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LATTICE ENERGIES AND THERMOCHEMISTRY OF HEXAHALOMETALLATE(IV) COMPLEXES, A_2MX_6, WHICH POSSESS THE ANTIFLUORITE STRUCTURE

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I. Introduction

Salts having the general formula A_2MX_6 are formed by both transition and main-group elements (M) in the formal oxidation state (IV), where A is an alkali metal, thallium, or ammonium and X is a halogen. Accordingly, a study of such salts, in this chapter confined to those having the antifluorite (K_2PtCl_6) structure, generates interesting data embracing a wide section of the periodic table. This chapter concerns the role lattice energy plays in the thermochemistry of these salts.

Since this chapter went to press a similar study of the lattice energies of salts of general formula A_2MX_6 possessing noncubic structures has been made and will appear shortly (*40a*).

This study describes the attention that lattice energies of A_2MX_6 salts have received to date in the literature, reports some recent studies from this laboratory of the lattice energies of such salts as calculated using a new minimization procedure (*38, 39*), and, on the basis of these latter results, also presents estimates of the lattice energies of A_2MX_6 salts where M = Hf, Nb, Ta, Ru, and Sb to complete the study. All the salts considered (with the exception of a handful for which we estimate the lattice energy from thermochemical data) for which we have carried out an accurate evaluation of the lattice energy possess the antifluorite (K_2PtCl_6) structure, having a unit cell length a_0 and an M—X bond distance d ($d = u.a_0$) as the only variants from structure to structure.

Lattice energies have been the subject of isolated studies (*16, 19, 22, 29, 36, 40, 51, 53, 68–70*) for isolated salts over the last decade and a half. Figure 1 represents the situation prior to the study that is the main subject of this article.

Figure 1 gives the salts, in periodic order, for which lattice energies had been reported prior to the commencement of this present study.

Table I gives the detailed results and references associated with Fig. 1 and indicates the type of calculation used to establish the lattice of the twenty-two A_2MX_6 salts considered.

A. THERMOCHEMICAL CYCLE

Incorporating the lattice energy into the Born–Fajans–Haber cycle:

$$\begin{tikzcd}
 & 2A(c) + M(c) + 3X_2(ss) \arrow[dl, "\Delta H_f^{\circ}(A_2MX_6)(c)"'] \arrow[dr, "2\Delta H_f^{\circ}(A^+)(g) + \Delta H_f^{\circ}(MX_6{}^{2-})(g)"] & \\
A_2MX_6(c) \arrow[rr, "U_{POT}(A_2MX_6)"] & & 2A^+(g) + MX_6{}^{2-}(g)
\end{tikzcd}$$

IVA	VA	VIA	VIIA	VIII			IVB	VB	VIB
							Cs_2GeCl_6		
K_2ZrCl_6	K_2NbCl_6 Rb_2NbCl_6 Cs_2NbCl_6	Na_2MoCl_6 K_2MoCl_6 Rb_2MoCl_6 Cs_2NbCl_6				K_2PdCl_6	K_2SnCl_6 Rb_2SnCl_6		Rb_2TeCl_6
K_2HfCl_6	K_2TaCl_6 Rb_2TaCl_6 Cs_2TaCl_6		K_2ReCl_6 Cs_2ReCl_6 Cs_2ReBr_6		$(NH_4)_2IrCl_6$	K_2PtCl_6 K_2PtBr_6 K_2PtI_6 Cs_2PtCl_6 $(NH_4)_2PtCl_6$ $(NH_4)_2PtBr_6$	Rb_2PbCl_6		

FIG. 1. Calculated and estimated lattice energies for A_2MX_6 salts: pre-1977.

