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Double Halide Ion Affinities of Metal Tetrahalides and Associated Bond Strengths

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Double halide ion affinities corresponding to the process:

$$MX_4(g) + 2X^-(g) \rightarrow MX_6^{2-}(g)$$

are calculated (M = Ti, Si, Ge, X = F; M = Ti, Zr, Hf, Nb, Ta, Mo, W, Os, Ge, Sn, Pb and Te, X = Ti; M = Ti, X = Br) from lattice energy studies and acceptor power towards Cl⁻ is as follows:

$$\begin{array}{ccccccc|ccc}
TiCl_4 & & & & & & & GeCl_4 & & \\
\wedge & & & & & & & \vee & & \\
ZrCl_4 & < & NbCl_4 & < & MoCl_4 & & & SnCl_4 & > & TeCl_4 \\
\wedge & & \wedge & & \wr & & & \wedge & & \\
HfCl_4 & > & TaCl_4 & > & WCl_4 & > & OsCl_4 & PbCl_4 & &
\end{array}$$

Homo and heterolytic bond structures are then calculated and the transition metal–chlorine bond strengths show the following periodic trends:

$$\begin{array}{ccccccccccccc}
Ti{-}Cl & & & & & & & & & & & & \\
\vee & & & & & & & & & & & & \\
Zr{-}Cl & < & Nb{-}Cl & < & Mo{-}Cl & & & & < & & & & Pd{-}Cl \\
\vee & & \vee & & \vee & & & & & & & & \vee \\
Hf{-}Cl & < & Ta{-}Cl & < & W{-}Cl & < & Re{-}Cl & < & Os{-}Cl & > & Ir{-}Cl & < & Pt{-}Cl
\end{array}$$

The actinide metal–clorine bond strengths are in the order:

$$Th{-}Cl > U{-}Cl > Pu{-}Cl$$

Introduction

In 1967, Pearson and Mawby [1], in a review of metal–halogen bond strengths, considered only one hexahalometallate(IV) ion, TiF_6^{2-}; no *systematic* study of bond strengths over the transition metal, main-group or actinides for MX_6^{2-} ions has since been made. There have, however, been a number of isolated studies, based on lattice energy calculations, of the enthalpies of formation of the hexahalometallate(IV) ions, $\Delta H_f^\ominus(MX_6^{2-})(g)$ and hence of the metal–halogen bond strengths and associated halide ion affinities of the parent tetrahalides (where values of $\Delta H_f^\ominus(MX_4)(g)$ are available). Specifically Webster and Collins [2] and Jenkins and Smith [3] considered $SnCl_6^{2-}$ and $TeCl_6^{2-}$; De Jonge [4] and Hartley [5] have studied $PtCl_6^{2-}$ and $PtBr_6^{2-}$ while Jenkins [6] treated the former ion; Welsh, Brill, Thompson, Wood and Gearhart [7] have studied $GeCl_6^{2-}$, $SnCl_6^{2-}$, $PbCl_6^{2-}$ while Westland *et al.* [8, 9] has considered $ZrCl_6^{2-}$, $HfCl_6^{2-}$, $NbCl_6^{2-}$, $TaCl_6^{2-}$ and $SnCl_6^{2-}$. The only actinide metal–halogen bond strengths to be calculated have been those derived from the studies of Volovenko, Suglobova, Chirkst and Volkov [10, 11] on UCl_6^{2-} and UBr_6^{2-}.

The calculation of lattice energies of salts containing complex anions of the type MX_6^{2-} has been extensively explored recently by Jenkins and Pratt [12–14]. These studies have generated lattice energies for the salts A_2MX_6 where A is an alkali metal or ammonium X is a halogen, usually F, Cl or Br and M = Ti, Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Si, Ge, Sn, Pb, Sb, Se, Te, Po, Ce, Th, U, Pu and Bk using a systematic approach to salts with available crystal structures. Though ancillary thermodynamic data does not exist ($\Delta H_f^\ominus(A_2MX_6)(c)$ or $\Delta H^\ominus(MX_4)(g)$) for many of the salts for which lattice energies have been calculated, nevertheless, data for double halide ion affinities and bond energies for nearly thirty ions can now be obtained and compared.

