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Some features of the thermochemistry of coordination compounds

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CONTENTS

ABBREVIATIONS

ac	acetamide
an	aniline
acy	acetylhydrazine
bipy	2,2′-bipyridine
bipyo	2,2′-bipyridine *N*,*N*′-dioxide
cyt	cytosine
da	diacetamide
dce	1,2-dichloroethane
dma	*N*,*N*-dimethylacetamide
dmf	*N*,*N*-dimethylformamide

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dmu	*N,N'*-dimethylurea
dta	*N,N*-dimethylthioacetamide
dtf	*N,N*-dimethylthioformamide
en	ethylenediamine
hmpa	hexamethylphosphine oxide
mu	methylurea
mpy	*m*-methylpyridine
mcyt	1-methylcytosine
opy	*o*-methylpyridine
py	pyridine
phen	1,10-phenanthroline
pip	piperidine
ppy	*p*-methylpyridine
pya	*N*-(2-pyridil)acetamide
pyo	pyridine *N*-oxide
ta	thioacetamide
tu	thiourea
tmu	tetramethylurea
ttu	1,1,3,3-tetramethyl-2-thiourea
tbpo	tribenzylphosphine oxide
tepo	triethylphosphine oxide
tppo	triphenylphosphine oxide
ur	urea

A. SCOPE

In recent years, considerable effort has been invested on the thermochemistry of coordination compounds. Quite understandably, these studies focus mainly on organometallic compounds, which reflects the advances in this field in the last three decades [1]. In addition, thermochemical data of adducts contribute to our understanding of this important class of compounds, which, for example, serve as models for important biological systems [2].

In the eary sixties, Mortimer included in his book [3] a chapter which contained thermochemical data for molecular addition compounds formed with classical acceptors of the boron group elements and some electron donor bases of the nitrogen and oxygen group elements. The author stressed that much more thermochemical information was needed for these complexes and cited, as an example, the reaction of triphenylphosphine oxide with transition metal halides. Coincidentally, our first publication in this area dealt with the thermochemistry of adducts of this ligand with zinc chloride group elements [4].

A review in 1970 of the thermochemistry of adducts dealt mainly with pyridine and related ligands, and described some enthalpies, determined generally by means

of differential scanning calorimetry [5]. However, due to the large uncertainty inherent in these determinations, it is not possible to derive, with any precision, thermochemical parameters such as the mean metal–ligand bond enthalpy. Moreover, the enthalpies of sublimation of the adducts are generally unknown and difficult to obtain. In a more recent review, calorimetric measurements on crystalline adducts, methods used to characterize these compounds in the gaseous state, and mean metal–ligand bond enthalpy determinations were described [6].

The present review covers the thermochemical data for adducts of zinc halide group elements with mono- or bidentate nitrogen, oxygen or sulphur donor atom ligands, and also some adducts of arsenium halide group elements. The majority of data for these adducts was obtained via reaction–solution calorimetric measurements in our laboratory. Based on assumptions which were established to give the best approximation, the mean metal–ligand bond enthalpies for nearly one hundred compounds have been determined. In addition, thermochemical data for dithiocarbamate chelate complexes are also summarized and correlations between these parameters are discussed. The thermodynamic data for homogeneous non-aqueous solution and heterogeneous equilibria, obtained through calorimetric titration, can be used to establish acidity and basicity orders and to characterize adsorption phenomena on silica gel surfaces and intercalation properties of organic polar molecules in inorganic crystalline lamellar compounds.

B. A BRIEF HISTORY

In the course of the development of coordination chemistry in Brazil, there has been continuous scientific activity over the years in the area of adducts. This field of investigation started in 1934 with the arrival of Prof. H. Rheinboldt, from the University of Bonn, at the newly founded University of São Paulo where he established a chemistry school which profoundly influenced various future generations of chemists [7].

Rheinboldt was already an established researcher in this field when he arrived in Brazil due to his extensive activities as Pfeiffer's disciple and collaborator. Pfeiffer, who was Werner's disciple, started to apply, in a systematic way, Werner's theory to complexes which are formed by the association of simple organic molecules. Rheinboldt started his collaboration with Pfeiffer at the beginning of 1922 and for more than ten years their research was devoted to explaining this new molecular class of compounds.

With the establishment and progress of Rheinboldt's new school, the ideas which he stimulated in his students resulted in the study of diverse facets of the chemistry of adducts. Presently, research activities are focused on the preparation, structural characterization through vibrational, electronic and nuclear magnetic resonance spectroscopies, mechanical quantum calculations, and thermochemistry of adducts.

C. GENERAL CONCEPTS

Molecular compounds, molecular complexes or adducts are compounds formed by the interactions of neutral molecular species, where one molecule donates a pair of electrons (Lewis base) to the other acceptor species (Lewis acid) [8]

$$:B + A \rightarrow A:B$$

Normally, the above notation is used to represent the pair of electrons in the bond formed in this general acid–base Lewis neutralization reaction. However, to simplify this representation, only one point will be used between the acid and base, and the adduct will be represented in this review as A · B.

The adduct A · B can be found in the solid, liquid or gas phase and even dispersed in solution. When the species involved are ionic, the complex formed is not normally called an adduct. The acid involved in adduct formation is generally a metallic halide. Historically, the first adduct, which was described in the literature in 1857, was obtained by reacting zinc chloride with urea to give $ZnCl_2 \cdot 2ur$ [9].

From the theoretical point of view, adducts constitute excellent models for the study of molecular interactions and for the chemical bond itself. Different preparations lead to diverse compounds with the same interacting atoms, but with bond distances and energies within a broad range of values. These studies are of fundamental importance in various areas such as protein interactions with diverse molecules, sensitizer–acceptor centres of taste and smell, immunological recognition, adsorption of pigment on fibres, catalysts, etc.

From the practical point of view, adducts constitute a great number of intermediates in organic and inorganic reactions and, more recently, have been utilized in the purification and production of fine semiconductor materials.

D. SOME FEATURES OF ACID–BASE INTERACTIONS

In the course of establishing donor–acceptor interaction, an increase of coordination of the acid and an energy gain associated with the adduct, as a whole, occurs simultaneously [10]. The structural features have been extensively explored by several techniques, which provide a detailed description of the changes which occur on coordination. However, the energetic features that attend the system can be most conveniently obtained from thermochemical data, which is the main objective of this review.

The generalized concept of bonding in adducts is that of a bond of low attainment and, therefore, a weak bond [8]. However, in the extreme case, the gaseous adduct Xe—Xe [11] and dma—I_2 [12] in dichloromethane solution have homo- and heteronuclear enthalpy values of 2.2 and 10.9 kJ mol^{-1}, while in the piperidine adduct with antimony pentachloride, $SbCl_5 \cdot pip$ [8], the Sb—N enthalpy of interaction is 231 kJ mol^{-1}. The latter value is comparable with Sb—Cl and C—N

interactions, which are 250 and 280 kJ mol^{-1}, respectively [13]. This diversity of values shows that various interactive processes are important in adduct formation and contribute to the energy in the total process. From the point of view of interactions which occur in solution, such as solute–solvent, solvent–solvent, adsorbent–adsorbate, enzyme substrate and others, the energetic content involved in these processes is, in the majority of cases, low. Since these interactions resemble those involved in adduct formation, knowledge of the energetic adducts can give important information for understanding interactions in solution. Furthermore, a large number of biological processes involve the active participation of metals in chemical functions. A well-known case is haemoglobin, where iron is coordinated by a porphyrin ring forming iron–nitrogen bonds and the free position is used to accommodate the oxygen molecule to form an adduct. The Mo—S—Fe bonds are the active centres in nitrogenase, where some micro-organisms use enzymes to fix nitrogen from the atmosphere in plants. DNA polymerase, whose function is to replicate DNA molecules, contains Zn—O bonds. In an anti-tumour therapy, the Pt—N and Pt—O bond formation with cytosine and adenine bases is involved. The photosynthetic process in green plants is carried out by chlorophyll, which has a magnesium atom centred in a porphyrin system [2,6,14].

These examples are illustrative of a large class of enzymes whose activity can be better understood if the energies involved in the formation or breakage of bonds during the reaction process is known. However, there is a shortage of thermochemical data available for complexes which can be applied to enzymes. The majority of these data have been determined in aqueous solution, while the energies of the metal–ligand interaction need to be calculated from the gaseous state data.

It is worthwhile mentioning here some results with Vaska's compounds, which are very useful as inorganic models. These compounds show a great ability to catalyze organic reactions, such as olefin hydrolysis, and even to exchange gaseous oxygen reversibily, as does haemoglobin. In chlorobenzene, the oxygen uptake by these compounds is thermochemically similar to that found in haemoglobin and other haemoprotein oxygenation [15].

E. THE ADDUCTS

In the great majority of themochemical studies, the adducts were prepared from organic solutions of the metal halides, MX_n, by the addition of ligand, L, in variable proportions, normally dissolved in the same solvent

$$MX_n(c,l) + bL(c,l) \rightarrow MX_n \cdot bL(c,l)$$

This review mainly covers two series of acids: (i) the pronounced acids of the nitrogen group, AsX_3 (X = Cl, Br, I), $SbCl_3$ and $BiCl_3$, which react readily in presence of the bases to give an adduct with distorted geometry due to the presence of the lone pair electrons centred on the coordinated atom; (ii) the halides of the zinc group

MX_2 (M = Zn, Cd, Hg and X = Cl, Br, I), which are less well studied than the neighbouring transition elements, probably because they have a d^{10} configuration and lack the stabilization energy of the crystal field environment. The increase in size or polarizability of the atoms in the triad Zn, Cd, Hg results in interesting features associated with the bond. Moreover, these metals have enormous biological, industrial and environmental importance, especially in the case of zinc [14] whose biochemistry ranks foremost in the field of enzymology.

