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INFLUENCE OF ION SIZE ON THE STABILITY OF CHLOROPLUMBATES CONTAINING $PbCl_5^-$ OR $PbCl_6^{2-}$

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The enthalpies of formation of $PbCl_4$, $PbCl_5^-$ and $PbCl_6^{2-}$, originating from quantum mechanics, have enabled the thermodynamic behaviour of these ions with respect to Cl^- detachment to be assessed. The stability of salts containing $PbCl_5^-$ and $PbCl_6^{2-}$ as a function of the dimensions of these anions and complementary cations was studied using an approach combining the Kapustinskii–Yatsimirskii equation with basic thermochemical relationships.

It was found that hexachloroplumbates of monovalent metal cations will not dissociate into metal chlorides and $PbCl_4$, provided the complementary cations are suitably large in size. Hexachloroplumbates of divalent metal cations have not yet been synthesised since no known metal cations attain the requisite large size. Such salts will not dissociate if the divalent metal cations are able to complex suitably large electron-donating ligands. The pentachloroplumbates of both monovalent and divalent metal cations are unstable, since no known metal cations have appropriately large ionic radii. The approach adopted appears to be useful for the examination of the thermal behaviour, stability and reactivity of chloroplumbates.

Keywords: *hexachloroplumbates, pentachloroplumbates, reactivity, stability, thermochemistry*

Introduction

Lead (Pb) has the ability to form the hexachloroplumbate ($PbCl_6^{2-}$) anion, which occurs in salts containing simple monovalent metal cations [1, 2] or the cations of various organic nitrogen bases [1–6]. There is only one report on the formation of hexachloroplumbates containing simple divalent metal cations [7], but these findings have not been confirmed [8]. One of the present authors therefore attempted to synthesise hexachloroplumbates containing divalent metal cations complexed with several organic nitrogen bases [9, 10]. The apparent stability of these compounds provided an opportunity to investigate their thermal properties. The conclusion drawn from earlier investigations was that hexahalogenometallates could be isolated in the crystalline form only if the dimensions of the complementary ions exceeded certain values [11–13]. The principal objective of the present work was to develop this idea in order to discover what the dimensions of monovalent or divalent metal cations and $PbCl_5^-$ or $PbCl_6^{2-}$ should be for the relevant salts to be energetically stable. A secondary aim was to demonstrate the usefulness of computations in predicting enthalpies of formation and the stability of gaseous $PbCl_4$, $PbCl_5^-$ and $PbCl_6^{2-}$. Owing to their interesting features and behaviour, the thermochemistry and thermal properties of compounds containing complex metal anions are ongoing subjects of interest [14, 15].

Experimental

Methods

The geometries and energies of $PbCl_4(g)$, $PbCl_5^-(g)$ and $PbCl_6^{2-}(g)$ at constrained T_d (tetrahedral), D_{3h} (bipyramidal) and O_h (octahedral) symmetry, respectively, were determined at the MP2 level of theory [16] employing 6–311+G(d) (for Cl) [17,18] and LanL2DZ (for Pb) [19] basis sets and Baker′s optimisation procedure [20]. The validity of the geometry optimizations was proven in the subsequent Hessian (second derivatives of the energy *vs.* nuclear coordinates) calculations followed by normal mode analyses [21]. The bond lengths and vibrational harmonic frequencies so obtained were subsequently used to convert the zero-point energy, as well as the entropy and thermal energy contributions at 298.15 K and standard pressure (0), to the enthalpy and Gibbs free energy terms using statistical thermodynamics routines [22]. The enthalpies and Gibbs free energies of formation of gaseous $PbCl_4$, $PbCl_5^-$ and $PbCl_6^{2-}$ were obtained by following the basic rules of thermodynamics [23]. In these calculations, the values of thermochemical quantities for $Cl_2(g)$ and $Pb(s)$ predicted at the above-mentioned level of theory were used (in the latter case, the energy of $Pb(g)$ was lowered by 195.2 kJ mol^{-1}, i.e. by the heat of its volatilisation) [24]. Quantum chemistry calculations were carried out with the Gaussian03 code [25].