Defining halide ion affinities for gaseous tetrahedralides MX_4 as the enthalpy change, ΔH_X. for the process:

$$MX_4(g) + 2X^-(g) \rightarrow MX_6^{2-}(g)$$

we can obtain the double halide ion affinity data given in Table I. These figures are generated using the equation:

$$\Delta H_X = \Delta H_f^\ominus(MX_6^{2-})(g) - \Delta H_f^\ominus(MX_4)(g) - 2\Delta H_f^\ominus(X^-)(g) \qquad (1)$$

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TABLE I. Double Halide Ion Affinities, $\overline{\Delta H_X}$ for MX_4 ($kJ\ mol^{-1}$).

MX_4	$\overline{\Delta H_X}$ ($kJ\ mol^{-1}$)	$\Delta H_f^\ominus(MX_4)(g)$ Subsidiary Data ($kJ\ mol^{-1}$)	Reference
TiF_4	−228	−1552	[15]
$TiCl_4$	−76	−763.2	[15]
$ZrCl_4$	−164	−870.3	[15]
$HfCl_4$	−259	−889.0	[15]
$NbCl_4$	−171	−561	[16]
$TaCl_4$	−222	−561	[16]
$MoCl_4$	−192	−386.3	[17]
WCl_4	−188	−305	[15]
$OsCl_4$	−181	−79	[15]
$TiBr_4$	−125	−549.3	[15]
SiF_4	−138	−1615	[15]
GeF_4	−242	−1190	[19]
$GeCl_4$	+7	−496	[15]
$SnCl_4$	−192	−472	[15]
$PbCl_4$	−163	−285	[7]
$TeCl_4$	−153	−246	[2]

obtaining $\Delta H_f^\ominus(MX_6^{2-})(g)$ from lattice energy studies, taking $\Delta H_f^\ominus(MX_4)(g)$ from the literature indicated in Table I and assuming $\Delta H_f^\ominus(F^-)(g) = -271\ kJ\ mol^{-1}$, $\Delta H_f^\ominus(Cl^-)(g) = -246\ kJ\ mol^{-1}$ and $\Delta H_f^\ominus(Br)(g) = -234\ kJ\ mol^{-1}$ [18].

The halide ion affinities are such that the order of acceptor power towards the Cl^- gaseous ion is as follows:

$$\begin{array}{ccccccc|ccc} \mathrm{TiCl_4} &&&&&&& \mathrm{GeCl_4} && \\ \wedge &&&&&&& \vee && \\ \mathrm{ZrCl_4} & < & \mathrm{NbCl_4} & < & \mathrm{MoCl_4} &&& \mathrm{SnCl_4} & > & \mathrm{TeCl_4} \\ \wedge && \wedge && \wr &&& \wedge && \\ \mathrm{HfCl_4} & > & \mathrm{TaCl_4} & > & \mathrm{WCl_4} & > & \mathrm{OsCl_4} & \mathrm{PbCl_4} && \end{array}$$

This order corresponds to that found by Westland and coworkers [8, 9] for M = Zr, Hf, Nb and Ta, except that they find $ZrCl_4$ is a better acceptor than $NbCl_4$. The lattice energies obtained by our new minimisation procedure are much lower than those obtained by Gelbman and Westland [9] using the Kapustinskii equation.

The data calculated for $\Delta H_f^\ominus(MX_6^{2-})(g)$ can be used to calculate homo, $\overline{E(M-X)}_{hom}$, and heterolytic, $\overline{E(M-X)}_{het}$ bond energies (the latter being referred to as coordinate bond energy, c.b.e.), these are defined:

$$\overline{E(M-X)}_{hom} = -\frac{1}{6}\Delta H_f^a(MX_6^{2-})(g) \qquad (2)$$

the enthalpy of the process ($\Delta H_f^a(MX_6^{2-})(g)$):

$$M(g) + 6X(g) + 2e \rightarrow MX_6^{2-}(g)$$

being involved.

$$\overline{E(M-X)}_{het} = -\frac{1}{6}\Delta H_f^i(MX_6^{2-})(g) = \frac{1}{6}\text{c.b.e.} \qquad (3)$$

involves the enthalpy ($\Delta H_f^i(MX_6^{2-})(g)$) of the reaction:

$$M^{4+}(g) + 6X^-(g) \rightarrow MX_6^{2-}(g)$$

For reactions at high temperature and in certain redox processes (atom transfer mechanisms), $\overline{E(M-X)}_{hom}$ is an appropriate index of relative reactivity, while for the process of complexes dissociating into ions, $\overline{E(M-X)}_{het}$ and the associated coordinate bond energy, (c.b.e.), are more useful.

Table II gives the results for the bond energies and in Figure 1 we show that the calculated coordinate bond energies may be used in the form of a Huish–Pryce plot [21] to estimate data for the corresponding bromides, the results being given in Table III.