TABLE I

Lattice Energy Calculations for A_2MX_6 Salts, Pre-1977. Energies in kJ mol^{-1}[a]

Complex Ion $MX_6{}^{2-}$	Counter Ion A^+	Webster and Collins (*69*) 1963	Efimov and Belorukova (*19*) 1967	Tsintsius and Smirnova (*68*) 1969	Hartley (29) 1972		Lister (53) *et al.* 1974						Welsh *et al.* (*70*) 1974	Lal and Westland (*51*) 1974	Gelbman and Westland (*22*) 1975	Jenkins and Smith (*40*) 1975	Burgess and Cartwright (*10a*) 1975	De Jonge (*16*) 1976	Jenkins (*36*) 1976	Makhij and Westlan (*54a*) 1977
		(j)	(g)	(g)	(b)	(c)	(d)	(e)	(e)	(f)	(c)	(g)	(j)	(c)	(a)	(k)	(b)	(e)	(h)	(c)
$ZrCl_6{}^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	(1571)	—	—	—	—	—
$ZrBr_6{}^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1501
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1464
$HfCl_6{}^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	(1574)	—	—	—	—	—
$HfBr_6{}^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1464
$NbCl_6{}^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	1586	—	—	—	—	—	—
	Rb^+	—	—	—	—	—	—	—	—	—	—	—	—	1569	—	—	—	—	—	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	1540	—	—	—	—	—	—
$TaCl_6{}^{2-}$	K^+	—	—	1582	—	—	—	—	—	—	—	—	—	1586	—	—	—	—	—	—
	Rb^+	—	—	1565	—	—	—	—	—	—	—	—	—	1569	—	—	—	—	—	—
	Cs^+	—	—	1540	—	—	—	—	—	—	—	—	—	1540	—	—	—	—	—	—
$MoCl_6{}^{2-}$	Na^+	—	1638	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	K^+	—	1602	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Rb^+	—	1567	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Cs^+	—	1537	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$ReCl_6{}^{2-}$	K^+	—	—	—	—	—	1448	1231	1170	1437	1555	1508	—	—	—	—	1506	—	—	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1453	—	—	—

$ReBr_6^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1399	—	—	—
$IrCl_6^{2-}$	NH_4^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1505	—	—	—
$PdCl_6^{2-}$	K^+	—	—	—	1519	1573	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$PtCl_6^{2-}$	K^+	—	—	—	1540	1598	1461	1327	1274	1450	1572	1521	—	—	—	—	1521	1323[b]	1468	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1459	1337		—
	NH_4^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1507	—	—	—
$PtBr_6^{2-}$	K^+	—	—	—	1452	1506	1388	—	1301	1377	1498	1445	—	—	—	—	1451	1299	—	—
	NH_4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1439	—	—	—
PtI_6^{2-}	K^+	—	—	—	—	—	1264	—	—	—	1421	1317	—	—	—	—	—	—	—	—
$GeCl_6^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	1404	—	—	—	—	—	—	—
$SnCl_6^{2-}$	K^+	—	—	—	—	—	1425	—	—	1414	1533	1484	1370	—	(1586)	—	—	—	—	—
	Rb^+	1551	—	—	—	—	—	—	—	—	—	—	—	—	—	1259	—	—	—	—
$SnBr_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$PbCl_6^{2-}$	Kb^+	—	—	—	—	—	—	—	—	—	—	—	1335	—	—	—	—	—	—	1505
$TeCl_6^{2-}$	Rb^+	1578	—	—	—	—	—	—	—	—	—	—	—	—	—	1197	—	—	—	—

[a] Column heads: (a) Estimated from lattice energies calculated in reference 51 using relationships proposed in Gelbman and Westland (*22*). (b) Born–Mayer equation (*6*). (c) Kapustinskii equation (*46*). (d) Empirical. (e) Extended Born–Lande equation (*5*). (f) Simple Born–Lande equation (*5*). (g) Alternative Kapustinskii equation (*46*). (h) Direct minimization equation (*35*). (j) Wood's method (*2, 18, 21, 72, 73*). (k) Extended Huggins and Mayer equation (*33*).