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Results and discussion

Properties of $PbCl_5^-$ and $PbCl_6^{2-}$

A search of the Inorganic Structural Data Base [26] revealed that only X-ray powder diffraction data are available for $(NH_4)_2PbCl_6$, K_2PbCl_6, Rb_2PbCl_6 and Cs_2PbCl_6 [27, 28]. The predicted value of the Pb–Cl bond length in octahedral $PbCl_6^{2-}$ agrees reasonably well with the one estimated on the basis of the above-mentioned structural information (Table 1) [29, 30]. Presumably, then, the bond lengths predicted for chloroplumbate anions are good approximations of actual values. The values of $\Delta_{f,298}H^0$ for gaseous $PbCl_6^{2-}$ (–927 [34] or –940 [30] kJ mol^{-1}) , derived from the thermochemical cycle, correlate very well with those predicted computationally at an advanced level of theory (Table 1). On the other hand, the predicted value of –438 kJ mol^{-1} for $\Delta_{f,298}H^0[PbCl_{4(g)}]$ is a long way from the values of this quantity (range: –282 to –287 kJ mol^{-1}) extracted from the available thermochemical data [1, 37]. The latter data may, however, be uncertain, since the compound is highly unstable and the experimental data may be encumbered with an error that is difficult to estimate. Having examined several quantum chemistry methods and basis sets, we selected an approach yielding enthalpies of formation for $PbCl_4$ and $PbCl_6^{2-}$ that are the closest to the literature values. We thus regard the predicted $\Delta_{f,298}H^0$ of gaseous $PbCl_4$ and chloroplumbate anions as optimal for studying the stability of salts containing the latter ions. On the other hand, some of the computed thermochemical data are the first such characteristics ever calculated for chloroplumbate anions. The vibrational frequencies found for $PbCl_6^{2-}$ compare reasonably well with the literature values (Table 1). This leads us to believe that the frequencies predicted for both anions are good approximations of actual values.

The stability of chloroplumbate anions can be examined in the light of the following dissociation processes:

$$PbCl_6^{2-}(g) \rightarrow PbCl_5^-(g) + Cl^-(g) \qquad (1)$$
$$\Delta_{r,298}H^0 = -157 \text{ kJ mol}^{-1}$$

$$PbCl_5^-(g) \rightarrow PbCl_4(g) + Cl^-(g) \qquad (2)$$
$$\Delta_{r,298}H^0 = 195 \text{ kJ mol}^{-1}$$

Table 1 Structural, thermochemical and spectral characteristics of chloroplumbate ions

Entity	Symmetry	Pb–Cl bond length/Å		Thermochemical data^{a,b}			Vibrational frequencies/cm^{-1}		
		This work^a	Ref.	$\Delta_{f,298}H^0$/ kJ mol^{-1}	$\Delta_{f,298}G^0$/ kJ mol^{-1}	$_{298}S^0$/ J mol^{-1} K^{-1}	Mode^c	Value	
								This work^a	Ref.
$PbCl_5^-$	D_{3h}	2.44; 2.48		–866	–828	430	e’ (ν_7)	49	
							e’ (ν_6)	128	
							a_2’’ (ν_4)	143	
							e’’ (ν_8)	147	
							a_1’ (ν_2)	237	
							a_2’’ (ν_3)	279	
							a_1’ (ν_1)	288	
							e’ (ν_5)	301	
$PbCl_6^{2-}$	O_h	2.52	2.49 [29, 30]	–942	–888	486	t_{2u} (ν_6)	82	76 [29]
							t_{2g} (ν_5)	132	137–141 [29, 31–34]
							t_{1u} (ν_4)	135	137–142 [29, 32–35]
							e_g (ν_2)	201	206–215 [29, 31–34]
							t_{1u} (ν_3)	240	258–262 [29, 32–35]
							a_{1g} (ν_1)	255	281–285 [29, 31–34]

^{a}computationally predicted values for gaseous entities, ^{b}literature value of $\Delta_{f,298}H^0$ [$PbCl_6^{2-}(g)$] (in kJ mol^{-1})= –927 [36] or –940 kJ mol^{-1} [30], ^{c}singly (a), doubly (e) and triply (t) degenerate vibrations for which $\Delta_{r,298}H^0$ were obtained by taking the standard enthalpies of formation of chloroplumbate anions from Table 1, the above-mentioned value of $\Delta_{f,298}H^0[\mathrm{PbCl_4}(g)]$ (–438 kJ mol^{-1}) and assuming $\Delta_{f,298}H^0[\mathrm{Cl^-}(g)]=-233$ kJ mol^{-1} [11–13].