Adduct formation with a series of bases having oxygen or nitrogen as donor atom, which form mono- or bidentate bonds with metallic ions [16], were explored as were some sulphur atom donors. A list of bases and the respective abbreviations are found at the beginning of this article.

As a general procedure, the adducts were always well characterized by elemental analysis, infrared spectroscopy, thermal analysis, and mass spectrometry. The objective of the last two techniques was to verify the behaviour of the adducts in the gaseous phase [17].

The melting intervals of the adducts are not reproducible after cooling and reheating. It was observed through thermogravimetric curves that some adducts lost mass even before the fusion point. The mass losses confirmed the stoichiometry of the complexes and can occur in distinct stages, corresponding to the initial departure of ligands and, finally, to the complete sublimation of halide [17]. With the mercury halides, both halide and ligand sublime completely or separately. The adducts with oxo-ligands readily form residues, especially with zinc and cadmium halides. Normally, the lack of a well-defined inflection in the thermogravimetric curves indicates that, during the process of decomposition, several reactions occur simultaneously, such as the loss of ligand, ligand decomposition, and volatilization of the metal halide [17].

The mass spectra of the adducts show ligand fragmentation, which is enriched in the case of mercury, antimony and bismuth adducts by the presence of halides [17,18]. With triphenylphosphine oxide, the mass spectrum showed the presence of zinc halide [4]; however, the adduct parent ion was not detected in any case.

(i) Thermochemistry of adducts

The main objective of thermochemical studies is to acquire data for the adduct AB in the condensed phase followed by other enthalpic results such as enthalpy of sublimation ($\Delta_c^g H_m^\circ$) from which the mean metal–ligand bond enthalpy $\bar{D}$(A—B) in the gas phase can be obtained. A general outline involving the whole process, including the enthalpy of decomposition ($\Delta_M H_m^\circ$) and atomization ($\Delta_{atom} H_m^\circ$), is represented in Fig. 1.

In order to access the first stage, the standard molar enthalpy of formation of the adduct in the condensed phase ($\Delta_f H_m^\circ$), reaction–solution calorimetric measurements must be carried out in an appropriate solvent for the following general

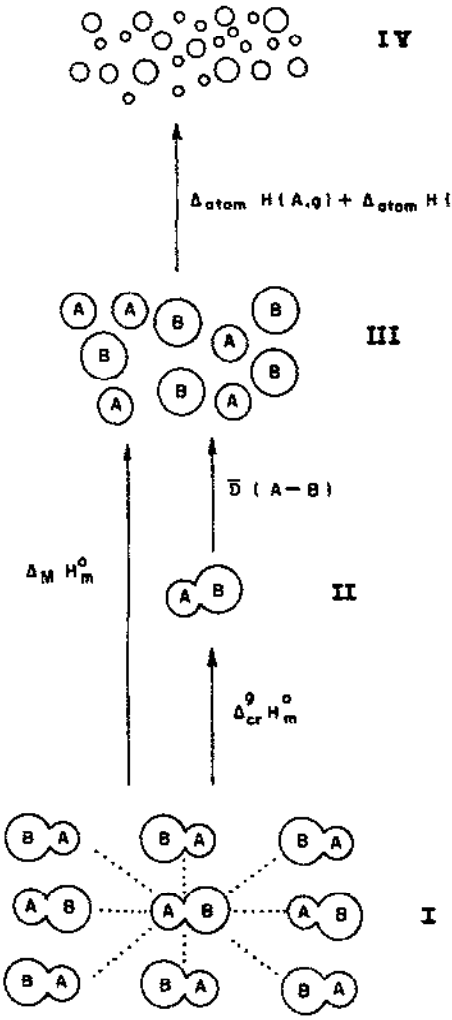

Fig. 1. A schematic representation of the thermochemistry of adducts: (I) intramolecular, AB, and intermolecular (···) interactions; (II) associated AB molecules in an ideal gas; (III) A and B molecules in an ideal gas; and (IV) atomisation of molecules in an ideal gas.

thermochemical cycle with a strict control of the stoichiometry of each individual reaction in the cycle

$MX_n(c,l) + \text{solvent} = \text{soln. A}$ $\Delta_1 H^o_m$

$aL(c,l) + \text{soln. A} = \text{soln. B}$ $\Delta_2 H^o_m$

$MX_n \cdot aL(c,l) + \text{solvent} = \text{soln. C}$ $\Delta_3 H^o_m$

$\text{soln. B} = \text{soln. C}$ $\Delta_4 H^o_m$

The standard molar enthalpy of the final reaction

$$MX_n(c,l) + aL(c,l) = MX_n \cdot aL(c,l) \qquad \Delta_r H^\circ_m$$

can be obtained by the application of Hess' law to the cycle

$$\Delta_r H^\circ_m = \Delta_1 H^\circ_m + \Delta_2 H^\circ_m - \Delta_3 H^\circ_m$$

where strict stoichiometric control gives $\Delta_4 H^\circ_m = 0$, since the participation of the solvent in the cycle is cancelled.

The thermochemical data for all adducts studied in our laboratory are summarized in Tables 1 and 2. The halides of the zinc group elements with some mono- or bidentate ligands containing oxygen or nitrogen donor atoms are listed in Table 1 and the halides of the arsenic group elements with monodentate ligands with nitrogen, oxygen or sulphur donor atoms are listed in Table 2.

The donor strength of the ligand toward a specific acceptor can be represented by $\Delta_r H^\circ_m$ values, which in this case reflect the Lewis acidities of a group of metal halides [35]. In considering the acid–base strengths, comparisons should be made for adducts of the same stoichiometry in which crystal enthalpies, reorganization enthalpies, etc. can be assumed to be the same. To illustrate this behaviour, Table 3 presents $\Delta_r H^\circ_m$ values for adducts of the halides of the zinc group elements with dmf [19], and antimony and bismuth chlorides with dma, dmf and tmu [18]. For bis adducts of dmf, the acidity order is $ZnBr_2 > ZnI_2 > ZnCl_2 > CdI_2 > CdCl_2$.

With the zinc halides, the order $ZnI_2 > ZnBr_2 > ZnCl_2$ based on the mono-adducts, contrasts with the inverse order of the halides in the cadmium series, where the acidity order $HgCl_2 > HgBr_2$ is observed. However, the relative acceptor acidity varies in the order Zn > Cd > Hg for bis adducts [19]. For MCl_3 (M = Sb, Bi) adducts, the acidity order $BiCl_3 > SbCl_3$ [18] contrasts with a previously proposed order [36]. The basicity order tmu > dma > dmf [18] is consistent in both series of adducts and correlates closely with the donor number of the ligands [37]. Identically, for urea and its derivatives, the basicity order tmu > dmu > mu > ur [25] was observed. For *N*,*N*-dimethyl-*N'*-methylurea (trmu), which is missing in this sequence, a graph of $\Delta_r H^\circ_m$ versus ligand molar mass for $ZnCl_2 \cdot 2L$ and $MCl_2 \cdot L$ (M = Cd, Hg) was used to obtain the desired values by interpolation, as can be seen in Fig. 2. However, $\Delta_r H^\circ_m$ values for zinc and cadmium urea adducts deviate from the linear correlation. Presumably, hydrogen bonding affects the formation of the adduct in the solid phase and results in a larger enthalpy of formation when the acid is relatively hard, like zinc, rather than soft, as in the case of mercury. The intermediate hardness of cadmium places it in both positions [8].