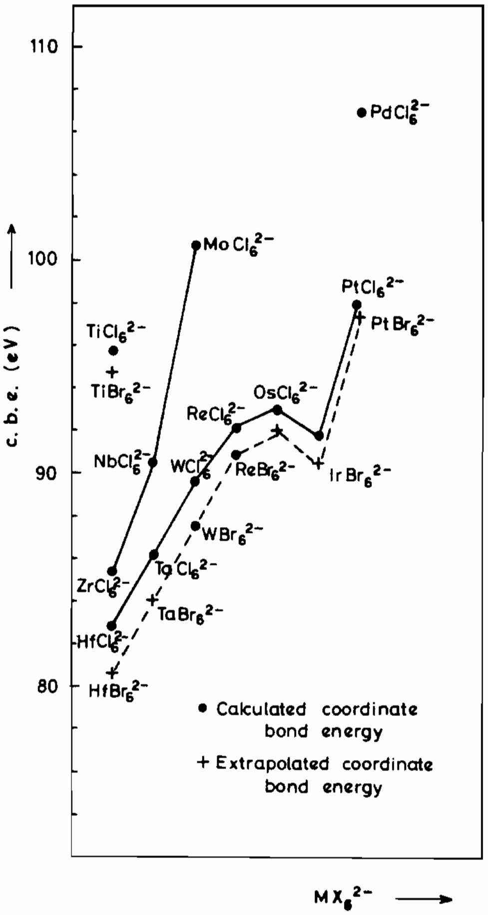

Figure 1.

The order of halogen–metal bond strengths, depends on the definition used (homolytic or coordinate), in itself an interesting point. In the case of the coordinate bond energy, the definition of $\overline{E(M-X)}_{het}$ leads to the following trends:

TABLE II. Bond strength, $\overline{E(M{-}X)}_{hom}$, and Coordinate Bond Strength, $\overline{E(M{-}X)}_{het}$, for M–X bonds and Total Coordinate Bond Energy, c.b.e., in MX_6^{2-} Gaseous Ions (1 eV = 96.5 kJ mol^{-1}).

M–X		Bond Strength $\overline{E(M{-}X)}_{hom}$ (kJ mol^{-1})	Coordinate Bond Strength $\overline{E(M{-}X)}_{het}$ (kJ mol^{-1})	Total Coordinate Bond Energy for MX_6^{2-} c.b.e. = $6\overline{E(M{-}X)}_{het}$ (eV)
Transition Metal–Halogen Bonds	Ti–F	544	1692	105.2
	Ti–Cl	422	1542	95.9
	Zr–Cl	477	1375	85.5
	Hf–Cl	497	1336	83.1
	Nb–Cl	446	1461	90.8
	Ta–Cl	464	1388	86.3
	Mo–Cl	409	1620	100.7
	W–Cl	427	1443	89.7
	Re–Cl	403	1483	92.2
	Os–Cl	378	1496	93.0
	Ir–Cl	363	1478	91.9
	Pd–Cl	309	1723	107.1
	Pt–Cl	347	1577	98.0
	Ti–Br	380	1525	94.8
	W–Br	370	1411	87.7
	Re–Br	355	1460	90.8
	Pt–Br	313	1567	97.4
Main Group Metal–Halogen Bonds	Si–F	538	1877	116.7
	Ge–F	471	1821	113.2
	Ge–Cl	347	1672	104.0
	Sn–Cl	365	1519	94.5
	Pb–Cl	310	1518	94.4
	Te–Cl	302	1516	94.2
Actinide Metal–Halogen Bonds	Th–Cl	507	1357	84.4
	U–Cl	468	–	–
	Pu–Cl	434	–	–

(i) the Si–F bond energy (the largest considered here) is greater than that for Ge–F;

(ii) the following Periodic trends are evident in the metal–chlorine coordinate bond strengths in MCl_6^{2-} ions:

$$\overbrace{\begin{array}{ccccccccccccc}
\text{Ti–Cl} & & & & & & & & & & & & \\
\vee & & & & & & & & & & & & \\
\text{Zr–Cl} & < & \text{Nb–Cl} & < & \text{Mo–Cl} & & & & < & & & & \text{Pd–Cl} \\
\vee & & \vee & & \vee & & & & & & & & \vee \\
\text{Hf–Cl} & < & \text{Ta–Cl} & < & \text{W–Cl} & < & \text{Re–Cl} & < & \text{Os–Cl} & > & \text{Ir–Cl} & < & \text{Pt–Cl}
\end{array}}^{\text{transition metal–chlorine bond energies}}
\quad\Bigg|\quad
\overbrace{\begin{array}{ccc}
\text{Ge–Cl} & & \\
\vee & & \\
\text{Sn–Cl} & \approx & \text{Te–Cl} \\
\wr\wr & & \\
\text{Pb–Cl} & &
\end{array}}^{\substack{\text{main group}\\ \text{metal–chlorine}\\ \text{bond energies}}}$$

