters of Rb_2TeCl_6 obtained in the previous section were used for the lattice energy calculation. Early work by Engel [4,30] established the crystal structure of Rb_2SnCl_6 which is isomorphous with Rb_2TeCl_6 and K_2PtCl_6. In the following lattice energy calculations on Rb_2SnCl_6 ($a = 10{\cdot}099$ Å) the chlorine atom (x,0,0) has one variable parameter which was taken as 0·240.

The Madelung Constant.—The Madelung constant (A_δ) was calculated using the method of Wood [40] for the process:

$$Rb_2MCl_6(\text{cryst}) \longrightarrow 2Rb^+(\text{gas}) + [MCl_6]^{2-}(\text{gas}) \qquad (2)$$

M = Te or Sn.

The characteristic distance used was the cube root of the molecular volume and the constant was evaluated for various charge distributions within the anion. In case I a $-2{\cdot}0$ charge on atom M; case II a $-0{\cdot}286$ charge on M and each of the six chlorines; in case III, zero charge on M and $-0{\cdot}333$ on each chlorine atom; in case IV $+1{\cdot}0$ charge on M and $-0{\cdot}5$ charge on each chlorine atom, and in case V a $+4{\cdot}0$ charge on M and $-1{\cdot}0$ charge on each chlorine atom. Five shells were calculated for each model, the error resulting from the omission of the fifth shell being in all cases less than 0·1% of the value of A_δ. The results are shown in Table 2. The coulombic energy of the lattice for process (2) is calculated as $U_{\text{Coul}} = A_\delta e^2 N_0/r_\delta$ where N_0 (Avogadro's Number) $= 6{\cdot}023 \times 10^{23}$ mol^{-1}, $e = 4{\cdot}803 \times 10^{-10}$ e.s.u., 1 kcal $= 4{\cdot}184 \times 10^{10}$ erg, $r_\delta =$ (Molecular volume)$^{\frac{1}{3}}$ Å, 1 Å $= 10^{-8}$ cm.

TABLE 2

Madelung constants for Rb_2MCl_6 (M = Te or Sn)

Model	Charge distribution [a]	$A_\delta(Rb_2TeCl_6)$ [b]	$A_\delta(Rb_2SnCl_6)$ [c]
I	$Rb_2^{(1+)}[M^{(2\cdot0-)}Cl_6^{(0)}]$	7·32460 [d]	7·32460 [d]
II	$Rb_2^{(1+)}[M^{(0\cdot286-)}Cl_6^{(0\cdot286-)}]$	6·72299	6·78211
III	$Rb_2^{(1+)}[M^{(0)}Cl_6^{(0\cdot333-)}]$	6·60384	6·67439
IV	$Rb_2^{(1+)}[M^{(1+)}Cl_6^{(0\cdot5-)}]$		6·32265
V	$Rb_2^{(1+)}[M^{(4+)}Cl_6^{(1-)}]$	4·81659	5·10065

[a] The charges on the atoms are given as superscripts in parentheses. [b] Madelung constant for the process $Rb_2TeCl_6(c) \longrightarrow 2Rb^+(g) + [TeCl_6]^{2-}(g)$. Te–Cl distance is 2·5255 Å; $r_\delta = 6{\cdot}44639$ Å. [c] Madelung constant for the process $Rb_2SnCl_6(c) \longrightarrow 2Rb^+(g) + [SnCl_6]^{2-}(g)$. Chlorine co-ordinate taken as 0·24, 0, 0; Sn–Cl distance (2·42376 Å); $r_\delta =$ (molecular volume)$^{1/3}$ (6·36197 Å). [d] The literature value for model I (the calcium fluoride structure) is 7·33058, ref. 50 and T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 158.