The standard molar enthalpy of formation of the adduct in the condensed phase could be obtained from $\Delta_r H^\circ_m$ values by means of the expression

$$\Delta_f H^\circ_m \text{ (adduct)} = \Delta_r H^\circ_m + b\Delta_f H^\circ_m \text{ (ligand)} + \Delta_f H^\circ_m \text{ (halides)}$$

The enthalpies of formation of the metal halides have been tabulated in the literature

TABLE 1

Summary of thermochemical measurements on the adducts of the halides of zinc group elements with oxygen and nitrogen donor atoms

Compound	M	X	Non-isolated adduct	Ref.
Compound with one MY bond				
$MX_2 \cdot dmf$	Zn, Cd, Hg	Cl, Br, I	HgI_2	19
$MX_2 \cdot dma$	Cd, Hg	Cl, Br		20,21
$MX_2 \cdot tmu$	Cd, Hg	Cl, Br		22
$MX_2 \cdot dmu$	Cd, Hg	Cl, Br		23
$MX_2 \cdot mu$	Cd, Hg	Cl, Br		24
$MX_2 \cdot ur$	Cd, Hg	Cl, Br, I	HgI_2	25
$MX_2 \cdot py$	Cd, Hg	Cl		26
$HgCl_2 \cdot pyo$	Hg	Cl		17
Compound with two MY bonds				
$MX_2 \cdot 2tepo$	Zn, Cd, Hg	Cl		27
$MX_2 \cdot 2tppo$	Zn, Cd, Hg	Cl, Br, I		4,28
$ZnCl_2 \cdot 2tbpo$	Zn	Cl		27
$MX_2 \cdot 2hmpa$	Zn, Cd, Hg	Cl, Br, I		29
$MX_2 \cdot 2dmf$	Zn, Cd	Cl, Br, I	$CdBr_2$	19
$MX_2 \cdot 2dma$	Zn, Cd	Cl, Br, I	$CdCl_2$ and $CdBr_2$	20,21
$MX_2 \cdot da$	Zn, Cd	Cl, Br, I		30
$HgX_2 \cdot 2da$	Hg	Cl, Br		30
$MX_2 \cdot 2tmu$	Zn, Cd	Cl, Br, I	$CdCl_2$ and $CdBr_2$	22
$MX_2 \cdot 2dmu$	Zn, Hg	Cl, Br	$HgBr_2$	23
$ZnX_2 \cdot 2mu$	Zn	Cl, Br		24
$MX_2 \cdot 2ur$	Zn, Cd	Cl, Br, I	$CdCl_2$	25
$ZnCl_2 \cdot 2py$	Zn	Cl		26
$MX_2 \cdot 2pyo$	Zn, Cd	Cl		17
$MCl_2 \cdot bipy$	Zn, Cd, Hg	Cl		26
$MCl_2 \cdot bipyo$	Cd, Hg	Cl		17
$MCl_2 \cdot phen$	Zn, Cd, Hg	Cl		26
$MX_2 \cdot pya$	Zn, Hg	Br		31
Compounds with three MY bonds				
$CdBr_2 \cdot 3dmu$	Cd	Br		23
$ZnCl_2 \cdot 1.5bipyo$	Zn	Cl		17
Compounds with four MY bonds				
$MX_2 \cdot pya$	Zn, Cd, Hg	Cl, I	HgI_2	32
$CdBr_2 \cdot 2pya$	Cd	Br		32

TABLE 2

Summary of thermochemical measurements on the adducts of the halides of arsenic group elements with nitrogen, oxygen and sulphur donor atoms

Adduct	L	Ref.
$AsCl_3 \cdot L$	py, mpy, ppy, ac, dma, ta, dtf, tmtu	33,34
$AsBr_3 \cdot L$	ac, dma, dtf, dta, ttu	34
$AsI_3 \cdot L$	mpy, ppy, ac, dma, ta, tu, dtf, dta, ttu	33,34
$AsCl_3 \cdot 2L$	tu	34
$AsBr_3 \cdot 2L$	ppy, ta, tu	33,34
$AsI_3 \cdot 2L$	py	33
$AsBr_3 \cdot 3L$	mpy	33
$2AsCl_3 \cdot 3L$	dmta	34
$2AsBr_3 \cdot 3L$	py	33
$SbCl_3 \cdot L$	dmf, dma, tmu	18
$SbCl_3 \cdot 2L$	tmu	18
$BiCl_3 \cdot 2L$	dmf, dma, tmu	18
$BiCl_3 \cdot 3L$	dma, tmu	18

[38], as have those of many ligands [39]. The data for pya [32], mu [24], dmu [23] and bipy [26] were determined through combustion calorimetry. For urea and R-urea (R = methyl, dimethyl, trimethyl and tetramethyl) compounds, a correlation between the energy of combustion and the molar mass (M) of urea and R-ureas, $\Delta_c H^\circ_m/\text{kJ mol}^{-1} = 49.14M + 2305.15$ is observed with less than 1% error [24].

The standard molar enthalpies of formation of pyO and bipyO [17] were determined from solution–reaction calorimetry. These determinations were based on

TABLE 3

$\Delta_f H^\circ_m$ values (kJ mol^{-1}) of adducts of the halides of zinc elements with dmf, and antimony and bismuth chlorides with dma, dmf, and tmu

Adduct	$\Delta_f H^\circ_m$	Adduct	$\Delta_f H^\circ_m$
$ZnCl_2 \cdot 2dmf$	-81.37 ± 0.77	$ZnCl_2 \cdot dmf$	-52.39 ± 0.41
$ZnBr_2 \cdot 2dmf$	-90.79 ± 0.48	$ZnBr_2 \cdot dmf$	-53.78 ± 0.57
$ZnI_2 \cdot 2dmf$	-86.56 ± 0.74	$ZnI_2 \cdot dmf$	-57.50 ± 0.28
		$CdCl_2 \cdot dmf$	-26.84 ± 0.18
$CdI_2 \cdot 2dmf$	-54.39 ± 0.27	$CdBr_2 \cdot dmf$	-35.61 ± 0.36
$BiCl_3 \cdot 2tmu$	-83.88 ± 0.83	$CdI_2 \cdot dmf$	-30.72 ± 0.18
$BiCl_3 \cdot 2dma$	-82.36 ± 0.83	$HgCl_2 \cdot dmf$	-23.09 ± 0.42
$BiCl_3 \cdot 2dmf$	-66.15 ± 0.61	$HgBr_2 \cdot dmf$	-19.02 ± 0.19
$SbCl_3 \cdot 2tmu$	-76.96 ± 0.42	$SbCl_3 \cdot tmu$	-44.86 ± 0.27
		$SbCl_3 \cdot dma$	-37.96 ± 0.16
		$SbCl_3 \cdot dmf$	-27.82 ± 0.15

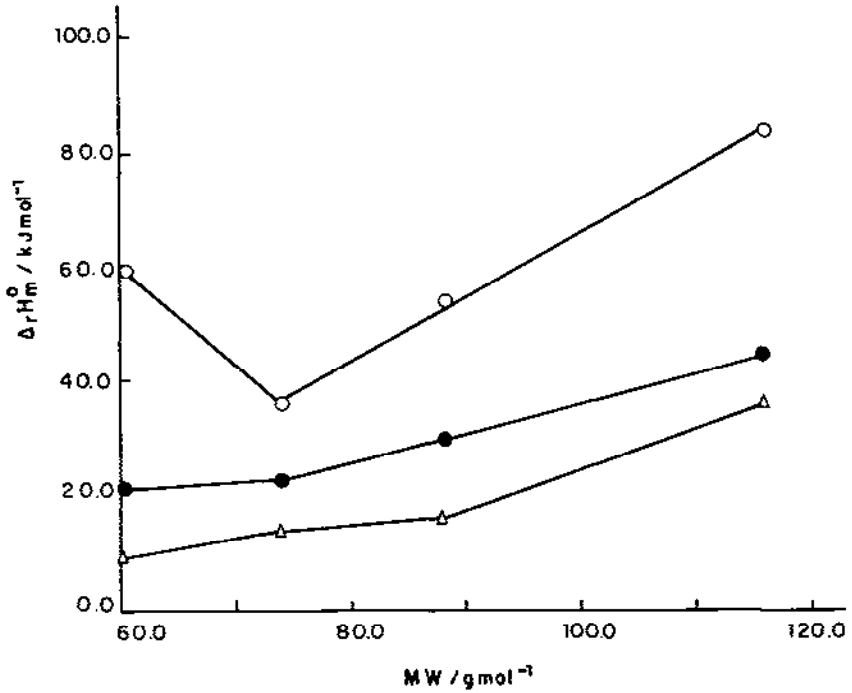

Fig. 2. A plot of $\Delta_r H_m^o$ against molecular weight of the ligand (MW): ○, $ZnCl_2 \cdot 2L$; ●, $CdCl_2 \cdot L$, and △, $HgCl_2 \cdot L$. L = ur, mu, dmu and tmu.

the ability of titanium(III) in $TiCl_3$–HCl solutions as calorimetric solvent, to reduce heterocyclic amine *N*-oxides [40].

From $\Delta_r H_m^o$ values, the enthalpies for the reactions

$$MX_n \cdot bL(c) = MX_n(c) + bL(g) \qquad \Delta_D H_m^o$$

$$MX_n \cdot bL(c) = MX_n(g) + bL(g) \qquad \Delta_M H_m^o$$

can be obtained by means of thermodynamic cycles to provide information about the energetics of formation of solid adducts from gaseous reagents or to demonstrate the facility of releasing ligands during heating (see Fig. 1). From cycles

$$\Delta_D H_m^o = -\Delta_r H_m^o + b\Delta_c^g H_m^o(L)$$

and

$$\Delta_M H_m^o = \Delta_D H_m^o + \Delta_c^g H_m^o(MX_n)$$

The last terms in both expressions are the enthalpies of sublimation of the ligand (L) and halides (MX_n). These enthalpies of sublimation of metal halides are known and have been tabulated [38,41,42]; however, the values of the ligands must normally

be determined. The enthalpies of sublimation can be obtained from the expression

$$\Delta_c^g H_m^\circ(298\ \mathrm{K}) = \int_{298}^{T_{fus}} \mathrm{Cp(c)d}T + \Delta_c^l H_m^\circ(T_{fus}) + \int_{T_{fus}}^{T_{vap}} \mathrm{Cp(l)d}T + \Delta_l^g H_m^\circ(T_{vap}) - \int_{298}^{T_{vap}} \mathrm{Cp(g)d}T$$

The determination of the enthalpy of sublimation ($\Delta_c^g H_m^\circ$) will be illustrated for bipy [26] where differential scanning calorimetry can be used. In this case, a sharp peak at 342 K corresponds to fusion, from which the enthalpy of fusion 19.9 ± 0.2 kJ mol^{-1} was calculated. The heat capacities of the solid and liquid forms were also determined by this technique as 0.21 and 0.23 kJ K^{-1} mol^{-1}, respectively. The mean standard enthalpy of vaporization was calculated by means of Riedel–Planck–Miller equations [43,44] giving 41.55 ± 0.33 kJ mol^{-1}. Finally, the heat capacity in the gas phase was estimated by means of the method of generalized vibrational assignment [43,44] from the expression $\mathrm{Cp(g)} = -6.95 \times 10^{-2} + 8.77 \times 10^{-4}T - 4.50 \times 10^{-7}T^2$. From these values, the enthalpy of sublimation, calculated from the above expression, is 67 kJ mol^{-1}.