[b] As corrected by DeJonge (*17*).

where (ss) indicates standard state (for $A = NH_4$ we must replace $U_{POT}(A_2MX_6)$ by $\{U_{POT}[(NH_4)_2MX_6] + 3RT\}$, the following equations are generated:

$$U_{POT}(A_2MX_6) = 2\Delta H_f^{\theta}(A^+)(g) + \Delta H_f^{\theta}(MX_6{}^{2-})(g) - \Delta H_f^{\theta}(A_2MX_6)(c) \tag{1}$$

for salts where A = K, Rb, Cs, Tl, and Ag, and

$$\begin{aligned} U_{POT}((NH_4)_2MX_6) = {} & 2\Delta H_f^{\theta}(NH_4{}^+)(g) + \Delta H_f^{\theta}(MX_6{}^{2-})(g) \\ & - \Delta H_f^{\theta}((NH_4)_2MX_6)(c) - 3RT \end{aligned} \tag{2}$$

for the ammonium salts.

We use these equations and the relationships:

$$\begin{aligned} \Delta H_f^{\theta}(MX_6{}^{2-})(g) = {} & \Delta H_f^{\theta}(MX_6{}^{2-})(aq) - 2\Delta H_f^{\theta}(H^+)(g) - 2\Delta H^{\theta}_{\text{hyd}}(H^+)(g) \\ & - \Delta H^{\theta}_{\text{hyd}}(MX_6{}^{2-})(g) \end{aligned} \tag{3}$$

$$\overline{\Delta H}_{X(ss)} = \Delta H_f^{\theta}(MX_6{}^{2-})(g) - 2\Delta H_f^{\theta}(X^-)(g) - \Delta H_f^{\theta}(MX_4)(ss) \tag{4}$$

to obtain enthalpies of hydration, $\Delta H^{\theta}_{\text{hyd}}(MX_6{}^{2-})(g)$, and enthalpies of formation, $\Delta H_f^{\theta}(MX_6{}^{2-})(g)$, for the gaseous ions as well as halide (X^-) ion affinities for MX_4 in the state (ss), where (ss) = (g), (l), or (c).

B. BOND STRENGTH

We can define the metal–halogen bond strength in the $MX_6{}^{2-}$ ion in two ways. First, with reference to the homolytic fission of the bond:

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

in which case the enthalpy change, $-\Delta H_f^{a}(MX_6{}^{2-})(g)$ of the reaction above can be employed as a measure of the average (homolytic) bond energy, $\overline{E(M - X)}_{\text{hom}}$, defined as:

$$\overline{E(M - X)}_{\text{hom}} = -\tfrac{1}{6}\Delta H_f^{a}(MX_6{}^{2-})(g) \tag{5}$$

Second, with reference to the heterolytic fission of the bond:

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

we can define an average (heterolytic) bond energy, $\overline{E(M - X)_{het}}$, using the enthalpy change, $-\Delta H_f^i(MX_6^{2-})(g)$ of the reaction thus:

$$\overline{E(M - X)_{het}} = -\tfrac{1}{6}\Delta H_f^i(MX_6^{2-})(g) \tag{6}$$

This latter bond energy has been referred to by Basolo and Pearson (*1*) as the coordinate bond energy and is recommended by them as the more informative for the study of ions of the type MX_6^{2-} on the grounds (i) that in common substitution reactions it is heterolytic, rather than homolytic fission, that occurs in the M–X bonds, (ii) that no process corresponding to:

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

really exists, and (iii) that the ionic nature of the metal halogen bonds makes it natural to think of complexes dissociating into ions. However, at high temperature the homolytic fission occurs, and thus for consideration of reactions at high temperature and in certain redox reactions involving atom-transfer mechanisms, the former $\overline{E(M - X)_{hom}}$ definition may be more appropriate. Consequently we have chosen to cite both bond energies in what follows, although coordinate (heterolytic) bond energies, $\overline{E(M - X)_{het}}$, for the most part feature in our discussion.

The "total coordinate bond energy" (c.b.e.) defined by Pearson and Mawby (*58*) is defined as $6\overline{E(M - X)_{het}}$ = c.b.e. for MX_6^{2-} ions.

Figure 2 gives the energy diagram related to the above definitions.

C. Scope of Review

Figure 1 presented details of the calculations of the lattice energies of A_2MX_6 salts prior to the main studies reported here. Figure 3 shows the compounds that have received attention as a result of our *recent* minimization method in addition to values that have been estimated from these studies. Deriving from these lattice energies, using ancillary thermochemical data where available, we have computed halide ion affinitions as defined in Eq. (4), and these have been obtained for the compounds MX_4(ss) as indicated in Fig. 4.