Other calculations on the Madelung constant of the K_2PtCl_6 structure have been reported by Hoppe,[41] who gives a Madelung constant for process (2) of 3·21794 based on the Pt–K distance. When suitably converted to one based on the cube root of the molecular volume [multiplication by $1/(4^{\frac{1}{3}} \times 0{\cdot}4330)$] this gives A_δ (model V, $x/a = 0{\cdot}25$) of 4·68146, compared with our value of 4·81659.

van der Waals Energy.—The van der Waals energy was calculated from the formula proposed by London.[42,43]

$$U = \frac{3}{2R^6}\left(\frac{\varepsilon_i\varepsilon_j}{\varepsilon_i + \varepsilon_j}\right)\alpha_i\alpha_j = \frac{C_{ij}}{R^6} \qquad (3)$$

i and j refer to two atoms, separated by a distance R, and ε and α are the characteristic energy and polarisability respectively used to calculate the interaction constant (C_{ij}). The values used are shown in Table 3. The characteristic energies of Rb^+, Te^{4+}, and Sn^{4+} were taken as 90% of the second and fifth ionisation potential of the elements.[44] The values for Cl^- were taken from ref. 45. The polarisability of the Rb^+ and Sn^{4+} ions were taken from Pauling's tabulation of the molar refractivity [46] ($4/3\,\pi N\alpha = R_\infty$), Te^{4+} was obtained from the value for Sn^{4+} assuming that the polarisability varies as the cube of the ionic radius. Ionic radii were taken from Greenwood [47] [$r(Sn^{4+}) = 0{\cdot}71$; $r(Te^{4+}) = 0{\cdot}89$ Å; $\alpha(Sn^{4+}) = 0{\cdot}500 \times 10^{-24}$ cm^3].

TABLE 3

Characteristic energies and polarisabilities of ions

Ion	$10^{12}\varepsilon$/erg molecule^{-1}	$10^{24}\alpha$/cm^3
Rb^+	39·76	1·42
Te^{4+}	95·21	0·985
Cl^-	15·6	3·45
Sn^{4+}	131·3	0·50

The C_{ij} values were calculated from equation (3) and the values given in Table 3, and are listed in Table 4. The van

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[46] L. Pauling, *Proc. Roy. Soc.* (*A*), 1927, **114**, 181.

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der Waals sums (S_{ij}) were calculated over shells of unit cells by the method of D'Orazio and Wood.[48]

TABLE 4

Interaction constants (C_{ij}) and van der Waals sums (S_{ij})

Rb_2TeCl_6 [a]	$10^{60}C_{ij}$ erg cm^6 molecule^{-1}	S_{ij} *
Rb^+–Rb^+	60·1	33·06
Cl^-–Cl^-	139	533·27
Te^{4+}–Te^{4+}	69·3	6·69
Cl^-–Rb^+	82·3	857·48
Cl^-–Te^{4+}	68·3	68·99
Rb^+–Te^{4+}	58·8	82·54
Rb_2SnCl_6 [b]		
Rb^+–Rb^+	60·1	33·06
Cl^-–Cl^-	139·2	479·05
Sn^{4+}–Sn^{4+}	24·6	6·69
Cl^-–Rb^+	82·3	856·04
Cl^-–Sn^{4+}	36·1	67·5
Rb^+–Sn^{4+}	32·5	82·54

* For the process in equation (2).

[a] Taking (molecular volume)^3 = $0{\cdot}71763 \times 10^5$ Å^6. [b] Taking (molecular volume)^3 = $0{\cdot}66306 \times 10^5$ Å^6.

Calculation of the Lattice Energy.—Coulombic energies were calculated from the room temperature cell dimensions. The repulsion energies were calculated by the method of D'Orazio and Wood (ref. 48, equation 13) using a value of ρ of 0·33 Å taken from data on the alkali halides[49] and taking the anion to cation distance as the Rb–M distance. The lattice energy is taken as the sum of the three terms and ignores the zero point energy (see Table 5).