In Table 4, some selected thermochemical results for ligand with oxygen (tmu [22] and hmpa [29]) and nitrogen (py, bipy and phen [26]) donor atoms are listed. $\Delta_r H_m^\circ$ values for MCl_3 (M = Sb, Bi) show a variation with the number of ligands and present a higher exothermicity for adducts of bismuth compared with compounds of the same stoichiometry, i.e. $SbCl_3 \cdot 2$tmu and $BiCl_3 \cdot 2$tmu, gave -76.96 ± 0.42 and -83.88 ± 0.83 kJ mol^{-1}, respectively [18]. For a series of adducts of the same ligands and stoichiometry, this enthalpy increases from chloride ($ZnCl_2 \cdot 2$hmpa = -113.08 ± 0.79 kJ mol^{-1}) to iodide ($ZnI_2 \cdot 2$hmpa = -131.86 ± 0.86 kJ mol^{-1}). Within the same series, a decrease from $ZnCl_2$ ($ZnCl_2 \cdot$ bipy = -82.9 ± 0.5 kJ mol^{-1}) to $HgCl_2$ ($HgCl_2 \cdot$ bipy = -37.7 ± 0.9 kJ mol^{-1}) was observed. $\Delta_f H_m^\circ$, $\Delta_M H_m^\circ$ and $\Delta_D H_m^\circ$ have the same behaviour as $\Delta_r H_m^\circ$ in relation to the variation of the number of ligands in the MCl_3 series. While $\Delta_f H_m^\circ$ values decrease from chloride ($CdCl_2 \cdot 2$hmpa = -1462 kJ mol^{-1}) to iodide ($CdI_2 \cdot 2$hmpa = -1366 kJ mol^{-1}), which is the inverse order of $\Delta_r H_m^\circ$ values, $\Delta_M H_m^\circ$ and $\Delta_D H_m^\circ$ values do not present a regular trend and show a higher value for bromide (compare $CdX_2 \cdot 2$hmpa values, for one or both parameter series). For adducts $MCl_2 \cdot L$, $\Delta_f H_m^\circ$ values decrease from $ZnCl_2$ ($ZnCl_2 \cdot$ phen = -255 kJ mol^{-1}) to $HgCl_2$ ($HgCl_2 \cdot$ phen = -41 kJ mol^{-1}), as does $\Delta_D H_m^\circ$. However, a higher $\Delta_D H_m^\circ$ value for $CdCl_2 \cdot L$ was observed.

(ii) Metal–ligand bond in adducts

In order to characterize the strength of the metal–ligand bond in any coordination compound, it is of fundamental importance to estimate the standard enthalpy

TABLE 4

Some selected thermochemical results (kJ mol^{-1})

Adduct	$\Delta_r H_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_M H_m^\circ$	$\Delta_D H_m^\circ$
$SbCl_3 \cdot tmu$	-44.86 ± 0.27	-681	-164	96.0
$SbCl_3 \cdot 2tmu$	-76.96 ± 0.42	-968	-247	179.2
$BiCl_3 \cdot 2tmu$	-83.88 ± 0.83	-972	-300	186.1
$BiCl_3 \cdot 3tmu$	-112.19 ± 0.98	-1255	-381	266.5
$ZnCl_2 \cdot 2tmu$	-83.13 ± 0.96	-1006	-334	185
$ZnBr_2 \cdot 2tmu$	-88.68 ± 2.12	-926	-322	191
$ZnI_2 \cdot 2tmu$	-127.83 ± 2.87	-844	-350	130
$CdCl_2 \cdot tmu$	-44.68 ± 0.62	-690	-277	96
$HgCl_2 \cdot tmu$	-36.52 ± 0.47	-515	-170	88
$ZnCl_2 \cdot 2hmpa$	-113.08 ± 0.79	-1596	375	226
$ZnBr_2 \cdot 2hmpa$	-135.53 ± 1.18	-1532	380	249
$ZnI_2 \cdot 2hmpa$	-131.86 ± 0.86	-1408	365	245
$CdCl_2 \cdot 2hmpa$	-55.12 ± 0.81	-1514	349	168
$CdBr_2 \cdot 2hmpa$	-77.73 ± 0.67	-1462	342	191
$CdI_2 \cdot 2hmpa$	-94.58 ± 0.50	-1366	345	208
$HgCl_2 \cdot 2hmpa$	-63.97 ± 1.24	-1356	260	177
$HgBr_2 \cdot 2hmpa$	-65.42 ± 1.78	-1304	263	179
$HgI_2 \cdot 2hmpa$	-53.41 ± 0.78	-1227	255	167
$ZnCl_2 \cdot 2py$	-116.1 ± 1.0	-331	-346	197
$CdCl_2 \cdot py$	-46.8 ± 0.5	-338	-268	87
$HgCl_2 \cdot py$	-43.4 ± 0.4	-168	-166	84
$ZnCl_2 \cdot bipy$	-82.9 ± 0.5	-282	-299	150
$CdCl_2 \cdot bipy$	-53.9 ± 1.6	-229	-302	121
$HgCl_2 \cdot bipy$	-37.7 ± 0.9	-46	-188	105
$ZnCl_2 \cdot phen$	-83.5 ± 1.5	-255	-298	149
$CdCl_2 \cdot phen$	-61.7 ± 1.7	-210	-308	127
$HgCl_2 \cdot phen$	-60.0 ± 1.6	-41	-208	125

of adduct dissociation in the ideal gaseous state in order to remove contributions due to intermolecular forces. In principle, this operation depends on the characteristics of the compound. Since it has the facility to sublime, therefore, this is an appropriate condition to calculate the enthalpy of the metal–ligand bond. However, the ligand–metal bond in adducts is prone to suffer dissociation when submitted to sublimation.

Therefore, to characterize the adducts, it is necessary to determine the dissociation enthalpy in the gas phase for $MX_2 \cdot bL$ adducts (M = Zn, Cd, Hg and X = Cl, Br, I), which is given by

$$MX_2 \cdot bL(g) = MX_2(g) + bL(g) \qquad \Delta_g H_m^\circ$$

A measure of the strength of the metal–ligand bond can be given by:

$$\Delta_g H^\circ_m = -b\bar{D}(MY)$$

where $\bar{D}(MY)$ is the mean enthalpy of dissociation of MY, with Y being the donor atom bonded to M.

To obtain $\Delta_g H^\circ_m$, and consequently $\bar{D}(MY)$, thermochemical cycle I was applied, using $\Delta_r H^\circ_m$ determined experimentally through solution–reaction calorimetry.

$$\begin{array}{ccccc} MX_2(g) & + & bL(g) & \xrightarrow{\Delta_g H^\circ_m} & MX_2 \cdot bL(g) \\ \uparrow \Delta^g_c H^\circ_m(M) & & \uparrow b\Delta^g_c H^\circ_m(L) & & \uparrow \Delta^g_c H^\circ_m(ad) \\ MX_2(c) & + & bL(c,l) & \xrightarrow{\Delta_r H^\circ_m} & MX_2 \cdot bL(c) \end{array}$$

Scheme I.

The enthalpies of sublimation of metal halide, $\Delta^g_c H^\circ_m(M)$, and ligand, $\Delta^g_c H^\circ_m(L)$, can be determined by various techniques, such as calorimetry, vapour pressure measurements, etc., and are available in the literature [38,39,41,42]. The enthalpy of sublimation of the adduct, $\Delta^g_c H^\circ_m(ad)$, is not experimentally accessible because the adducts are prone to dissociate when sublimed.

In order to estimate the strength of the MY bond, the assumption that $\Delta^g_c H^\circ_m(L) = \Delta^g_c H^\circ_m(ad)$ was proposed [4]. At that time (1978), the justification for this assumption was based on the few available enthalpies of sublimation of some thiourea adducts of the type $MCl_2 \cdot 4tu$, which are in the 75–101 kJ mol^{-1} range. The sublimation enthalpy of the free ligand is 94 kJ mol^{-1} [45]. Other adducts have recently become available and their enthalpy values are close to that of the ligand, varying within ± 10 kJ mol^{-1}. These values are listed in Table 5. For these sublimable adducts the assumption is valid within the experimental errors [46]. This assumption is reasonable since the intermolecular forces in the adduct and ligand should be very similar since the crystalline structure of the ligand complex remain virtually unchanged [46].

