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Energetics of formation of adducts of *N*-methyl-2-pyrrolidone with zinc(II) family metal halides – A thermochemical study

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Abstract

Thermochemical data for adducts of *N*-methyl-2-pyrrolidone (NMP) with zinc(II), cadmium(II) and mercury (II) halides have been obtained from solution calorimetry. The technique provided the values for the dissolution enthalpies ($\Delta_i H^0$) of MX_2 (M = Zn, Cd, Hg; X = Cl, Br, I) metal halides, the NMP lactam and $MX_2.n$NMP adducts, which were used to determine the standard molar enthalpies of acid–base reaction in the condensed state ($\Delta_r H^0$) for the adducts, by using appropriate thermodynamic cycles. From $\Delta_r H^0$ values and literature data, the following thermochemical parameters have been calculated: standard enthalpy of formation ($\Delta_f H^0$), standard enthalpy of decomposition ($\Delta_d H^0$), standard lattice enthalpy ($\Delta_{latt} H^0$), standard enthalpy of acid–base reaction in the gaseous phase ($\Delta_g H^0$) and the mean dissociation enthalpy of the metal–oxygen bond, $\overline{D}$ (M–O) have been established. In order to evaluate the methyl group influence on the donor oxygen strength of the NMP lactam, the obtained thermochemical data are compared with those previously published for analogous 2-pyrrolydone (BuL) compounds. The influence of the ionic and covalent character of the metal halides has been taken into account in the metal–oxygen interaction processes. © 1997 Elsevier Science B.V.

Keywords: Adducts; Lactams; Metal halides; Metal–oxygen bonds; Solution calorimetry

1. Introduction

Thermochemical data for the formation of the adducts of 2-pyrrolidone (BuL) and ε-caprolactam (CL) with zinc(II), cadmium(II) and mercury(II) halides have been determined [1,2] recently from solution calorimetry. This study is a continuation of our interest in investigating the ability of cyclic amides (lactams) to form stable complexes with transition metals. Complexes in which metal–oxygen bonds are present, are important in biological processes such as replication of DNA molecules by DNA polymerase, which depends on the formation of zinc–oxygen bonds [3].

Lactams are of great interest in the study of biological systems, due to their structural similarity to cyclic peptides and proteins. Hence, the study of these species is useful in the attempt to elucidate the physical and chemical properties of peptidic bonds [4].

This survey deals with zinc(II) metal halides and their *N*-methyl-2-pyrrolidone (NMP) adducts, where we report a thermochemical study focused mainly on

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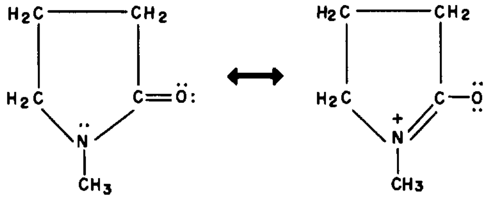

(I) (II)

Fig. 1. *N*-methyl-2-pyrrolidone (NMP).

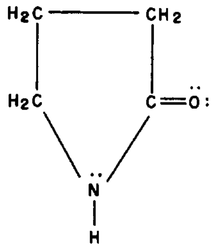

Fig. 2. 2-pyrrolidone (BuL).

evaluating the metal–oxygen interactions in the ZnX_2.2NMP (X = Cl, Br, I), MX_2.NMP (M = Cd, Hg; X = Cl, Br) and CdI_2.2NMP adducts. Studies concerned with structural aspects of some compounds with NMP have been carried out [5–7]. However, there are no thermochemical studies concerning the energetics of formation of compounds with this lactam.

The NMP structure is better described as a hybrid of resonance of the primary structures I and II (Fig. 1). From comparison with previous thermochemical data for BuL (Fig. 2) adducts [1], the relative base strength NMP > BuL is generally observed. Such an order is thought to be associated with the greater donor oxygen capacity of the NMP due to inductive effect of the methyl group. The metal–oxygen interaction processes are shown to be best correlated with the covalent character of the metal halides.

2. Experimental

2.1. Chemicals

The following solvents were obtained (Merck): Ethanol, methanol, *n*-hexane and ethyl acetate. They were purified [8] and kept dry.