$\mathrm{PbCl_6^{2-}}$ is energetically unstable in the context of reaction (1). It can exist only if a suitably high kinetic barrier to the process (1) exists. The results of advanced calculations, soon to be published, indicate that there is indeed a conspicuous barrier to this reaction. Kinetically stable $\mathrm{PbCl_6^{2-}}$ may thus occur in salts containing the appropriate complementary cations. On the other hand, $\mathrm{PbCl_5^-}$ appears to be energetically stable (positive $\Delta_{r,298}H^0$ for reaction (2)), so the possible formation of salts containing this anion will depend on the dimensions of the complementary cations.

Stability and reactivity of chloroplumbates

A compound is thermodynamically stable if at a given temperature (T) and at constant (usually standard) pressure (0) no chemical decomposition process (d) occurs for which the change in Gibbs free energy (G) ($\Delta_{d,T}G^0$) is negative. The parameters for which $\Delta_{d,T}G^0$ becomes negative thus determine the conditions for a compound's existence. Temperature changes usually enable conditions to be approached in which a compound becomes thermodynamically stable or unstable. Temperature-driven processes are known as thermal processes. But structural factors, such as the dimensions of ions, may influence thermodynamic stability; as will be demonstrated, they can affect the stability of salts containing the chloroplumbate anions $\mathrm{PbCl_5^-}$ and $\mathrm{PbCl_6^{2-}}$. A complete thermodynamic analysis would require knowledge of the enthalpy and entropy changes accompanying the reactions taking place along the reaction pathway. As in most cases the latter characteristics are neither available nor easily predictable, we restricted our considerations to an analysis of the enthalpy changes at a constant temperature of 298 K.

The enthalpy changes ($\Delta_{d,298}H^0$) accompanying the reactions

$$\mathrm{M(I)_n\,PbCl_{4+n}}(s)\rightarrow \mathrm{PbCl_4}(g)+n\mathrm{M(I)Cl}(s) \tag{3}$$

or

$$\mathrm{M(II)_m\,(PbCl_{4+m})_2}(s)\rightarrow 2\mathrm{PbCl_4}(g)+m\mathrm{M(II)Cl_2}(s) \tag{4}$$

where M(I) is a monovalent monatomic metal cation, M(II) is a divalent monatomic metal cation, and n and m=1, 2, can be assumed to be a measure of the energetic stability of chloroplumbates.

To make $\Delta_{d,298}H^0$ dependent on the ionic dimensions of the salts in question we need to consider the following hypothetical reactions, in which the enthalpy changes are in fact crystal lattice enthalpies ($\Delta_{c,298}H^0$):

$$\mathrm{M(I)_n\,PbCl_{4+n}}(s)\rightarrow n\mathrm{M(I)^+}(g)+\mathrm{PbCl_{4+n}^{n-}}(g) \tag{5}$$

$$\begin{gathered}\mathrm{M(II)_m\,(PbCl_{4+m})_2}(s)\rightarrow\\ m\mathrm{M(II)^{2+}}(g)+2\mathrm{PbCl_{4+m}^{m-}}(g)\end{gathered} \tag{6}$$

$$n\mathrm{M(I)Cl}(s)\rightarrow n\mathrm{M(I)^+}(g)+n\mathrm{Cl^-}(g) \tag{7}$$

$$m\mathrm{M(II)Cl_2}(s)\rightarrow m\mathrm{M(II)^{2+}}(g)+2m\mathrm{Cl^-}(g) \tag{8}$$

$\Delta_{c,298}H^0$ is related to crystal lattice energy ($\Delta_{c,298}E$) via the equation

$$\Delta_{c,298}H^0=\Delta_{c,298}E+\Delta\nu RT \tag{9}$$

where $\Delta\nu$ is the sum of the stoichiometric coefficients of the gaseous reactants in reactions (5)–(8).

$\Delta_{c,298}E$ is related to ionic dimensions via the Kapustinskii–Yatsimirskii relationship [38, 39]

$$\begin{gathered}\Delta_{c,298}E(\mathrm{kJ\ mol^{-1}})=\\ 120.2\frac{(\Sigma x)z_\mathrm{C}z_\mathrm{A}}{r_\mathrm{C}+r_\mathrm{A}}\left[1-\frac{0.0345}{r_\mathrm{C}+r_\mathrm{A}}+0.087(r_\mathrm{C}+r_\mathrm{A})\right]\end{gathered} \tag{10}$$

where (Σx) is the total number of ions in the stoichiometric unit of the compound, z_C and z_A denote the numerical (absolute) values of the relative charges of cation (C) and anion (A), and r_C and r_A are the thermochemical radii of ions (in nm).