Some selected $\bar{D}$(M–N) and $\bar{D}$(M–O) values for MCl_2 (M = Zn, Cd, Hg) are plotted in Fig. 3. For adducts of the same stoichiometry, $\bar{D}$ values show a slight increase (phen, bipy [26]) or a slight decrease (pyo [17], dmf [19], bipyo [17]) from zinc to cadmium, followed by a considerable drop to the much less strongly bonded mercury. The proximity of $\bar{D}$(M–O) values for da [30] may be related to the behaviour of the ligand in acting as a monodentate adduct with mercury. A strong increase from zinc to cadmium is observed for adducts of different stoichiometries (py [26], tmu [22], ur [25]) and are higher for monodentate ligands (compare py

TABLE 5
Some enthalpies of sublimation of adducts and their respective ligands at 298 K

Compound	$\Delta_c^g H_m^\circ$ (kJ mol^{-1})	Ref.
Cytosine (cyt)	147.2 ± 2.6	46
1-Methylcytosine (mcyt)	141.8 ± 8.8	46
Thiourea (tu)	93.7 ± 10	45
$MnCl_2 \cdot 2cyt$	153 ± 21	46
$CdCl_2 \cdot 2mcyt$	145 ± 20	46
$HgCl_2 \cdot 2myct$	159 ± 19	46
$ZnCl_2 \cdot 4tu$	90 ± 20	45
$CdCl_2 \cdot 4tu$	75 ± 20	45
$HgCl_2 \cdot 4tu$	101 ± 20	45

and bipy, and pyo and bipyo). Also, the $\bar{D}$(M—O) value for dmf is higher than that of the bidentate da adduct. *N*-Oxide ligands have lower $\bar{D}$ values, as can be seen by comparing pyo and py, and bipyo and bipy. It seems that the electronic effect of the methyl groups on the nitrogen atom of urea results in an increase of the $\bar{D}$(M—O) values in the tmu adducts. In general, $\bar{D}$ values decrease for the halides in the order Cl > Br > I for a given ligand and metal.

Table 1 presents nearly one hundred adducts studied thermochemically in our laboratory and are classified by the nature of the ligand bonding. The majority of these ligands are monodentate in character and therefore add one or two molecules to the acid and are classified as one or two MY bonds, respectively. Exceptionally, dmu forms $CdBr_2 \cdot 3dmu$ [23], which has three MY bonds. The ability of diacetamide [30] to act as a mono- or bidentate ligand is reflected in both formulations, $MX_2 \cdot da$ and $HgX_2 \cdot 2da$, which can be easily distinguished by infrared spectroscopy [47]. Identically, the bidentate coordination of *N*-(2-pyridyl)acetamide through the carbonyl oxygen and pyridinic nitrogen forms the adducts $MX_2 \cdot pya$ [48]. The other bidentate ligands bipy, bipyo and phen are also classified as two MY bonds. The change in stoichiometry of the adducts of pya leads to four MY bonds. Due to the use of bipyo in bridging the zinc atom in the adduct $ZnCl_2 \cdot 1.5$ bipyo [17], it is defined as three MY bonds.

Based on the decomposition reaction of the adducts

$$MX_2 \cdot bL(c) = MX_2(g) + bL(g) \qquad \Delta_M H_m^\circ$$

the expression

$$\Delta_M H_m^\circ = \Delta_r H_m^\circ + \Delta_c^g H_m^\circ(M) + b\Delta_c^g H_m^\circ(L)$$

was derived by applying Hess' law to Scheme 1. Since all terms on the right-hand side of the expression are experimentally accessible, $\Delta_M H_m^\circ$ can be calculated without

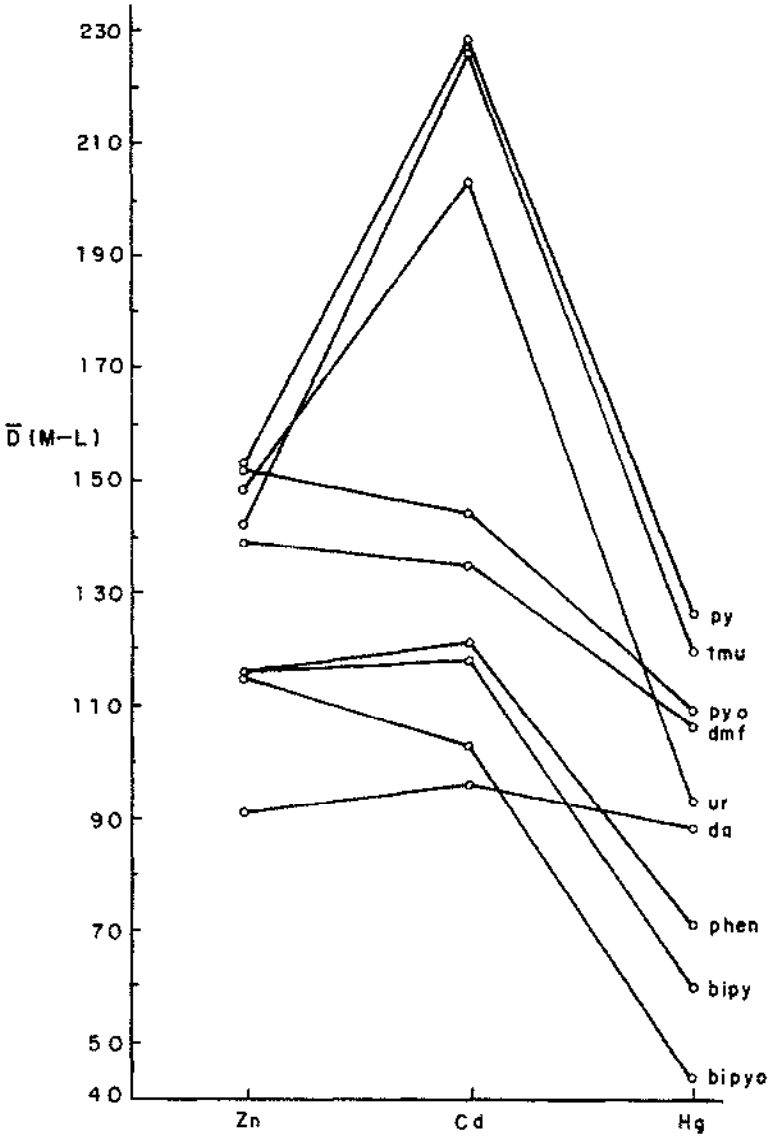

Fig. 3. A plot of $\bar{D}$(M–N) and $\bar{D}$(M–O) values obtained for the $MCl_2 \cdot bL$ adducts of zinc, cadmium and mercury.

approximations. This parameter is correlated with the $\bar{D}$(MY) calculated assuming that $\Delta_c^g H_m^o(\text{ad}) = \Delta_c^g H_m^o(\text{L})$. These parameters can be fit to the straight line equation

$$\bar{D}(\text{MY}) = p\Delta_M H_m^o + q$$

where the constant $p = 1/b$, b is the number of monodentate ligands in the adduct and $q = (1/b)\Delta_c^g H_m^o(\text{ad})$. The adducts of general formula $MX_2 \cdot 2L$ gave $p = 0.48 \pm 0.07$

(expected $1/b = 0.5$) and $q = -26 \pm 22$ with a correlation coefficient (r) of 0.9527 for 52 adducts. The compounds $MX_2 \cdot L$ showed $p = 0.95 \pm 0.19$ (expected $1/b = 1.0$) and $q = -55 \pm 42$ with $r = 0.9116$ for 30 adducts. In these correlations, there is no loss of fundamental information linked to the stoichiometry of the adducts. Based on this hypothesis, some $\bar{D}$(M–Y) values were calculated for $MCl_2 \cdot bL$ adducts studied by us, and aniline [49] and thiourea [50] adducts; they are listed in Table 6. Other approximations, such as the geometric means of the enthalpies of sublimation of the ligands and halides, were also tested, but resulted in poorer correlations [16].

From the data listed in Table 6, the following observations can be deduced: (i) for the same M bonded to ligands with identical Y atoms in two different stoichiometries, $\bar{D}$(M–Y) values are higher for the monoadduct. For example, the $\bar{D}$(Cd–O) values are 209 ± 8 and 142 ± 9 kJ mol^{-1} for $n = 1$ and 2, respectively, where n is the number of Y atoms bonded to M; (ii) the preceding assertion is not valid for bidentate ligands. For example, $\bar{D}$(Zn–N) = 116 kJ mol^{-1} for bipy and phen ($n = 1$), and $\bar{D}$(Zn–N) = 152 ± 1 kJ mol^{-1} for py and an ($n = 2$); (iii) for bisadducts, a general trend $\bar{D}$(Zn–Y) > $\bar{D}$(Cd–Y) > $\bar{D}$(Hg–Y) is observed. The same behaviour

TABLE 6
Some $\bar{D}$(MY) values (kJ mol^{-1}) for $MCl_2 \cdot bL$ adducts

Bond	n[a]	$\bar{D}$(MY)[b]	N[c]	Way of bonding[d]	Ligand
ZnO	2	146 ± 10	11	m	tepo, tppo, tbpo, hmpa, dmf, dma, tmu, dmu, mu, ur, pyo
ZnO	1	201	1	m	dmf
ZnN	2	152 ± 1	2	m	py, an
ZnN	1	116	2	b	bipy, phen
ZnS	2	148	1	m	tu
CdO	2	142 ± 9	5	m	dmf, dma, tmu, dmu, mu, ur, pyo
CdO	1	109 ± 8	6	m	dmf, dma, tmu, dmu, mu, ur
CdO	1	103	1	b	bipyo
CdN	1	228	1	m	py
CdN	1	120 ± 2	2	b	bipy, phen
CdS	2	142	1	m	tu
HgO	2	92	1	m	dmu
HgO	1	102 ± 10	10	m	tepo, tppo, hmpa, dmf, dma, tmu, dmu, mu, ur, pyo
HgN	1	126	1	m	py
HgN	1	66 ± 6	2	b	bipy, phen
HgS	2	104	1	m	tu

[a]Number of Y atoms bonded to M.
[b]Mean value ± standard deviation.
[c]Number of compounds used for the mean calculation.
[d]Ligands bonded mono- (m) or bidentate (b) to metal.

is shown by the monoadducts originating from bidentate ligands; (iv) $\bar{D}$(Hg–Y) is always smaller in comparison with the respective adduct of zinc and cadmium, even in the case of a sulphur donor atom where a favourable bond would be expected [51].