2.1.1. Metal halides (Aldrich)

$ZnCl_2$ was prepared in our laboratory, according to a literature procedure [9]. $CdBr_2 \cdot 4H_2O$ and $CdCl_2 \cdot 2.5H_2O$ were made anhydrous by the Pascal [10] and Moeler [11] procedures, respectively. The remaining metal halides were dried under vacuum before use and were approximately 98% pure as measured by analysing the metal content from EDTA titration [12,13]. All the metal halides were handled in a dry nitrogen atmosphere using a glove-bag.

2.1.2. N-methyl-2-pyrrolidone (Riedel de Haen)

Benzene was added to the reagent grade, fractionally distilled at ambient pressure, and then distilled under reduced pressure at 341 K [8].

2.2. Preparation of the adducts

All the adducts were prepared under anhydrous conditions and using a vacuum/nitrogen system. Attempts to obtain an adduct of NMP with HgI_2, by varying reagents, the proportion of solvents, heating temperature as well as stirring time and reflux, were unsuccessful. The procedures adopted to prepare the adducts are described below.

2.2.1. ZnX_2.2NMP (X = Cl, Br)

The $ZnCl_2$.2NMP adduct was obtained by dissolving, the ligand in a mixture of solvents, ethyl acetate/2,2 dimethoxypropane (1 : 1) and the pure zinc chloride was added to the resulting solution in a ratio corresponding to the desired stoichiometry. The resulting solution was refluxed by heating at 353 K for 1 h. On evaporation of the solvent under vacuum, a white solid was precipitated on adding *n*-hexane under stirring. The mixture was filtered and the solid was washed with a solution of ethyl acetate/*n*-hexane (1 : 2), then dried under vacuum for 16 h. The $ZnBr_2$.2NMP adduct was obtained in the same way, but from a mixture of methanol and 2,2-dimethoxypropane (1 : 1).

2.2.2. CdX_2.NMP (X = Cl, Br)

$CdCl_2$ and $CdBr_2$ were added to the ethanolic solution of the ligand at molar ratios 1 : 2.5. The mixtures were maintained under reflux for 8 and

2 h, respectively. The adducts were filtered and washed several times with ethyl acetate and dried under vacuum for 8 h.

2.2.3. HgX_2.NMP (X = Cl, Br)

These adducts were obtained by adding the appropriate anhydrous halide, dissolved in ethanol, to the ligand dissolved in the same solvent, at a 1 : 1 stoichiometric ratio. After stirring for 1 h, the solvent was evaporated, then *n*-hexane was added in order to enhance the precipitation of the adducts, which were filtered and washed with ethyl acetate/*n*-hexane (1 : 2). The adducts were dried under vacuum for 9 h.

2.2.4. $MI_2$2NMP (M = Zn, Cd)

The procedure used in the preparation of these adducts was similar to that described for the CdX_2.NMP adducts. The differences lie in the molar ratios of metal/ligand, of 1 : 3, and the ethanol was removed from solutions and replaced by a mixture ethyl acetate/*n*-hexane (1 : 2) to precipitate the solid.

The majority of these adducts were extremely sensitive to moist air, thus all manipulations were performed in a dry nitrogen atmosphere.

2.3. Techniques used to characterize the adducts

2.3.1. Elemental analysis

The metal content of the adducts was determined by standard methods [12,13], and carbon, hydrogen and nitrogen contents were determined by using a Perkin–Elmer 240 Element Analyzer.

2.3.2. Infrared spectroscopy

The infrared spectra were obtained in the 4000–400 cm^{-1} range on a Perkin–Elmer 283B spectrophotometer, using the Nujol mull technique, with a polystyrene film as reference.

2.3.3. Melting points (m.p.)

The m.p. of the adducts were determined by using an HWS SG2000 apparatus with the samples in sealed capillary tubes.

2.3.4. Thermogravimetry

Thermogravimetry determinations were carried out using a Perkin–Elmer TGA7 thermobalance with a dynamic flux of dry nitrogen and a heating of 5°C min^{-1}.

2.4. Calorimetric procedures

Calorimetric measurements were performed using a Parr 1451 Solution Calorimeter adapted to a system of electric calibration. The calorimeter's performance and procedure are outlined in a previous paper [1]. For the $CdCl_2$.NMP and $HgCl_2$.NMP adducts, a 2 M HCl solution was used as the calorimetric solvent, and for the remaining adducts ethanol was used. The choice of solvents was made on their capacity to dissolve ligands, halides and adducts. All calorimetric determinations were carried out at 298.15 K.