Figure 1 shows these to be entirely in accordance with trends found by Pearson and Mawby, in their review [1], to exist in the divalent and trivalent halides of the first transition series.

(iii) parallel trends to those shown above for the metal–chlorine bond strengths are shown in the metal–bromine bonds and in all cases:

$$\overline{E(M{-}Cl)}_{het} > \overline{E(M{-}Br)}_{het}$$

The alternative definition, $\overline{E(M{-}X)}_{hom}$, leads to bond strengths whose periodic trends, both horizontally across the period and vertically down the group, are the complete reverse (except that $\overline{E(Os{-}Cl)}_{hom} > \overline{E(Ir{-}Cl)}_{hom}$) of those shown in (ii) above. Although the relationship:

$$\overline{E(M{-}Cl)}_{hom} > \overline{E(M{-}Br)}_{hom}$$

is preserved.

TABLE III. Extrapolated c.b.e. Values from Figure I (eV).

M–X	Extrapolated Values	
	c.b.e. (eV)	$\overline{E(M{-}Br)}_{het}$ (kJ mol^{-1})
Hf–Br	80.6	1296
Ta–Br	82.0	1319
Os–Br	92.0	1480
Ir–Br	90.4	1454
Pt–Br	97.3	1565

The trend in the $\overline{E(M{-}Cl)}_{hom}$ for the actinide elements is:

$$Th{-}Cl > U{-}Cl > Pu{-}Cl$$

as would be expected.

References

1 R. G. Pearson and R. J. Mawby, *Halogen Chemistry, 3,* 55 (1967).
2 M. Webster and P. M. Collins, *J. Chem. Soc. Dalton,* 588 (1963).
3 H. D. B. Jenkins and B. T. Smith, *J. Chem. Soc. Faraday I, 72,* 353 (1976).
4 R. M. DeJonge, *J. Inorg. Nucl. Chem., 38,* 1821 (1976).
5 F. R. Hartley, *Nature (Phys. Sci.), 236,* 75 (1972).
6 H. D. B. Jenkins, *J. Phys. Chem., 81,* 850 (1977).
7 W. A. Welsh, T. B. Brill, P. T. Thompson, R. M. Wood and R. C. Gearhart, *Inorg. Chem., 13,* 1797 (1974).
8 D. Lal and A. D. Westland, *J. Chem. Soc. Dalton,* 2505 (1974).
9 P. Gelbman and A. D. Westland, *J. Chem. Soc. Dalton,* 1598 (1974).
10 V. M. Vdovenko, I. G. Suglobova and D. E. Chirkst, *Soviet Radiochem., 16,* 205 (1974).
11 V. M. Vdovenko, V. A. Volkov and I. G. Suglobova, *Soviet Radiochem., 16,* 364 (1974).
12 H. D. B. Jenkins and K. F. Pratt, *Adv. Inorg. Chem. Radiochem., 22,* 1 (1979).
13 H. D. B. Jenkins and K. F. Pratt, *Prog. Solid State Chem., 14* (1979) in press.
14 H. D. B. Jenkins and K. F. Pratt, *Proc. Roy. Soc., A356,* 115 (1977).
15 V. B. Parker, D. D. Wagman and W. H. Evans, "Selected Values of Chemical Thermodynamic Properties", N. B. S. Technical Note 270, National Bureau of Standards, Washington, U. S. Department of Commerce (1971).
16 D. A. Stull, "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Michigan, U.S.A. (1960–66).
17 D. S. Barnes, "Computer Analysis of Thermochemical Data – Cr, Mo and W Compounds", University of Sussex, June (1974).
18 J. D. Cox, "Computer Analysis of Thermochemical Data – Halogen Compounds", University of Sussex, September (1972).
19 P. Gross, C. Haymann and J. J. Bingham, *Trans. Faraday Soc., 62,* 2388 (1966).
20 F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York (1958).
21 N. S. Hush and M. N. L. Pryce, *J. Chem. Phys., 28,* 244 (1958).