(iii) Some general comments

The variation of the mean metal–ligand bond enthalpy across the periodic table demands the existence of a series of convenient complexes, for which the experimental calorimetric measurements could provide sufficient thermochemical data to estimate or to calculate the mean metal–donor atom ligand bond enthalpy. A class of compounds useful for this kind of determination is the hexacoordinated complexes, where knowledge of the hexacoordinated cation–anion distance is required, but for which published data are scarce. An interesting series of these thermochemical data was early related to hexamine complexes for calcium and some first transition divalent elements. A graph of the enthalpy of formation of $[M(NH_3)_6]^{2+}$ in the gaseous phase against the atomic number of the elements exhibits a smooth curve through the values for calcium, manganese and zinc complexes, due to the ligand field stabilization energies [52].

After determination of the standard enthalpy of the crystalline hexacoordinated complex, the molar lattice enthalpy can be obtained by the use of a convenient equation, since the total cation–anion distance is known [53]. Application of these values to the thermochemical cycle with other auxiliary data, leads to determination of the enthalpy of formation of the cation complex and consequently the mean metal–ligand bond enthalpy. For hexakis(urea)calcium bromide, $\bar{D}$(Ca–O) = 295 ± 9 kJ mol^{-1} [54]. This value is higher than the corresponding calcium–nitrogen enthalpy, calculated from the hexamine complex [52], which gave 190 kJ mol^{-1}.

A mean nickel–sulphur bond enthalpy for hexakis(thiourea)nickel(II) cation of 263 kJ mol^{-1} [55] and the corresponding values for hexaaquo and hexamine complexes of 236 and 295 kJ mol^{-1}, respectively, were recalculated from literature data [52,56]. The order of the mean nickel–ligand bond enthalpies, O < N < S, was interpreted to be due to the soft behaviour of nickel(II) [55]. The higher $\bar{D}$(Ca–O), in comparison with the corresponding nickel value, seems to be associated with the strong characteristic of the calcium to bond oxygen ionically [54].

Another feature of these adducts is the correlation between standard enthalpies of formation of crystalline compounds and enthalpies of formation of ligands in their standard reference state (rs) [57,58]. Among others, one correlation will be used to illustrate this behaviour. For example, a plot of $\Delta_f H^\circ_m$ ($ZnCl_2 \cdot 2L$,c) versus the enthalpy of formation of several oxygen ligands L gave the following correlation for all points with a coefficient $r = 0.998$

$$\Delta_f H^\circ_m(ZnCl_2 \cdot 2L,c) = (2.076 \pm 0.048)\Delta_f H^\circ_m(L,rs) - (456.8 \pm 17.0)$$

Two important observations can be added: (i) the estimated $\Delta_f H^\circ_m$(c) values obtained from this equation agree with the experimental values within

ca. $\pm$ 20 kJ mol^{-1}, and (ii) the angular coefficients correspond to the stoichiometry of the series of the adducts considered.

The strong Lewis acidity character revealed by MCl_3 (M = Sb, Bi) in the presence of Lewis bases gives rise to the possibility of the formation of more than one adduct with the same ligand, depending on the experimental stoichiometry of the reaction [18]. Surprisingly, $SbCl_3$ with dmf and dma formed viscous liquid adducts. Taking advantage of this property, the barrier to internal rotation of dma in $SbCl_3 \cdot$dma was determined [59] from total lineshape analysis of the ^{13}C NMR spectra of the neat liquid, without apparent dissociation and the spectroscopic data showed a coordination through the oxygen of the carbonyl group to antimony [18]. The Arrhenius energy of activation for the hindered rotation about the CN bond was found to be 73.8 $\pm$ 1.1 kJ mol^{-1}, and the enthalpy and entropy of activation, 71.0 $\pm$ 1.2 kJ mol^{-1} and -5 ± 4 J K^{-1} mol^{-1}, respectively. A decrease of the rotational barrier by a small amount on formation of this adduct was observed in comparison with those values for neat dma:Ea = 79.5 $\pm$ 0.4, $\Delta H^{\neq}$ = 76.6 $\pm$ 0.4 kJ mol^{-1} and $\Delta S^{\neq} = 3 \pm 4$ J mol^{-1} K^{-1} [60]. This behaviour contrasts with an increase of 10–15 kJ mol^{-1} for similar complexes of BF_3 [61], $SnCl_4$ [62], $TiCl_4$ [62] and $SbCl_5$ [62,63] with *N*,*N*-dimethylamides. The decrease was interpreted by the greater stabilisation of the transition state by using some participation of the nitrogen atom of the ligand in coordinating the antimony. While this structure would not be expected for most amide complexes because of steric or electronic considerations, the results obtained with this isolated liquid adduct can contribute a valuable source to explain the decrease in rotational barrier of the other amide adducts [62,64].

In order to evaluate the techniques used to obtain thermochemical data, the cobalt(II) chloride–acetonitrile system was studied using calorimetry [65] and compared with vapour pressure and DSC measurements. The adducts $CoCl_2 \cdot bCH_3CN$ (b = 1, 2 and 3) were carefully isolated. The infrared spectrum of the tris-adduct led to the suggestion that the metal is tetrahedrally bonded by two ligands and two chlorides, with a third uncoordinated site present in the crystal [66].

Reaction-solution calorimetry of this system led to the determination of the enthalpy of the reactions

$$CoCl_2(c) + bCH_3CN = CoCl_2 \cdot bCH_3CN \qquad \Delta_r H^{\circ}_m$$

and consequently the respective enthalpies of decomposition. Table 7 summarizes the thermochemical results obtained using these three different techniques.

The enthalpy of decomposition obtained through vapour-pressure measurements [67] are quite precise in the experimental range of temperatures for which the pressure was collected and an excellent linearity of ln$p$ versus $1/T$ was observed. These values agree with those obtained by reaction–solution calorimetry [65], with small differences which could be attributed to the different temperatures used in the experimental work. However, the DSC results [68] for bis and trisadducts are

TABLE 7

Standard enthalpy of reaction and decomposition (kJ mol^{-1}) of $CoCl_2$ adducts at different temperatures (K) by using solution-reaction calorimetry (cal), vapour pressure (vp) and differential scanning calorimetry (DSC)

Adduct	$\Delta_r H_m^\circ$	$\Delta_D H_m^\circ$	Temperature (K)	Technique	Ref.
$CoCl_2 \cdot CH_3CN$	-22.92 ± 0.78	56.04 ± 0.91	298.15	cal	65
		60.4 ± 0.4	318–354	vp	67
$CoCl_2 \cdot 2CH_3CN$	-34.07 ± 0.80	100.35 ± 1.06	298.15	cal	65
		107.7 ± 0.7	298–349	vp	67
		76.4 ± 0.9	350	DSC	68
$CoCl_2 \cdot 3CH_3CN$	-47.32 ± 0.76	146.74 ± 1.15	298.15	cal	65
		155.4 ± 0.9	288–354	vp	67
		103.4 ± 2.9	320	DSC	68

considerably lower than the other determinations. Assuming the same purity of the adducts, the $\Delta_D H_m^\circ$ values do not distinguish different ligand bonding environments, as was suggested by infrared [66]. More importantly, the DSC values, although obtained outside of the standard temperature range, are significantly different from those obtained from other measurements, which suggests that many systems studied by DSC should be carefully re-analysed.

F. THE CHELATES

(i) Introduction

Dithiocarbamates comprise a structurally related group of sulphur-chelating agents which has a strong tendency to coordinate metals. There has been increasing interest not only in their coordination chemistry [69–71], but also in many applications [72] such as the use of the ligands for trace-metal determination in foods, pharmaceutical products, biological samples, and in the environment with appropriate analytical techniques.

The thermochemistry of these chelates is being continuously investigated and many features of these compounds studied. An interesting review on the thermochemistry of metal dithiocarbamate complexes and related compounds, published a decade ago, emphasized the volatility, thermal decomposition mechanisms and solution thermochemistry [73]. The authors observed that, since the majority of thermochemical data refers only to the first row transition metals, it is difficult to establish trends within the periodic table and that many thermal properties do not correlate with the structure of the complexes. Therefore, they suggested that the acquisition of additional thermochemical data could give important information to relate structure properties of the ligands with the thermochemistry.