By combining Eqs (3), (5), (7), (9) and (10), the relationship reflecting the stability of chloroplumbates containing monovalent metal cations can be obtained

$$\begin{gathered}\Delta_{d,298}H^0[(\mathrm{M(I)_n\,PbCl_{4+n}}(s)]=\\ (1-n)RT+\Delta_{f,298}H^0[\mathrm{PbCl_4}(g)]+n\Delta_{f,298}H^0[\mathrm{Cl^-}(g)]\\ -\Delta_{f,298}H^0[\mathrm{PbCl_{4+n}^{n-}}(g)]\\ -120.2\frac{2n}{\Sigma r(\mathrm{I})}\left[1-\frac{0.0345}{\Sigma r(\mathrm{I})}+0.087\Sigma r(\mathrm{I})\right]\\ +120.2\frac{n(n+1)}{\Sigma r(\mathrm{II})}\left[1-\frac{0.0345}{\Sigma r(\mathrm{II})}+0.087\Sigma r(\mathrm{II})\right]\end{gathered} \tag{11}$$

where $\Sigma r(\mathrm{I})=r(\mathrm{M(I)})+r(\mathrm{Cl^-})$ and $\Sigma r(\mathrm{II})=r(\mathrm{M(I)})+r(\mathrm{PbCl_{4+n}^{n-}})$.

By combining Eqs (4), (6), (8), (9) and (10) the corresponding relationship reflecting the stability of chloroplumbates containing divalent metal cations is

$$\begin{gathered}\Delta_{d,298}H^0[(\mathrm{M(II)_m\,PbCl_{4+m}}(s)]=\\ 2(1-m)RT+2\Delta_{f,298}H^0[\mathrm{PbCl_4}(g)]+2m\Delta_{f,298}H^0[\mathrm{Cl^-}(g)]\\ -2\Delta_{f,298}H^0[\mathrm{PbCl_{4+m}^{m-}}(g)]\\ -120.2\frac{6m}{\Sigma r(\mathrm{III})}\left[1-\frac{0.0345}{\Sigma r(\mathrm{III})}+0.087\Sigma r(\mathrm{III})\right]\\ +120.2\frac{2m(m+2)}{\Sigma r(\mathrm{IV})}\left[1-\frac{0.0345}{\Sigma r(\mathrm{IV})}+0.087\Sigma r(\mathrm{IV})\right]\end{gathered} \tag{12}$$

where $\Sigma r(\mathrm{III})=r(\mathrm{M(II)})+r(\mathrm{Cl^-})$ and $\Sigma r(\mathrm{IV})=r(\mathrm{M(II)})+r(\mathrm{PbCl_{4+m}^{m-}})$.

The chemical entities to which the thermodynamic quantities correspond are indicated in the square brackets in relationships (11) and (12).

To predict $\Delta_{d,298}H^0$ values, the following enthalpies of formation (f) were assumed (in kJ mol^{-1}): $\Delta_{f,298}H^0[PbCl_4(g)]=-438$; $\Delta_{f,298}H^0[PbCl_5^-(g)]$ and $\Delta_{f,298}H^0[PbCl_6^{2-}(g)]$ – taken from Table 1; $\Delta_{f,298}H^0[Cl^-(g)]=-233$ [11–13]. It was assumed that the thermochemical radius of Cl^-= 0.181 nm [11–13] and that of $PbCl_6^{2-}(g)$=0.372 nm [6].

Energetic stability of chloroplumbates in relation to ionic dimensions

Figures 1–4 show plots of the dissociation enthalpies ($\Delta_{d,298}H^0$) of chloroplumbates, calculated using Eqs (11) or (12), *vs.* the radii of monovalent or divalent cations and the complementary chloroplumbate anions. The areas of positive $\Delta_{d,298}H^0$ values represent energetic stability, whereas the areas of negative $\Delta_{d,298}H^0$ stands for energetic instability. The curves corresponding to $\Delta_{d,298}H^0=0$ indicate the threshold values of the thermochemical radii of cation and anion for energetic stability.