3. Results and discussion

3.1. Characterization of the adducts

All the results of metal, carbon, hydrogen and nitrogen contents of the adducts were in strict agreement with their proposed formulation. The temperature interval (ΔT) over which melting occurred and/or decomposition, and the onset of decomposition in the thermogravimetric determinations (T_d) are shown in Table 1. For $ZnCl_2$.2NMP, $CdBr_2$.2NMP and CdI_2.2NMP adducts, the m.p. results were not reproducible on cooling after melting and subsequent reheating, suggesting that these adducts melt with decomposition. This fact is confirmed as the beginning of the decomposition in thermogravimetric determinations occurs at temperatures lower than the m.p. range. The ZnI_2.2NMP adduct had m.p. range (386.6–387) K reproducible, and decomposition found by thermogravimetry begins at 408 K, so confirming melt without decomposition. The $CdCl_2$.NMP adduct does not melt until 523 K, although thermogravimetric results show that the decomposition begins at 341 K. Thermogravimetric curve for $HgBr_2$.NMP adduct showed that the mass loss occurs in one step, suggesting a possible decomposition or vaporization. However, this adduct has a defined m.p. range, once reproducibility of the m.p. for the previously melted sample was observed. Reproducible m.p. was not observed for the $HgCl_2$.NMP adduct, and decomposi-

Table 1
Beginning of decomposition in thermogravimetric determinations (T_d), temperature interval (ΔT) of melting points and/or decomposition in m.p. determinations, and absorption frequences (cm^{-1}) of the CONH group of $MX_2.n$NMP adducts

Compounds	ΔT (K)	T_d (K)	ν(CO)	$\Delta\nu$(CO)	ν(CN)	$\Delta\nu$(CN)
NMP		1682	—	1505	—	
$ZnCl_2$.2NMP	318.0–318.2	687	1627	−55	1505	0
$CdCl_2$.NMP	[a]	341	1649	−33	1507	+2
$HgCl_2$.NMP	396.0–396.4	374	1638	−44	1508	+3
$ZnBr_2$.2NMP	359.0–359.3	305	1630	−52	1506	+1
$CdBr_2$.NMP	441.1–441.3	304	1650	−32	1505	0
$HgBr_2$.NMP	359.2–359.5	370	1670	−12	1506	+1
ZnI_2.2NMP	386.6–387.0	408	1630	−52	1507	+2
CdI_2.2NMP	371.4–371.7	304	1650	−32	1508	+3

[a] Did not melt until 523 K.

tion observed from thermogravimetry begins at temperature lower than the melting point range, hence melt with decomposition occurs. Except for these mercury adducts, which lost mass continuously without any perceivable inflection, the thermogravimetric curves for all the remaining adducts showed that the mass loss occurs in two distinct steps. In the first step, the ligand is released and this is followed by loss of the metal halide. In this case, it was observed that the mass loss was consistent with the stoichiometry of the adducts.

The wavenumber of the CO and CN stretchings are shown in Table 1. As can be seen, the wavenumber of ν(CO) for all adducts decreases in relation to the 1682 cm^{-1} value of the free ligand, and the band at 1505 cm^{-1}, due to ν(CN), is practically not affected, indicating that coordination occurs through the oxygen atom of the NMP lactam.

3.2. Thermochemical determinations

The standard molar enthalpies of acid–base reactions in the condensed state ($\Delta_r H^0$) of the adducts were determined from dissolution enthalpies ($\Delta_i H^0$) of metal halides, ligand and adducts, obtained by calorimetric methods in solution. Thermodynamic cycles 1 and 2 were used to calculate $\Delta_r H^0$. The choice of the appropriate thermodynamic cycle was determined according to the best experimental conditions, such as the solubility of reagents and the thermal effect values produced.