Taking into account our interest in group elements, dithiocarbamate complexes were also studied. Thus, bis(diethyldithiocarbamato)zinc(II) was first prepared and studied by reaction–solution calorimetry [74]. This compound associates as dimers in the solid state with the metal surrounded by five sulphur atoms [75] with one long zinc–sulphur bond in a weak coordination position. Its acidic nature is revealed by its ability to form adducts with primary and secondary aliphatic amines, and pyridine [76]. Crystal structure determination of the pyridine adduct shows that the zinc atom is located in a five-coordinate site [77]. Thermodynamic data for the addition of pyridine, 4-methylpyridine and 2,2′-bipyridine in 1:1 molar ratio in benzene solution have also been obtained through calorimetric titration [78] and no evidence of dimerization was noticed in this medium.

Various nitrogen bidentate ligands form adducts with zinc dialkyldithiocarbamates and the crystal structure determination of the monomeric phen adduct shows the metal centred in an octahedral site, with the ZnS_2C unit nearly planar [79].

The analogous cadmium compounds and their derivatives are known to be efficient therapeutic chelating agents [80]. Bis(diethyldithiocarbamato)cadmium(II) has a dimeric centrosymmetric structure, where the metal is essentially tetracoordinated by sulphur atoms with a fifth longer contact being observed owing to the binuclear nature of the complex in solid state. The acidity of this chelate was also calorimetrically explored in benzene solution in reactions with pyridine [78]. Furthermore, this chelate reacts with bipy and phen in organic solvents to produce the adduct, $Cd(S_2CNEt_2)_2 \cdot L$ (L = bipy, phen), as observed for other similar chelates [81,82]. Crystal structure determinations for both adducts show their monomeric nature with the metal hexacoordinated by four sulphur atoms from chelating dithiocarbamate groups, plus two nitrogen atoms from the added ligands in a distorted octahedral geometry [83].

The strong tendency for sulphur atoms in (dialkyldithiocarbamato)mercury(II) compounds to bridge the metal atoms and thus increase the coordination number was pointed out in an interesting review [84]. For example, in the α- and β-bis(diethyldithiocarbamato) complexes, the former [85] has a dimeric structure with one of the four sulphur atoms bonded to each metal, giving rise to a coordination number of five, while in the β-compound, all ligands are bridging, leading to a chain polymer with the metal centred in an octahedral site [86]. The Lewis acidity of these chelates was not cited [84]. However, the reaction of bischelate with phen in an organic solvent leads to an adduct whose crystal structure determination shows that the metal is asymmetrically bonded to both diethyldithiocarbamate ligands, plus both heteroatom of phen in a strongly distorted geometry [87].

(ii) Thermochemistry of chelates

The standard molar enthalpy of formation of zinc chelate was determined at 298.15 K, based on the general reaction [74]

$$ZnCl_2(c) + 2[NH_2Et_2][S_2CNEt_2](c) = Zn(S_2CNEt_2)_2(c) + 2NH_2Et_2Cl(c) \quad \Delta_r H^\circ_m$$

For this determination, the following sequence of reactions was performed calorimetrically.

$$ZnCl_2(c) + \text{acetone} = \text{soln. A} \quad \Delta_1 H^\circ_m$$

$$\text{soln. A} + 2[NH_2Et_2][S_2CNEt_2](c) = \text{soln. B} \quad \Delta_2 H^\circ_m$$

$$2NH_2Et_2Cl(c) + \text{acetone} = \text{soln. C} \quad \Delta_3 H^\circ_m$$

$$\text{soln. C} + Zn(S_2CNEt_2)_2(c) = \text{soln. D} \quad \Delta_4 H^\circ_m$$

$$\text{soln. B} = \text{soln. D} \quad \Delta_5 H^\circ_m$$

From the standard molar enthalpy values for each stage of the thermodynamic cycle, $\Delta_r H^\circ_m = -96.21 \pm 0.53$ kJ mol^{-1} was obtained. From the enthalpy of formation of diethylammonium chloride obtained by dissolving the salt in basic medium [88]

$$NH_2Et_2Cl(c) + OH^-(aq) = NHEt_2(l) + H_2O(l) + Cl^-(aq)$$

which gave $\Delta_f H^\circ_m$ (NH_2Et_2Cl,c) $= -359.73 \pm 1.22$ kJ mol^{-1}, the standard molar enthalpy of formation of the solid chelate was determined to be -289.65 ± 4.9 kJ mol^{-1}. Using the transpiration method of sublimation of the chelate, $\Delta^g_c H^\circ_m = 142.7 \pm 2.5$ kJ mol^{-1} [89], and the standard molar enthalpy of formation of the chelate in the gas state, $\Delta_f H^\circ_m$ [$Zn(S_2CNEt_2)_2$,g] $= -147.0 \pm 5.0$ kJ mol^{-1}.

The homolytic or heterolytic breakages of the zinc–sulphur bond in the chelate in the gaseous phase were also calculated, neglecting the reorganization energy associated with the ligand upon complexation and assuming the equivalence of four zinc–sulphur bonds. Taking into account the recent $\Delta_f H^\circ_m$ [$HS_2CN(C_2H_5)_2$,g] $= 33.2 \pm 3.8$ kJ mol^{-1} value [90] and by using the auxiliary data, D(S–H) $= 385 \pm 4$ [90] and $\Delta_f H^\circ_m$ (H,g) $= 218.00 \pm 0.01$ kJ mol^{-1} [74], the enthalpy of formation of the radical $\Delta_f H^\circ_m$ [$S_2CN(C_2H_5)$,g] $= 200.2 \pm 5.5$ kJ mol^{-1} was recalculated. From these values, the mean zinc–sulphur bond enthalpy, $\bar{D}$(Zn–S) $= \Delta_f H^\circ_m$ [$Zn(S_2CNEt_2)_2$,g]/4 gave 170 ± 3 kJ mol^{-1}.

The standard enthalpies of formation of crystalline $M(S_2CNH_2)_2$ chelates are -190 and -145 kJ mol^{-1} for zinc and cadmium, respectively [91]. Assuming that the enthalpy of sublimation of both chelates is 115 ± 15 kJ mol^{-1} [92] and using the above auxiliary data, the enthalpy of formation of the ligand in the gaseous phase was estimated by the group additivity method as $\Delta_f H^\circ_m$ [(HS_2CNH_2),g] $=$ 87.2 kJ mol^{-1}. Consequently, the mean metal–sulphur enthalpies of 178 and 164 kJ mol^{-1} were recalculated for zinc and cadmium, respectively. These values are listed in Table 8.

The standard enthalpy of formation of bis(diethyldithiocarbamato)nickel(II) and copper(II) complexes were first determined, through ligand replacement reactions where the pentane-2,4-dionato group is replaced by the diethyldithiocarbamato

TABLE 8

Standard molar enthalpies for dithio- and diethyldithiocarbamate chelates (kJ mol^{-1}), and mean metal–sulphur bond distance (pm)

Chelate	$\Delta_r H_m^\circ$	$\Delta_r H_m^\circ$ (c)	$\Delta_c^g H_m^\circ$	$\Delta_f H_m^\circ$ (g)	$\bar{D}$(M–S)	$\bar{d}$(M–S)
$Zn(S_2CNH_2)$	−49.2[a]	−190.4	115 ± 15	−75	178	–
$Cd(S_2CNH_2)$	−83.6[a]	−144.9	115 ± 15	−30	164	–
$Ni(S_2CNEt_2)$	116.54 ± 0.76[b]	−233.8 ± 3.6	157.3 ± 6	−76.5 ± 5.0	227 ± 3	220
$Cu(S_2CNEt_2)_2$	84.42 ± 0.63[c]	−170.2 ± 3.6	162.6 ± 5	−7.6 ± 5.0	187 ± 3	231
$Zn(S_2CNEt_2)_2$	−96.21 ± 0.53[d]	−289.7 ± 4.9	142.7 ± 2.5[e]	−147.0 ± 5.0	170 ± 3	240

[a] Enthalpy of precipitation [91].
[b] Ref. 94.
[c] Ref. 93.
[d] Ref. 74.
[e] Ref. 89.

group, by using reaction–solution calorimetry [92]. From these thermochemical data, mean metal–sulphur bond enthalpies of 193 ± 13 and 143 ± 13 kJ mol^{-1} were obtained for nickel and copper, respectively. Using a new series of auxiliary data, the values 175 ± 18 and 123 ± 17 kJ mol^{-1} were recalculated for the same sequence of metals [6]. Two years later, we again recalculated these values as 245 ± 4 and 202 ± 4 kJ mol^{-1}, respectively [74].

The variation of $\bar{D}$(M–S) values illustrates that these determinations depend not only on the experimental thermochemical results but also, upon the auxiliary data, which refer mainly to the ligands. Thus, the accuracy of these calculations is dependent on the set of auxiliary data, especially on the enthalpy of sublimation of the chelate and the standard enthalpy of formation of the dithionic acid, and consequently the corresponding enthalpy of the radical in the gaseous phase. For example, more precise $\bar{D}$(M–S) values were recently determined for the same series of chelates by using a redetermined set of thermochemical auxiliary data. Thus, $\bar{D}$(M–S) changed to 227 ± 2 and 187 ± 3 kJ mol^{-1}, for nickel and copper(II), respectively [93,94]. These values are also added in Table 8.