The change in coulombic energy with charge distribution is very much larger than for Ga[$GaCl_4$] for example[45] and it becomes desirable to narrow the limits set by the limiting but highly unreasonable (in chemical terms) models I and V. Pauling's electroneutrality principle[50] seems a useful rule and taking Pauling electronegativity values (2·1 Te; 3·0 Cl) gives a '20% ionic Te–Cl bond' with a resulting charge distribution close to that for model II. Intuitive limits might be 360—325 kcal mol^{-1} for the coulombic part of the lattice energy and hence a lattice energy of 334 ± 17 kcal mol^{-1} for Rb_2TeCl_6. Similarly for Rb_2SnCl_6 a lattice energy of 342 ± 17 kcal mol^{-1} represents likely limits. N.q.r. spectroscopy has been used to give an estimate of ionic character,[1] but it is not clear that the values obtained for [$SnCl_6$]$^{2-}$ are those appropriate for the lattice energy calculation.

TABLE 5

Lattice energy (kcal mol^{-1})

Rb_2TeCl_6	I	II	III	IV	V
Coulombic energy (U_{coul}) [a]	377·2	346·3	340·2		248·1
van der Waals energy (U_{VDW})	31·4	31·4	31·4		31·4
Repulsion energy (U_{rep})	−42·1	−39·8	−39·4		−32·5
Lattice energy	366·5	337·9	332·2		247·0
Rb_2SnCl_6					
Coulombic energy (U_{coul}) [b]	382·3	354·0	348·4	330·0	266·2
van der Waals energy (U_{DVW})	31·4	31·4	31·4	31·4	31·4
Repulsion energy (U_{rep})	−43·1	−40·9	−40·5	−39·1	− 34·3
Lattice energy	370·6	344·5	339·3	322·3	263·3

[a] r_δ = 6·44639 Å. [b] r_δ = 6·36197 Å.

Thermochemical Results

Experimental.—Rb_2TeCl_6 was prepared by the method given earlier; rubidium chloride (AnalaR grade) was dried at 105° prior to use, tellurium tetrachloride was prepared by the method of Suttle and Smith[51] and Rb_2SnCl_6 was prepared by the method of Brauer[29] (Found: Cl, 42·80. Calc. for Rb_2SnCl_6: Cl, 42·34%). Tin tetrachloride was distilled *in vacuo* into the fragile calorimetric bulbs which were sealed off. Solid samples were loaded into the bulbs in a dry box.

The detailed design and specifications of the microcalorimeter are given in ref. 28 and we present below a brief outline of the procedure. The calorimeter was tested by measuring the heat of solution of potassium chloride in water. Several runs gave an average value of +4·23 ± 0·23 kcal mol^{-1}, which compares well with the literature value +4·19 ± 0·01 kcal mol^{-1}.[52] The initial temperature of the calorimeter was adjusted to 25·0 ± 0·5 °C. The reactions were initiated by breaking the ampoules under 30 ml of 0·93M hydrochloric acid. Rb_2TeCl_6 was found to be not very soluble and early runs were observed to have undissolved material in the calorimeter. Smaller samples with efficient stirring were adopted. The endothermic heats of solution were determined by the constant temperature method. For the exothermic reactions the temperature was recorded for periods before and after the reaction or calibration by plotting thermistor resistance against time at one minute intervals. Calibration procedures were such as to be as close as possible to the reaction conditions. The heats of solution were calculated from the following relationships.

Heat produced in the calorimeter = $Q \times r$ where Q (the heat supplied electrically) = I^2RS/J. I is the current (in A) flowing through the heater (resistance R Ω) for time S (s) and J is the mechanical equivalent of heat.

$$r = \log\,(R_1{}^i/R_1{}^f)/\log\,(R_2{}^i/R_2{}^f)$$

where i and f denote the initial and final thermistor resistance and 1 and 2 refer to the reaction and calibration respectively. The relationship between temperature (T/K) and resistance (R) of the thermistor is of the form $R_T = R_\infty\,e^{B/T}$ where R_∞ and B are constants and this may be used to derive the expression for r above.

The molar heat of solution is then 1000 $Q.r/m$ where m is the amount of sample (in mmol).