The bond strengths of the metal–halogen bonds indicated in Fig. 5 have been obtained using the approach described in Section I,B above.

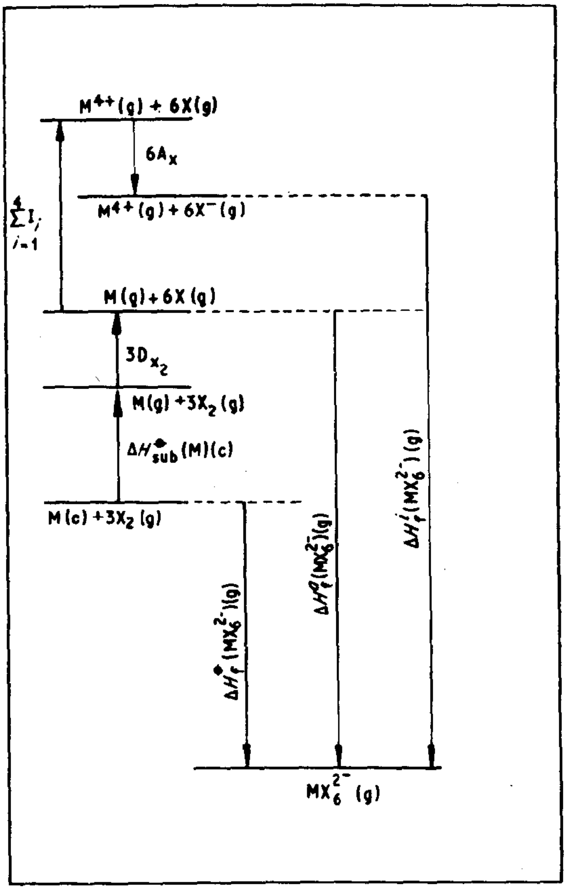

FIG. 2. Energy-thermodynamic correlation for bond-energy definitions.

We proceed now to a discussion of the method which is the main source of the lattice energies referred to in this chapter. The results are discussed in Section VIII and classified by ion type in periodic order in Section V. The lattice energies fall into three categories: (i) those derived from our new approach; (ii) those estimated on the basis of the results in (i); (iii) those obtained by other workers.

The study on the whole adds up to the generation of a systematic scheme for the examination of bond energies and other thermochemical properties across the periodic table to an extent not previously achieved.

IVA	VA	VIA	VIIA	← VIII →			IVB	VB	VIB
							K_2SiF_6 Rb_2SiF_6 Cs_2SiF_6 $(NH_4)_2SiF_6$		
K_2TiCl_6 K_2TiBr_6 Rb_2TiCl_6 Rb_2TiBr_6 Cs_2TiCl_6 Cs_2TiBr_6 $(NH_4)_2TiCl_6$		Cs_2CrF_6	K_2MnCl_6 Rb_2MnF_6 Rb_2MnCl_6 Cs_2MnF_6 Cs_2MnCl_6 $(NH_4)_2MnCl_6$		Rb_2CoF_6 Cs_2CoF_6	K_2NiF_6 Rb_2NiF_6	Cs_2GeCl_6		K_2SeBr_6 Rb_2SeCl_6 Cs_2SeCl_6 $(NH_4)_2SeCl_6$ $(NH_4)_2SeBr_6$
K_2ZrCl_6 Rb_2ZrCl_6 Cs_2ZrCl_6	K_2NbCl_6 Rb_2NbCl_6 Cs_2NbCl_6	Na_2MoCl_6 K_2MoCl_6 Rb_2MoCl_6 Cs_2MoCl_6	K_2TcCl_6 Rb_2TcCl_6	K_2RuCl_6		K_2PdCl_6 Rb_2PdCl_6 Cs_2PdCl_6 $(NH_4)_2PdCl_6$	K_2SnCl_6 Rb_2SnCl_6 Rb_2SnBr_6 Rb_2SnI_6 Cs_2SnCl_6 Cs_2SnBr_6 Cs_2SnI_6 $(NH_4)_2SnCl_6$ $(NH_4)_2SnBr_6$	Rb_2SbCl_6	K_2TeCl_6 Rb_2TeCl_6 Cs_2TeCl_6 Cs_2TeBr_6 Cs_2TeI_6 $(NH_4)_2TeCl_6$ $(NH_4)_2TeBr_6$
K_2HfCl_6	K_2TaCl_6 Rb_2TaCl_6 Cs_2TaCl_6	K_2WCl_6 K_2WBr_6 Rb_2WCl_6 Rb_2WBr_6 Cs_2WCl_6 Cs_2WBr_6	K_2ReCl_6 $K2ReBr_6$ Rb_2ReCl_6 Cs_2ReCl_6 $(NH_4)_2ReCl_6$	K_2OsCl_6 K_2OsBr_6 Cs_2OsCl_6 $(NH_4)_2OsCl_6$	$(NH_4)_2IrCl_6$	K_2PtCl_6 K_2PtBr_6 Rb_2PtCl_6 Cs_2PtCl_6 $(NH_4)_2PtCl_6$	Rb_2PbCl_6 Cs_2PbCl_6 $(NH_4)_2PbCl_6$		Cs_2PoBr_6 $(NH_4)_2PoCl_6$ $(NH_4)_2PoBr_6$