cycle 1

$$\begin{tikzcd}
\text{MX(s)} & + & \text{nNMP(l)} \arrow[rr, "\Delta_r H^\circ"] & & \text{MX}_2\text{.nNMP(s)} \\
+ & & + & & + \\
\text{calorimetric solvent} \arrow[rr, "\Delta_1 H^\circ"] & & \text{MX}_2\text{(solvent)} \arrow[d, "\Delta_2 H^\circ"] & & \text{calorimetric solvent} \arrow[d, dash, "\Delta_3 H^\circ"] \\
& & \text{MX}_2\text{.nNMP(solvent)} & & {} \arrow[ll]
\end{tikzcd}$$

cycle 2

$$\begin{tikzcd}
\text{MX(s)} & + & \text{nNMP(l)} \arrow[rr, "\Delta_r H^\circ"] & & \text{MX}_2\text{.nNMP(s)} \\
+ & & + & & + \\
\text{nNMP(solvent)} \arrow[d, "\Delta_5 H^\circ"] & & \text{calorimetric solvent} \arrow[ll, "\Delta_4 H^\circ"'] & & \text{calorimetric solvent} \arrow[d, dash, "\Delta_3 H^\circ"] \\
\text{MX}_2\text{.nNMP(solvent)} & & & & {} \arrow[llll]
\end{tikzcd}$$

From thermodynamic cycles 1 and 2, it is derived respectively, by applying Hass′ law: $\Delta_r H^0 = \Delta_1 H^0 + \Delta_2 H^0 - \Delta_3 H^0$ and $\Delta_r H^0 = n\Delta_4 H^0 + \Delta_5 H^0 - \Delta_3 H^0$. The dissolution enthalpies $\Delta_2 H^0$, $\Delta_3 H^0$, $\Delta_4 H^0$ and $\Delta_5 H^0$ were obtained by applying the least square method [14] to at least six individual determinations, whose values are listed in Table 2 together with the previously obtained $\Delta_1 H^0$ values [15,16].

Using $\Delta_r H^0$ values and the auxiliary data listed in Table 3 [17–21], the values of the standard molar enthalpies $\Delta_f H^0(MX_2.n\text{NMP}) = \Delta_r H^0 + n\Delta_f H^0(\text{NMP}) + \Delta_f H^0(MX_2)$, $\Delta_d H^0(MX_2.n\text{NMP}) = -\Delta_r H^0 + n\Delta_{vap} H^0(\text{NMP})$, and $\Delta_{latt} H^0(MX_2.\text{NMP}) = \Delta_r H^0 - \Delta_{sub} H^0(MX_2) - n\Delta_{vap} H^0(\text{NMP})$ were obtained. In these expressions $\Delta_{sub} H^0$ is the standard molar enthalpy of sublimation, and $\Delta_{vap} H^0$ is the standard

Table 2
Dissolution enthalpy values (kJ mol^{-1})

	$\Delta_i H^0$ (kJ mol^{-1})					
Adducts	$\Delta_1 H^0$	$\Delta_2 H^0$	$\Delta_3 H^0$	$\Delta_4 H^0$	$\Delta_5 H^0$	Solvent
$ZnCl_2.2NMP$	-43.33 ± 0.27 [a]	$+2.32 \pm 0.09$	$+21.67 \pm 0.39$			Ethanol
$CdCl_2.NMP$			$+21.95 \pm 0.14$	-26.07 ± 0.18	$+8.68 \pm 0.10$	2M HCl
$HgCl_2.NMP$			$+13.39 \pm 0.22$	-26.07 ± 0.18	$+2.91 \pm 0.04$	2M HCl
$ZnBr_2.2NMP$	-47.69 ± 0.37 [b]	-0.68 ± 0.03	$+38.35 \pm 0.62$			Ethanol
$CdBr_2.NMP$	-6.13 ± 0.12 [b]	$+1.40 \pm 0.04$	$+39.83 \pm 0.36$			Ethanol
$HgBr_2.NMP$	$+3.14 \pm 0.03$ [a]	$+2.05 \pm 0.05$	$+29.59 \pm 0.32$			Ethanol
$ZnI_2.2NMP$	-52.88 ± 0.35 [b]	-0.67 ± 0.03	$+43.06 \pm 0.68$			Ethanol
$CdI_2.2NMP$	-15.48 ± 0.19 [b]	-0.73 ± 0.02	$+47.35 \pm 0.62$			Ethanol

[a] Ref. [15].
[b] Ref. [16].