Results on Rb_2TeCl_6 and $TeCl_4$.—The heat of formation of Rb_2TeCl_6 (solid). The heats of solution of solid RbCl, $TeCl_4$, and Rb_2TeCl_6 were measured in 0·93M aqueous hydrochloric acid at 25 °C and the results are shown in Table 6. Hydrochloric acid was chosen to give soluble species and the evidence favours the presence of the [$TeCl_6$]$^{2-}$ ion. However, our results and their subsequent interpretation do not depend on any assumptions about the nature of solution species other than that $TeCl_4$ and Rb_2TeCl_6 give the same tellurium containing moiety. The heat of solution of RbCl in water has been reported as 4·0[53] and 4·50 kcal mol^{-1} at 298 K.[54]

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The enthalpy *change* at 298 K for the process

$$2\mathrm{RbCl(c)} + \mathrm{TeCl_4(c)} \longrightarrow \mathrm{Rb_2TeCl_6(c)}$$

may be calculated as $-11{\cdot}4$ kcal mol^{-1}. Using the standard heat of formation of RbCl ($-102{\cdot}91$) and $\mathrm{TeCl_4}$ ($-77{\cdot}2$ kcal mol^{-1} at 298 K) from circular 500,[55] the standard heat of formation of $\mathrm{Rb_2TeCl_6}$ is calculated to be $-294{\cdot}4$ kcal mol^{-1} at 298 K.

The enthalpy change for $2\mathrm{Cl^-(g)} + \mathrm{TeCl_4(g)} \longrightarrow [\mathrm{TeCl_6}]^{2-}\mathrm{(g)}$. The standard heat of formation of $[\mathrm{TeCl_6}]^{2-}$(g) at 298 K is given by the relationship

$$\Delta H_f{}^\circ\,[\mathrm{TeCl_6{}^{2-}(g)}] = U + \Delta H_f{}^\circ\,[\mathrm{Rb_2TeCl_6(c)}] - 2\Delta H_{\mathrm{sub}}(\mathrm{Rb}) - 2\,I.P.(\mathrm{Rb}) + \int_0^{298} [Cp(\mathrm{Rb_2TeCl_6(c)}) + 2Cp(\mathrm{e^-(g)}) - 2Cp(\mathrm{Rb(g)}) - Cp(\mathrm{TeCl_6{}^{2-}(g)})]\mathrm{d}T$$

where U (the calculated lattice energy) $= 334 \pm 17$; $\Delta H_f{}^\circ\,[\mathrm{Rb_2TeCl_6(c)}] = -294{\cdot}4$; $\Delta H_{\mathrm{sub}}(\mathrm{Rb}) = +19{\cdot}5$;[49] $I.P.(\mathrm{Rb}) = 96{\cdot}4$ kcal mol^{-1}.[44] The specific heat terms were neglected as those for $\mathrm{Rb_2TeCl_6}$ and $[\mathrm{TeCl_6}]^{2-}$ are uncertain but have opposite sign and should approximately cancel each other out while those for the electron ($1{\cdot}5$ kcal mol^{-1} [45]) and for rubidium ($1{\cdot}0$ kcal mol^{-1} [55]) are small. The resulting value of $\Delta H_f{}^\circ\,[\mathrm{TeCl_6{}^{2-}(g)}]$ is $-192{\cdot}2 \pm 17$ kcal mol^{-1}.