FIG. 3. Calculated and estimated lattice energies for A_2MX_6 salts: 1977.

IVA	VA	VIA	VIIA	← VIII →			IVB	VB	VIB
							SiF_4		
$TiCl_4$ $TiBr_4$						NiF_4	GeF_4 $GeCl_4$		
$ZrCl_4$	$NbCl_4$	$MoCl_4$				$PdCl_4$	$SnCl_4$		$TeCl_4$ $TeBr_4$
$HfCl_4$	$TaCl_4$	WCl_4 WBr_4	$ReCl_4$ $ReBr_4$	$OsCl_4$	$IrCl_4$	$PtCl_4$ $PtBr_4$	$PbCl_4$		

FIG. 4. Calculated halide ion affinities for MX_4 compounds.

IVA	VA	VIA	VIIA	← VIII →			IVB	VB	VIB
							Si-F		
Ti-Cl Ti-Br						Ni-F	Ge-F Ge-Cl		
Zr-Cl	Nb-Cl	Mo-Cl				Pd-Cl	Sn-Cl		Te-Cl Te-Br
Hf-Cl	Ta-Cl	W-Cl W-Br	Re-Cl Re-Br	Os-Cl	Ir-Cl	Pt-Cl Pt-Br	Pb-Cl		

FIG. 5. Calculated metal–halogen bond strengths.

II. Rigorous Lattice-Energy Calculation for A_2MX_6 Salts

A. THEORY

In the present study we have assigned a charge distribution (see Section II,B) in all cases to the $MX_6{}^{2-}$ ion, based where possible on experimental data already available. Within a given ion $MX_6{}^{2-}$ we have six atoms X bearing a charge q_X surrounding a central metal atom M bearing a charge q_M where:

$$q_M + 6q_X = -2 \tag{7}$$

The lattice potential energy of a salt A_2MX_6, $U_{POT}(A_2MX_6)$ is given by the sum of the electrostatic (U_{ELEC}), dipole–dipole dispersion (U_{dd}), dipole–quadrupole dispersion (U_{qd}), and repulsion (U_R) energies:

$$U_{POT}(A_2MX_6) = U_{ELEC} + U_{dd} + U_{qd} - U_R \tag{8}$$

and the condition that:

$$\left(\frac{\partial U_{POT}(A_2MX_6)}{\partial a}\right)_{a=a_0} = 0 \tag{9}$$

is used, and hence:

$$\left(\frac{\partial U_R}{\partial a}\right)_{a=a_0} = \left(\frac{\partial U_{ELEC}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{dd}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{qd}}{\partial a}\right)_{a=a_0} \tag{10}$$