molar enthalpy of vaporization. $\Delta_g H^0$ values were obtained for the thermodynamic equation:

$$MX_2(g) + nNMP(g) \xrightarrow{\Delta_g H^0} MX_2.nNMP(g) \quad (1)$$

from which one derives: $\Delta_g H^0(MX_2.nNMP) = \Delta_r H^0 + \Delta_{sub} H^0(MX_2.nNMP) - n\Delta_{vap} H^0(NMP) - \Delta_{sub} H^0(MX_2)$. The values of the mean enthalpy of dissociation of the metal oxygen bond, $\overline{D}$ (M–O), were determined from its relation with $\Delta_g H^0$, according to:

$$\overline{D}(M-O) = -\Delta_g H^0/n \quad (2)$$

Table 3
Auxiliary thermochemical data

Compounds	$-\Delta_f H^0$ (kJ mol^{-1})	$\Delta_{vap} H^0$ (kJ mol^{-1})	$\Delta_{sub} H^0$ (kJ mol^{-1})
NMP	262.2 [a]	44.45 [f]	
$ZnCl_2$	415.1 [b,c]		149.0 [c]
$CdCl_2$	391.5 [b,c]		181.2 [d]
$HgCl_2$	224.3 [b,c]		83.3 [e]
$ZnBr_2$	328.7 [b,c]		131.0 [e]
$CdBr_2$	316.2 [b,c]		151.5 [d]
$HgBr_2$	170.7 [b,c]		84.1 [e]
ZnI_2	208.0 [b,c]		120.0 [d]
CdI_2	203.3 [b,c]		137.7 [d]

[a] Ref. [17].
[b] Ref. [18].
[c] Ref. [19].
[d] Ref. [20].
[e] Ref. [21].
[f] From our laboratory, according to previously described procedure [1].

Since $\Delta_{sub} H^0(MX_2.nNMP)$ is experimentally inaccessible, the approximation which established that the enthalpy of sublimation of the adduct as equal to the enthalpy of sublimation or vaporization of the ligand [22–26] was utilized, in order to obtain $\Delta_g H^0(MX_2.nNMP)$ and, consequently, $\overline{D}$ (M–O). There are several arguments to support this assumption, which have been mentioned in our previous paper [2].

The thermochemical data for $MX_2.nNMP$ adducts are shown in Table 4. Relative basicity of ligands and relative acidity of metal halides have been evaluated by considering the $\Delta_r H^0$ parameter [27]. In this study, the adducts do not present the same stoichiometry. However, comparison of $\Delta_r H^0$ values is made by presuming that substitution of similar ligands in adducts of the same metal halide does not alter the coordination around the central atom. It is observed that the relative acidity order of the metal with relation to NMP decreases from zinc to mercury throughout the halide series. Concerning $\Delta_f H^0$ parameter, its values have been used to compare thermodynamic stability of adducts [28]. From this parameter, the thermodynamic stability sequence $ZnX_2.nNMP > CdX_2.nNMP > HgX_2.nNMP$ (X = Cl, Br, I for Zn and Cd, and Cl, Br for Hg) has been observed. The $\Delta_d H^0$, $\Delta_{latt} H^0$ and $\Delta_g H^0$ values also establish that the energetic interactions in the MX2.nNMP adducts decreases in the order: Zn > Cd > Hg, in accordance with the thermochemical behavior observed for the analogous BuL adducts [1]. $\overline{D}$ (M–O) values show that the donor–acceptor interaction in the NMP adducts follows the sequence Cd > Zn > Hg

Table 4
Thermochemical data for $MX_2.nL$ (L is NMP and BuL) adducts

$MX_2.nL$ adducts	$-\Delta_rH^0$		$-\Delta_fH^0$		Δ_dH^0		$-\Delta_{latt}H^0$		$-\Delta_gH^0$		$\overline{D}$ (M–O)	
	L = NMP	L = BuL	L = NMP	L = BuL	L = NMP	L = BuL	L = NMP	L = BuL	L = NMP	L = BuL	L = NMP	L = BuL
$ZnCl_2.2NMP$	63	73	1002	1061	152	157	301	306	256	264	128	132
$CdCl_2.NMP$	39	31	693	708	84	72	265	254	220	212	220	212
$HgCl_2.NMP$	37	28	523	539	81	70	164	153	120	111	120	111
$ZnBr_2.2NMP$	87	71	940	972	176	155	307	286	262	244	131	122
$CdBr_2.NMP$	45	39	623	642	89	81	241	232	196	191	196	191
$HgBr_2.NMP$	24	25	457	482	69	66	153	151	109	109	109	109
$ZnI_2.2NMP$	97	75	829	186	159	306	279	261	237	131	118	
$CdI_2.2NMP$	64	50	791	826	152	133	290	271	246	229	123	114

for chloride and bromide series, and Zn > Cd > Hg for iodide series.