The enthalpy change (ΔH_1) for the process below is calculated to be $-21{\cdot}8 \pm 17$ kcal mol^{-1} at 298 K.

$$2\mathrm{Cl^-(g)} + \mathrm{TeCl_4(g)} \xrightarrow{\Delta H_1} [\mathrm{TeCl_6}]^{2-}\mathrm{(g)} \qquad (4)$$

since

$$\Delta H_1 = \Delta H_f{}^\circ\,[\mathrm{TeCl_6{}^{2-}(g)}] - 2\Delta H_f{}^\circ\,[\mathrm{Cl^-(g)}] - \Delta H_f{}^\circ\,[\mathrm{TeCl_4(c)}] - \Delta H_{\mathrm{sub}}\,[\mathrm{TeCl_4(s)}]$$

where $\Delta H_f{}^\circ\,[\mathrm{TeCl_6{}^{2-}(g)}] = -192{\cdot}2$; $\Delta H_f{}^\circ\,[\mathrm{Cl^-(g)}] = -55{\cdot}8$;[56] $\Delta H_f{}^\circ\,[\mathrm{TeCl_4(c)}] = -77{\cdot}2$; $\Delta H_{\mathrm{sub}}\,[\mathrm{TeCl_4(s)}] = +18{\cdot}4$ kcal mol^{-1}.[57] The enthalpy of sublimation of $\mathrm{TeCl_4}$ was calculated from the temperature dependence of the vapour pressure. The gas phase molecular weight of $\mathrm{TeCl_4}$ favours the presence of monomers even though solution studies supporting polymeric and monomeric molecules have been published.[58] Tetrameric units occur in the solid state.[59]

An alternative (and equivalent procedure) is to consider the cycle below to obtain ΔH_1.

$$\begin{tikzcd}
2\mathrm{Rb^+(g)} + 2\mathrm{Cl^-(g)} + & \mathrm{TeCl_4(g)} \arrow[r, "\Delta H_1"] & 2\mathrm{Rb^+(g)} + [\mathrm{TeCl_6}]^{2-}\mathrm{(g)} \\
2\mathrm{RbCl(c)} + \arrow[u, "U'"] & \mathrm{TeCl_4(c)} \arrow[u] \arrow[r] & \mathrm{Rb_2TeCl_6(c)} \arrow[u]
\end{tikzcd}$$

$\Delta H_{\mathrm{diss}}\,[\mathrm{Cl_2(g)}] = +57{\cdot}8$ kcal mol^{-1} [49] and using numerical data already given U' calculates as 163 kcal mol^{-1}, in good agreement with literature values.[49]

Results on $\mathrm{Rb_2SnCl_6}$ *and* $\mathrm{SnCl_4}$.—*The heat of formation of* $\mathrm{Rb_2SnCl_6}$ (*solid*). The heat of reaction of liquid $\mathrm{SnCl_4}$ with aqueous hydrochloric acid ($0{\cdot}93$M) and the heat of solution of $\mathrm{Rb_2SnCl_6}$ in the same acid were determined. The results are presented in Table 6. The enthalpy for the following reaction was calculated as $-29{\cdot}4$ kcal mol^{-1} at 298 K.

$$2\mathrm{RbCl(c)} + \mathrm{SnCl_4(l)} \longrightarrow \mathrm{Rb_2SnCl_6(c)}$$

Using the standard heat of formation of RbCl ($-102{\cdot}91$) and $\mathrm{SnCl_4}$ ($-130{\cdot}3$ kcal mol^{-1} at 298 K) [55] the standard heat of formation of $\mathrm{Rb_2SnCl_6(c)}$ is calculated to be $-365{\cdot}5$ kcal mol^{-1} at 298 K.

The literature value for the heat of reaction of $\mathrm{SnCl_4}$ with water is $-28{\cdot}5$ kcal mol^{-1} at $283{\cdot}5$ K,[54] but the nature of the solution species under these conditions is not clear. There is strong Raman spectroscopic evidence for the presence of $[\mathrm{SnCl_6}]^{2-}$ ions in aqueous hydrochloric acid solutions of $\mathrm{SnCl_4}$ but other species exist at lower HCl concentrations.[60] Our thermochemical results are independent of any assumptions about the nature of solution species, other than that both $\mathrm{SnCl_4}$ and $\mathrm{Rb_2SnCl_6}$ in aqueous hydrochloric acid give rise to the same tin containing entities.