If, for a salt A_2MX_6, we regard it as consisting of two A^+ ions and an approximately spherical $MX_6{}^{2-}$ complex ion, the approach of Huggins and Mayer (*33*) renders a parametric form for the repulsion energy:

$$\begin{aligned} U_R = {} & \frac{1}{2} bC_{++} \exp\left(\frac{2\bar{r}_{A^+}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions}\\ A_i{}^+}} \exp\left(\frac{-R_{A^+A_i{}^+}}{\rho}\right)\right] \\ & + bC_{+-} \exp\left(\frac{\bar{r}_{A^+} + \bar{r}_{MX_6{}^{2-}}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \exp\left(\frac{-R_{A^+MX_{6i}^{2-}}}{\rho}\right)\right] \\ & + \frac{1}{2} bC_{--} \exp\left(\frac{2\bar{r}_{MX_6{}^{2-}}}{\rho}\right)\left[\sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \exp\left(\frac{-R_{MX_6{}^{2-}MX_{6i}^{2-}}}{\rho}\right)\right] \end{aligned} \tag{11}$$

applicable for this salt, where $C_{++} = 1.25$, $C_{+-} = 0.875$, and $C_{--} = 0.50$. All the distances involved in the summations are expressible as functions of a, the unit cell parameter, thus:

$$R_{ij} = a[(h + x_i - x_j)^2 + (k + y_i - y_j)^2 + (l + z_i - z_j)^2]^{1/2} = ak_{ij} \tag{12}$$

and hence U_R is differentiable and takes the form:

$$\begin{aligned} \left(\frac{\partial U_R}{\partial a}\right)_{a=a_0} = {} & -\frac{1}{2} bC_{++} \exp\left(\frac{2\bar{r}_{A^+}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions}\\ A_i{}^+}} \left(\frac{k_{A^+A_i{}^+}}{\rho}\right) \exp\left(\frac{-R_{A^+A_i{}^+}}{\rho}\right)\right] \\ & - bC_{+-} \exp\left(\frac{\bar{r}_{A^+} + \bar{r}_{MX_6{}^{2-}}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \left(\frac{k_{A^+MX_{6i}^{2-}}}{\rho}\right)\right. \\ & \left. \exp\left(\frac{-R_{A^+MX_{6i}^{2-}}}{\rho}\right)\right] \\ & -\frac{1}{2} bC_{--} \exp\left(\frac{2\bar{r}_{MX_6{}^{2-}}}{\rho}\right) \\ & \left[\sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \left(\frac{k_{MX_6{}^{2-}MX_{6i}^{2-}}}{\rho}\right) \exp\left(\frac{-R_{MX_6{}^{2-}MX_{6i}^{2-}}}{\rho}\right)\right] \end{aligned} \tag{13}$$

Herzig *et al.* (*32*) have expanded U_{ELEC}, the electrostatic energy for these salts, as a function of the cell length a, and an internal distance, d (corresponding to the M—X distance in the salt), and the charge distribution q_{X} on the terminal halogen atoms of the complex ion.

$$U_{\text{ELEC}} = K/a\left\{\alpha_0 + \left[\sum_{\substack{n=2\\ \text{even}}}^{\infty} \alpha_n (d/a)^n\right] q_{\text{X}} + \left[\sum_{\substack{n=2\\ \text{even}}}^{\infty} \beta_n (d/a)^n\right] q_{\text{X}}{}^2\right\} \tag{14}$$

whereupon

$$\left(\frac{\partial U_{\text{ELEC}}}{\partial a}\right)_{a=a_0} = \frac{K}{a_0}\left[\left(\frac{\partial M_{\text{ELEC}}}{\partial a}\right)_{a=a_0} - \frac{M_{\text{ELEC}}}{a_0}\right] \tag{15}$$

$$= -\frac{K}{a_0{}^2}\left[\alpha_0 + \sum_{\substack{n=2\\ \text{even}}}^{\infty} (n+1)\alpha_n \left(\frac{d}{a_0}\right)^n q_{\text{X}} + \sum_{\substack{n=2\\ \text{even}}}^{\infty} (n+1)\beta_n \left(\frac{d}{a_0}\right)^n q_{\text{X}}{}^2\right] \tag{16}$$