With a view to evaluate the donor capacity of NMP with relation to BuL, we consider the Δ_gH^0 and $\overline{D}$ (M–O) values. These are the best thermodynamic quantities to characterize the donor–acceptor interaction since, in the gaseous state, the contribution due to intermolecular forces are removed. An eminent fact that stands out from comparison of its values (Table 4) is a donor capacity order NMP > BuL, except for ZnC12.*n*L (L = BuL and NMP) where a BuL > NMP order is verified, and HgBr2.L where NMP = BuL is observed. The greater oxygen donor ability of the NMP lactam when compared with BuL, observed in a general way, is thought to be associated with the inductive effect of the methyl group in the NMP.

From our previous paper [1], it has been observed that there is some correlation between Δ_gH^0 values and energetic character of the bond energy of the metal

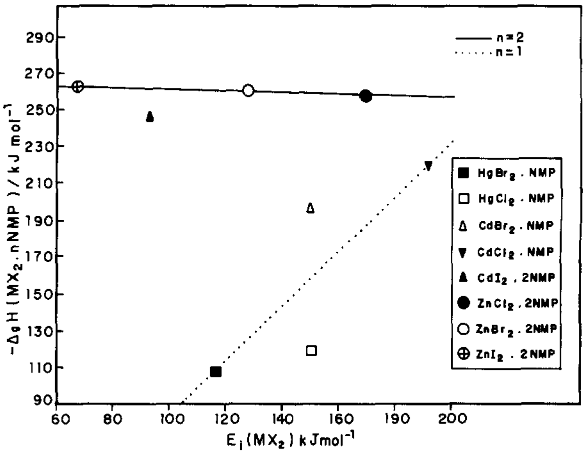

Fig. 3. $\Delta_gH^0(MX_2 \cdot nNMP)$ values vs. ionic energy (E_i) of the metal halides.

Table 5
Ionic energy (E_i) and covalent energy (E_c) of the bond energy of the metal halides [29]

Metal halides	E_i (kJ mol^{-1})	E_c (kJ mol^{-1})
$ZnCl_2$	168.1	160.2
$CdCl_2$	191.5	137.2
$HgCl_2$	150.1	74.4
$ZnBr_2$	126.7	149.3
$CdBr_2$	150.5	129.2
$HgBr_2$	116.7	71.5
ZnI_2	66.9	146.4
CdI_2	92.4	127.1

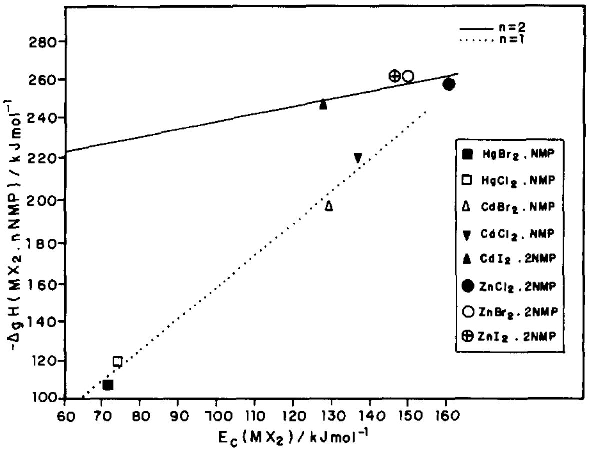

Fig. 4. $\Delta_gH^0(MX_2 \cdot nNMP)$ values vs. covalent energy (E_c) of the metal halides.

halides. Here, such correlation has been also examined. Plots of $\Delta_g H^0$(MX2.nNMP) values vs. ionic (E_i) and covalent (E_c) bond energies of the metal halides, whose values were obtained by Sanderson [29] (see Table 5), are shown in Figs. 3 and 4, respectively. A straight line is obtained for each series of points which distinguish adducts of 1 : 1 and 2 : 2 stoichiometry. As can be observed, a better correlation with the covalent energy is plausible, when it is substantial to argue that a greater influence of the covalent character of the metal halides can play a role in the investigation of these metal–oxygen interaction processes.

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