TABLE 6

Heats of solution in 30 ml of $0{\cdot}93$M hydrochloric acid at 25 °C

Compound	Wt/g	Amount/ mmol	q/cal	ΔH/kcal mol^{-1}
RbCl	0·1893	1·566	7·29	+4·66
RbCl	0·1126	0·931	4·28	+4·60
RbCl	0·0443	0·366	1·66	+4·54
RbCl	0·1321	1·093	5·38	+4·92
				Average 4·7 ± 0·3 *
$\mathrm{TeCl_4}$	0·1788	0·664	14·54	−17·05
$\mathrm{TeCl_4}$	0·2811	1·043	26·23	−17·46
$\mathrm{TeCl_4}$	0·4204	1·561	37·66	−17·30
				Average −17·3 ± 0·3 *
$\mathrm{Rb_2TeCl_6}$	0·0438	0·086	0·28	+3·27
$\mathrm{Rb_2TeCl_6}$	0·0437	0·086	0·29	+3·38
$\mathrm{Rb_2TeCl_6}$	0·0614	0·120	0·37	+3·07
$\mathrm{Rb_2TeCl_6}$	0·1568	0·307	1·22	+3·98
				Average 3·4 ± 0·6 *
$\mathrm{SnCl_4}$	0·8202	3·149	110·67	−31·22
$\mathrm{SnCl_4}$	0·8751	3·359	113·74	−31·55
$\mathrm{SnCl_4}$	0·8945	3·434	114·00	−31·38
				Average −31·4 ± 0·3 *
$\mathrm{Rb_2SnCl_6}$	0·0487	0·097	0·76	+7·86
$\mathrm{Rb_2SnCl_6}$	0·0505	0·101	0·65	+6·49
$\mathrm{Rb_2SnCl_6}$	0·0542	0·108	0·81	+7·50
$\mathrm{Rb_2SnCl_6}$	0·0355	0·071	0·52	+7·29
$\mathrm{Rb_2SnCl_6}$	0·0450	0·090	0·68	+7·60
				Average 7·34 ± 0·9 *

* Estimated 95% confidence limits.

The enthalpy and entropy change for $2\mathrm{Cl^-(g)} + \mathrm{SnCl_4(g)} \longrightarrow [\mathrm{SnCl_6}]^{2-}\mathrm{(g)}$. Using the calculated lattice energy, the standard heat of formation of $\mathrm{Rb_2SnCl_6(c)}$, ($-365{\cdot}5$); $\Delta H_{\mathrm{sub}}(\mathrm{Rb}) = 19{\cdot}5$; $I.P.(\mathrm{Rb}) = 96{\cdot}4$ kcal mol^{-1} and neglecting the specific heat terms, allows the standard heat of formation of $[\mathrm{SnCl_6}]^{2-}$(g) at 298 K to be calculated as $-255{\cdot}8 \pm 17$ kcal mol^{-1}.

The enthalpy change (ΔH_2) for the process below is calculated to be $-21{\cdot}7 \pm 17$ kcal mol^{-1} at 298 K using $\Delta H_f{}^\circ\,[\mathrm{SnCl_6{}^{2-}(g)}] = -255{\cdot}8$; $\Delta H_f{}^\circ\,[\mathrm{Cl^-(g)}] = -55{\cdot}8$;[56]

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$\Delta H_f°$ [$SnCl_4$(l)] = −130·3;[55] ΔH_{vap} [$SnCl_4$(l)] = +8·3 kcal mol^{-1}.[55]