where M_{ELEC} is the electrostatic Madelung constant based on a_0. The derivatives $(\partial U_{\text{dd}}/\partial a)_{a=a_0}$ and $(\partial U_{\text{qd}}/\partial a)_{a=a_0}$ are evaluated using the polarizabilities of Pirenne and Kartheuser (*59*), treating the ions $\text{MX}_6{}^{2-}$ as though they could be regarded as being comprised of six halide ions. The electron numbers were taken as 8, apart from the case where M = Tl, in which case the Herzfeld and Woolf formula (*31*) was employed. The summations necessary for the evaluation of the above derivatives took the form:

$$S_{\text{L}}^{\text{A}^+\text{A}^+} = 2\left[\sum_{\substack{\text{all ions}\\ \text{A}_i{}^+}}^{\text{AA}} (R_{\text{A}^+\text{A}_i{}^+})^{-\text{L}}\right] \tag{17}$$

$$S_{\text{L}}^{\text{A}^+\text{X}^-} = 2\left[\sum_{\substack{\text{all ions}\\ \text{X}_i{}^-}}^{\text{AX}} (R_{\text{A}^+\text{X}_i{}^-})^{-\text{L}}\right] \tag{18}$$

$$S_{\text{L}}^{\text{X}^-\text{X}^-} = 6\left[\sum_{\substack{\text{all ions}\\ \text{X}_i{}^-}}^{\text{XX}} (R_{\text{X}^-\text{X}_i{}^-})^{-\text{L}} - 4(R_{\text{X}^-\text{X}^-_{\text{cis}}})^{-\text{L}} - (R_{\text{X}^-\text{X}^-_{\text{trans}}})^{-\text{L}}\right] \tag{19}$$

where $R_{\text{X}^-\text{X}^-_{\text{cis}}}$ and $R_{\text{X}^-\text{X}^-_{\text{trans}}}$ are the halogen–halogen nearest and next-nearest neighbor distances in the same ion, $\text{MX}_6{}^{2-}$, and

$$U_{\text{dd}} = \tfrac{1}{2}[c_{++}S_6{}^{++} + c_{--}S_6{}^{--}] + c_{+-}S_6{}^{+-} \tag{20}$$

$$U_{\text{qd}} = \tfrac{1}{2}[d_{++}S_8{}^{++} + d_{--}S_8{}^{--}] + d_{+-}S_8{}^{+-} \tag{21}$$

where

$$c_{ij} = (2e^4 Q_i Q_j)/3(\epsilon_i + \epsilon_j) \tag{22}$$

$$d_{ij} = \tfrac{3}{2} c_{ij} [Q_i/p_i + Q_j/p_j] \tag{23}$$

$$Q_i = (3\alpha_i \epsilon_i)/2e^2 \tag{24}$$

α_i, ϵ_i, and p_i are the polarizability, characteristic energy, and electron number of the ion i and e is the electronic charge and, since

$$\left(\frac{\partial S_{\mathrm{L}}{}^{ij}}{\partial a}\right)_{a=a_0} = -\sum_{\substack{\text{all}\\ j}} k_{ij} L R_{ij}^{-(\mathrm{L}+1)} = \frac{-LS_{\mathrm{L}}{}^{ij}}{a_0} \tag{25}$$

we have

$$\left(\frac{\partial U_{\mathrm{dd}}}{\partial a}\right)_{a=a_0} = -\frac{6U_{\mathrm{dd}}}{a_0} \tag{26}$$

and

$$\left(\frac{\partial U_{\mathrm{qd}}}{\partial a}\right)_{a=a_0} = -\frac{8U_{\mathrm{qd}}}{a_0} \tag{27}$$