The thermochemical radii of monatomic ions are simply the ionic radii of these entities [11–13, 40]. As the thermochemical radius of $PbCl_6^{2-}$ is 0.372 nm [6], its salts containing monovalent cations of ionic radius >0.116 nm will be stable (Fig. 2). Therefore, Li^+ (r_C(I)=0.068 nm [11]) and Na^+ (r_C(I)=0.097 nm [11]) do not form hexachloroplumbates, whereas K^+ (r_C(I)=0.133 nm [11]), Rb^+ (r_C(I)=0.149 nm [11]) and Cs^+ (r_C(I)=0.167 nm [11]) do form such salts; this has been confirmed experimentally [1, 2]. Hexachloroplumbates containing divalent metal cations should be stable if their thermochemical radii are >0.273 nm (Fig. 4). The radii of divalent (monatomic) metal cations lie between 0.06–0.13 nm [11]. This means that it would be difficult to achieve conditions in which solid M(II)$PbCl_6$ could be isolated. As mentioned earlier, the existence of such salts has not actually been proven [7, 8]. The thermochemical radius of $PbCl_5^-$ is not known; however, we may expect it to be <0.372 nm, i.e. less than that of $PbCl_6^{2-}$. If we assume this value, Eqs (11) and (12) predict that M(I)$PbCl_5$ or M(II)$(PbCl_5)_2$ would be stable if the ionic radii of the complementary cations were >0.179 or >0.287 nm, respectively (Figs 1 and 3). None of the common monatomic monovalent or divalent metal ions attain these values [11], which explains why these salts have not been isolated.

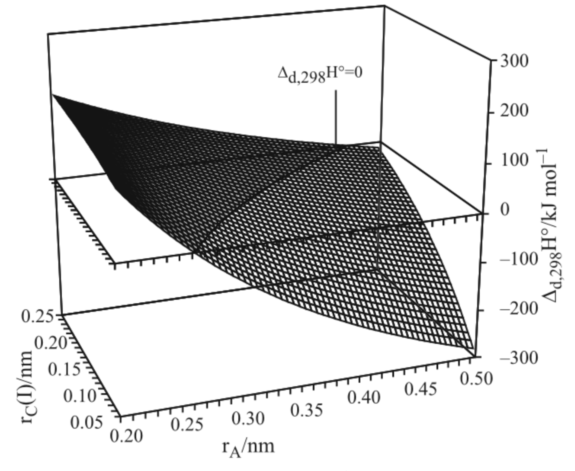

Fig. 1 Dissociation enthalpy ($\Delta_{d,298}H^0$) of pentachloroplumbates (Eq. (11)) *vs.* radii of monovalent cation (r_C(I)) and $PbCl_5^-$ (r_A)

Predictive possibilities of the proposed approach

As demonstrated above, Eqs (11) and (12) allow one to predict what the dimensions of the complementary ions

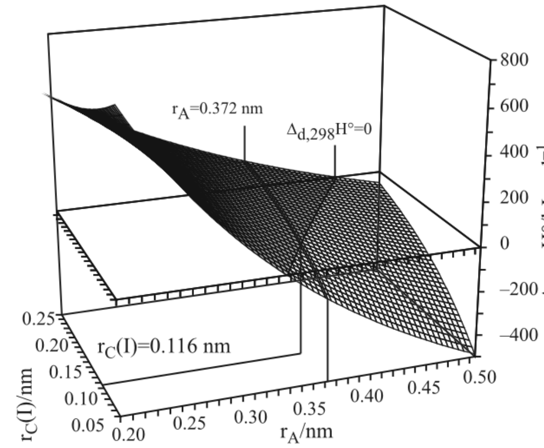

Fig. 2 Dissociation enthalpy ($\Delta_{d,298}H^0$) of hexachloroplumbates (Eq. (11)) *vs.* radii of monovalent cation (r_C(I)) and $PbCl_6^{2-}$ (r_A)