$$SnCl_4(g) + 2Cl^-(g) \xrightarrow{\Delta H_2} [SnCl_6]^{2-}(g) \qquad (5)$$

It is instructive to calculate the entropy change for equation (5)[61] using the vibrational frequencies for the $[SnCl_6]^{2-}$ ion.[62,63] In the absence of gas phase data, taking the experimental frequencies for solid Rb_2SnCl_6 as ν_1 (a_{1g}) = 316; ν_2 (e_g) = 241; ν_3, ν_4 (f_{1u}) = 312, 173; ν_5 (f_{2g}) = 171 cm^{-1} and the presumably calculated value for the inactive ν_6 (f_{2u}) vibration of 107 cm^{-1}[62] we find that $S°$ [$SnCl_6^{2-}$(g)] at 298 K is 101·90 cal deg^{-1} mol^{-1} [$S° = S_{trans}$ (43·11) + S_{rot} (25·33) + S_{vib} (33·45)]. [Taking two very different values of ν_6 (80 and 130 cm^{-1}) because of uncertainties in the value, changes $S°$ by about 3 entropy units]. Using the entropy of Cl^-(g) (39·46) and $SnCl_4$(g) (87·20 cal deg^{-1} mol^{-1}) at 298 K from Pitzer and Brewer[61] we find ΔS for the reaction in equation (5) is −64·22 cal deg^{-1} mol^{-1}. The very unfavourable entropy term arises primarily from the loss of translational entropy for the gas phase reaction under consideration.

SUMMARY AND DISCUSSION

The crystal structure of Rb_2TeCl_6 has been determined and the data interpreted in terms of a regular octahedral $[TeCl_6]^{2-}$ anion, with a Te–Cl bond length of 2·541(5) Å (corrected for rigid body motion of the anion).

The standard heat of formation of Rb_2TeCl_6(c) has been found to be −294·4 kcal mol^{-1} at 298 K. Using this value together with the calculated lattice energy and tabulated thermodynamic data, enables the enthalpy change (ΔH_1) for the reaction in equation (4) to be estimated as −21·8 ± 17 kcal mol^{-1} at 298 K. The calculation of the coulombic part of the lattice energy was found to be sensitive to the charge distribution within the anion, and one of the models examined (V) in which a large charge separation occurred, gave rise to a very small lattice energy. This calculation was thought to represent an unrealistic chemical situation and the limits of error (±17) represent likely limits based on chemical arguments.

Comparison of the thermochemical results with other main group halide species is difficult due to paucity of data but comparison with the Group III acceptor $GaCl_3$ with Cl^- ions to give $[GaCl_4]^-$ (ΔH = −80 ± 3 kcal mol^{-1} [45]) indicates the weakness of the interaction in the tellurium case. It is interesting that $[TeF_6]^{2-}$ has not been prepared although the $[TeF_5]^-$ ion is well known. Comparisons between the acceptor properties of Sn^{IV} and Te^{IV} present insight into the thermochemical effects of the lone pair of electrons.

The standard heat of formation of Rb_2SnCl_6(c) has been found to be −365·5 kcal mol^{-1} at 298 K. Using this value together with the calculated lattice energy enables the enthalpy change (ΔH_2) for the reaction in equation (5) to be estimated as −21·7 ± 17 kcal mol^{-1} at 298 K. The entropy change (−64·22 cal deg^{-1} mol^{-1} at 298 K) for equation (5) is calculated from the vibrational frequencies of the $[SnCl_6]^{2-}$ ion and as expected is unfavourable for complex formation due to the loss of translational entropy.

The equal value of ΔH_1 in equation (4) and ΔH_2 in equation (5) is fortuitous. The largest error in the thermodynamic quantities occurs in the lattice energy calculations, but if one accepts that for the two compounds Rb_2SnCl_6 and Rb_2TeCl_6, the anion charge distribution is similar,[1] then the enthalpy change for the two systems is the same to within a few kilocalories, though their numerical value remains uncertain to ±17 kcal mol^{-1}. Thus, measured by the enthalpy of reaction, $TeCl_4$ and $SnCl_4$ towards the chloride ion ligand, have the same, or very similar, acceptor power in the formation of the hexachloro-complex. It is important to note that the enthalpy change does not afford a direct comparison of bond strengths since a reorganisation energy of uncertain magnitude is involved. Indeed it is generally true that the discussion of enthalpy or free energy data of a chemical system, or the comparison of data from various chemical systems in terms of bond properties is a matter of some complexity.[22]

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