Substitution of Eqs. (13), (16), (26), and (27) into Eq. (10) gives us an equation of the form:

$$\theta_1 \exp\left(\frac{2\bar{r}_{\mathrm{MX}_6{}^{2-}}}{\rho}\right) + \theta_2 \exp\left(\frac{\bar{r}_{\mathrm{A}^+} + \bar{r}_{\mathrm{MX}_6{}^{2-}}}{\rho}\right) + \theta_3 \exp\left(\frac{2\bar{r}_{\mathrm{A}^+}}{\rho}\right) = \theta_4 \tag{28}$$

where

$$\theta_1 = \left\{-\frac{1}{2} bC_{--}\left[\sum_{\substack{\text{all ions}\\ \mathrm{MX}_{6i}^{2-}}} \left(\frac{k_{\mathrm{MX}_6{}^{2-}-\mathrm{MX}_{6i}^{2-}}}{\rho}\right) \exp\left(-\frac{R_{\mathrm{MX}_6{}^{2-}-\mathrm{MX}_{6i}^{2-}}}{\rho}\right)\right]\right\} \tag{29}$$

$$\theta_2 = \left[-2bC_{+-} \sum_{\substack{\text{all ions}\\ \mathrm{MX}_{6i}^{2-}}} \left(\frac{k_{\mathrm{A}^+-\mathrm{MX}_{6i}^{2-}}}{\rho}\right) \exp\left(-\frac{R_{\mathrm{A}^+\mathrm{MX}_{6i}^{2-}}}{\rho}\right)\right] \tag{30}$$

$$\theta_3 = \left[-bC_{++} \sum_{\substack{\text{all ions}\\ \mathrm{A}_i{}^+}} \left(\frac{k_{\mathrm{A}^+\mathrm{A}_i{}^+}}{\rho}\right) \exp\left(-\frac{R_{\mathrm{A}^+\mathrm{A}_i{}^+}}{\rho}\right)\right] \tag{31}$$

$$\theta_4 = \left[\frac{1}{a_0}\left(U_{\mathrm{ELEC}} + 6U_{\mathrm{dd}} + 8U_{\mathrm{qd}} - K\left(\frac{\partial M_{\mathrm{ELEC}}}{\partial a}\right)_{a=a_0}\right)\right] \tag{32}$$

In a particular salt, A_2MX_6, since we *know* the "basic" radius for the cation, A^+, $\bar{r}_{A^+}$ ($A = K, Rb, Cs, Tl, NH_4$), Eq. (28) becomes

$$\theta_1 \exp(2\bar{r}_{MX_6^{2-}}/\rho) + \eta_2 \exp(\bar{r}_{MX_6^{2-}}/\rho) + \eta_3 = 0 \tag{33}$$

where

$$\eta_2 = [\theta_2 \exp(\bar{r}_{A^+}/\rho)] \tag{34}$$

$$\eta_3 = [\theta_3 \exp(2\bar{r}_{A^+}/\rho) - \theta_4] \tag{35}$$

and hence we can solve Eq. (33) for $\bar{r}_{MX_6^{2-}}$:

$$\exp\left(\frac{\bar{r}_{MX_6^{2-}}}{\rho}\right) = \left[\frac{-\eta_2 \pm (\eta_2{}^2 - 4\theta_1\eta_3)^{1/2}}{2\theta_1}\right] \tag{36}$$

for a range of charge distributions on the $MX_6{}^{2-}$ ion as represented by q_X, θ_4 being itself a function of q_X by virtue of Eq. (21).

$$\theta_4 = \sum_{i=0}^{2} A_i q_X{}^i \tag{37}$$

and hence

$$\bar{r}_{MX_6^{2-}} = \rho \ln\left[\phi_0 + \left(\sum_{j=1}^{3} \phi_j q_X^{(j-1)}\right)^{1/2}\right] \tag{38}$$

where

$$\phi_3 = 4\theta_1 A_2 \tag{39}$$

$$\phi_2 = 4\theta_1 A_1 \tag{40}$$

$$\phi_1 = \eta_2{}^2 - 4\theta_1\theta_3[\exp(2\bar{r}_{A^+}/\rho) - A_0] \tag{41}$$

and

$$\phi_0 = (-\eta_2/2\theta_1) \tag{42}$$

In the present work, admitting a variable ρ parameter would introduce complications and, in the absence of compressibility data, makes the calculation of U_R difficult. Assumption that ρ is constant (taking the value to be 0.345 Å) within the framework of the present method is made prior to the solution of Eq. (38) and hence errors introduced by such an assumption will be minimized since $\bar{r}_{MX_6^{2}}$, which is determined in the study, has a close parametric relationship with ρ. From