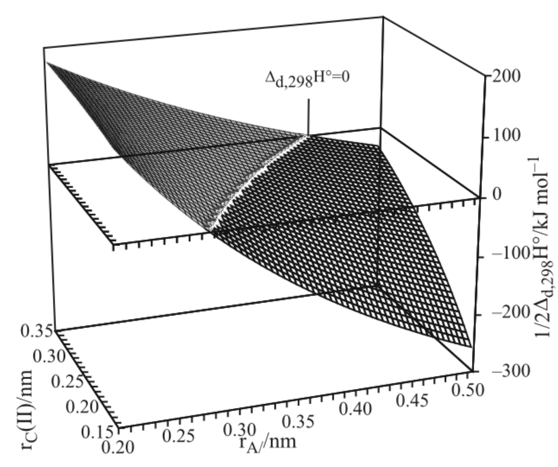

Fig. 3 Dissociation enthalpy ($\Delta_{d,298}H^0$) of pentachloroplumbates (Eq. (12)) *vs.* radii of divalent cation (r_C(II)) and $PbCl_5^-$ (r_A)

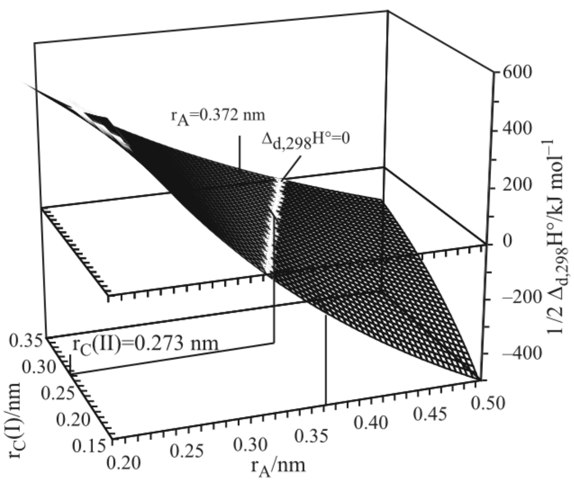

Fig. 4 Dissociation enthalpy ($\Delta_{d,298}H^0$) of hexachloroplumbates (Eq. (12)) *vs.* radii of divalent cation (r_C(II)) and $PbCl_6^{2-}$ (r_A)

would have be for chloroplumbates to be energetically stable. Earlier, we investigated the thermal stability of potassium, rubidium and caesium hexachloroplumbates and determined their thermal dissociation enthalpies on the basis of thermogravimetric data. These enthalpies can be predicted by using Eq. (11) and taking the thermochemical radii of K^+, Rb^+, Cs^+ and $PbCl_6^{2-}$ to be respectively equal to 0.133, 0.149, 0.167 and 0.372 nm [6,11]. The respective theoretical dissociation enthalpies obtained for K_2PbCl_6, Rb_2PbCl_6 and Cs_2PbCl_6 (34.6, 52.6 and 74.8 kJ mol^{-1}) are qualitatively comparable with the respective empirical values (156, 61.4 and 106 kJ mol^{-1}), derived on the assumption of equilibrium conditions for the dissociation process [2]. This qualitative agreement corroborates the model developed for investigating the stability and reactivity of chloroplumbates. It was shown above using Eq. (12) that it might be difficult to isolate the hexachloroplumbates of divalent monatomic cations. It was therefore decided to synthesise this type of salt by complexing cations with bipyridine and H_2O [9, 10]. Several such hexachloroplumbates were obtained, and their thermal properties were investigated by thermoanalytical methods [9, 10]. Unfortunately, however, thermal dissociation enthalpies determined on the basis of thermogravimetric traces are difficult to use for determining the thermochemical radii of complex cations (Eq. (12)). The experimentally determined thermodynamic characteristics correspond to complex multistep processes that are not reflected by the approach used here. Nevertheless, the model does provide an opportunity for predicting the behaviour of hexachloroplumbates containing complex divalent cations.

Conclusions

It is often hard to state why certain compounds are stable and others not, or why some compounds can be isolated and others not. The method developed here demonstrates a rational approach to the problem of the stability and thermal reactivity of chloroplumbates. It can be used to predict the stability of these compounds from ionic dimensions (thermochemical or ionic radii) and also their thermal dissociation enthalpies.

Quantum chemistry appears to be a useful tool for studying the stability and determining the properties of $PbCl_5^-$ and $PbCl_6^{2-}$. The existence of $PbCl_6^{2-}$ has been proven by the synthesis of salts containing this anion. As far as we know, no salts containing $PbCl_5^-$ have been isolated. The existence of this latter anion has, however, been demonstrated by electronic absorption spectroscopy [41].

Incorporation of the results of quantum chemistry computations into a model derived from the phenomenological relationships of thermodynamics provides a useful framework within which to consider the thermochemistry and behaviour of chloroplumbates.

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