The previously determined standard molar enthalpy of formation of solid $Zn(S_2CNEt_2)_2$ [74] and the following ligand replacement reaction in acetone as calorimetric solvent

$$Zn(acac)_2(c) + 2[NH_2Et_2][S_2CNEt_2](c)$$
$$= Zn(S_2CNEt_2)_2(c) + 2acacH(l) + 2Et_2NH(l) \qquad \Delta_r H_m^\circ$$

were used as the basis for thermochemical measurements. From $\Delta_r H_m^\circ = +(49.46 \pm 1.05)$ kJ mol^{-1} and the enthalpy of sublimation of the chelate 117 ± 3 kJ mol^{-1}, the standard molar enthalpy of the solid and gas chelate were

calculated to be -894.89 ± 6.88 and 777.9 ± 7.5 kJ mol^{-1}, respectively. These data yield $\bar{D}$(Zn–O) = 136 ± 11 kJ mol^{-1} [95].

Three other determinations of $\bar{D}$(Zn–O) should be mentioned here: (i) from an available $\Delta_r H^\circ_m$ value and an estimated $\Delta^g_c H^\circ_m = 45$ kJ mol^{-1}, $\bar{D}$(Zn–O) = 138 ± 4 kJ mol^{-1} [6]; (ii) the authors of this publication also used another estimate, $\Delta^g_c H^\circ_m = 90 \pm 10$ kJ mol^{-1}, which gave $\bar{D}$(Zn–O) = 155 ± 10 kJ mol^{-1} [96]; and (iii) in a more recent publication, $\Delta^g_c H^\circ_m = 136.6 \pm 8.3$ kJ mol^{-1}was used, which gave $\bar{D}$(Zn–O) = 139 ± 10 kJ mol^{-1} [97]. The discrepancy between these two last values was attributed to the preparation of the starting materials since the hygroscopicity of $ZnCl_2$ could affect the $\Delta_r H^\circ_m$ determination [97]. However, the sources of these differences could also be due to the auxiliary data used to calculate $\Delta_r H^\circ_m$ and other thermochemical data, such as the enthalpy of sublimation of the chelate, needed to derive the standard molar enthalpy of formation of the gaseous compound. Although our experimental calorimetric procedure was done by ligand replacement reaction, our $\bar{D}$(Zn–O) value is in good agreement with the recent determination [97].

The thermochemistry of dialkyldithiocarbamates with phosphorus group elements was based on determinations of the standard molar enthalpy of formation of chelates by means of reaction–solution calorimetry in acetone, which can be expressed in terms of the general reaction

$$ECl_3(l,c) + 3[NH_2R_2][S_2CNR_2](c) = E(S_2CNR_2)_3(c) + 3[NH_2R_2]Cl(c) \qquad \Delta_r H^\circ_m$$

where E represents the elements P, As, Sb and Bi, and R the ethyl or *n*-butyl radicals. $\Delta_r H^\circ_m$ values for these two series of chelates are listed in Table 9 with other standard molar enthalpies [98–100]. Using $\Delta_f H^\circ_m$ [$HS_2CN(C_2H_5)_2$,g] = -33.2 ± 3.8 kJ mol^{-1} [90], the standard molar enthalpy of di-*n*-butyldithiocarbamic acid was recalculated as -49.1 ± 3.8 kJ mol^{-1} by using the group additivity method [100]. The standard enthalpy of formation of the radical, 117.9 ± 5.5 kJ mol^{-1}, was obtained by using the same auxiliary data as before [74,90].

TABLE 9

Standard molar enthalpies for diethyl- and di-*n*-butyldithiocarbamate chelates (kJ mol^{-1}), and mean element–sulphur bond distance (pm)

Chelate	$\Delta_r H^\circ_m$	$\Delta_f H^\circ_m$ (c)	$\Delta^g_c H^\circ_m$	$\Delta_f H^\circ_m$ (g)	$\bar{D}$(E–S)	$\bar{d}$(E–S)
$P(S_2CNEt_2)_3$	-317.28 ± 2.22	-304.5 ± 7.6	143 ± 2	-161.5 ± 7.8	179.5 ± 3.0	257
$As(S_2CNEt_2)_3$	-132.16 ± 0.44	-104.5 ± 7.6	124 ± 3	19.7 ± 8.2	147.2 ± 3.1	260
$Sb(S_2CNEt_2)_3$	-112.08 ± 0.55	-161.8 ± 7.3	160 ± 2	-1.8 ± 7.5	144.1 ± 3.0	275
$Bi(S_2CNEt_2)_3$	-137.01 ± 0.99	-183.6 ± 7.3	213 ± 3	29.4 ± 7.9	129.7 ± 3.0	282
$P(S_2CNBu_2)_3$	-359.24 ± 5.45	-705.5 ± 7.3	136 ± 3	-569.5 ± 7.9	206.3 ± 3.1	257
$As(S_2CNBu_2)_3$	-111.51 ± 0.59	-443.1 ± 5.4	128 ± 3	-315.1 ± 6.2	161.8 ± 2.9	260
$Sb(S_2CNBu_2)_3$	-117.40 ± 1.21	-526.2 ± 2.5	179 ± 3	-347.2 ± 3.9	160.5 ± 2.8	276
$Bi(S_2CNBu_2)_3$	-125.00 ± 2.45	-530.7 ± 5.5	202 ± 3	-328.7 ± 6.3	148.3 ± 2.9	280

Attempts to sublime these chelates were unsuccessful; therefore the respective standard enthalpies of sublimation were determined by using the same procedure described in the adducts section. From DSC curves, the enthalpies of fusion, and solid and liquid heat capacities were obtained [100]. The standard enthalpies of vaporization were estimated by empirical methods and heat capacities for the gaseous phase by the generalized vibrational assignment method [43,44]. These values are also listed in Table 9 together with the mean element–sulphur bond enthalpies determined from the standard molar enthalpies of formation of chelates in the gaseous phase.

The main C–S stretching frequency of dialkyldithiocarbamate adducts normally appeared as a doublet. The separation of less than 20 cm^{-1} indicates an anisobidentate ligand with the two sulphur atoms bonding to the element with different distances [101,102]. This conclusion was confirmed by X-ray determinations of the chelates [103].

(iii) Some rationalization of the thermochemical data

The main standard molar enthalpies for dithio and diethyldithiocarbamate chelates are summarized in Table 9. The large values found for $\bar{D}$(Cu–S) and $\bar{D}$(Ni–S) suggest that the ethyl groups attached to the dithiocarbamate moiety contribute an additional increment to the $\bar{D}$(M–S) value, which could be interpreted as an inductive effect of this group. However, zinc complexes do not show this tendency and from these results it is inconclusive that the inductive effect is responsible for an effective contribution to the thermochemical values.

The metal–sulphur bond distances listed in Table 9 are the mean values, as a consequence of the anisobidentate behaviour of these ligands [102]. Another feature is that diethyldithiocarbamate chelates have a tendency to form a weak five-coordinate bonding with the central atom [75,77]. Assuming four-coordination for metal in chelates in the gaseous phase, the increasing metal–sulphur bond distances of 220 [70], 231 [70] and 240 pm [75] for nickel, copper and zinc complexes, respectively, is accompanied by a decrease in $\bar{D}$(M–S) values. It is worth comparing these data with those obtained with the phosphorus group elements which are listed in Table 9. The element–sulphur bond distances, derived from crystallographic determinations, are presented in Table 9 as mean distances. These values correlate with the mean element–sulphur bond enthalpies. The mean element–sulphur bond distances in di-*n*-butyldithiocarbamate complexes obtained by X-ray diffraction measurements are 276 and 280 pm for antimony and bismuth [100], which are very close to those of the corresponding compounds with diethyldithiocarbamate, i.e. 275 and 282 pm [98]. Since X-ray data are not available for phosphorus–sulphur and arsenic–sulphur in the diethyldithiocarbamate series, the same values as the equivalent complexes of di-*n*-butyldithiocarbamate were assumed. A graphic representation of the mean bond

enthalpy against the mean bond distance in Fig. 4 illustrates the behaviour of both thermochemical series of chelates [100].

From a simple bond-theory approach, one would expect the participation of d orbitals in bonds involving non-metals [104]. In this case, the formation of π bonds through the overlap of d orbitals of element and sulphur can explain the differences in enthalpies of E–S bonds. The higher $\bar{D}$(P–S) values found in both series suggested a strengthening via π bonding as a consequence of a better overlap of the d orbitals [105]. In going down the group, the diffuse d orbitals will overlap less, resulting in a larger distance and consequently, a lower mean element–sulphur bond enthalpy. The same sort of arguments can be applied with the hard/soft acid and base principle. The soft sulphur atom will form stronger π bonding with the softer acids, which decrease from phosphorus to bismuth [49]. Finally, the higher thermochemical result, about 15%, found with di-*n*-butyldithiocarbamate might be associated with the larger inductive effect of the di-*n*-butyl radicals, which overcame any possible steric effect [100].

The thermochemical data for the two series of dialkyldithiocarbamates involving copper [93] and nickel [94] chelates demonstrate a similar behaviour for the $\bar{D}$(M–S) variation as a function of the alkyl group attached to the nitrogen of the thioamide group. The increase in $\bar{D}$(M–S) in each series shows a dependency on the

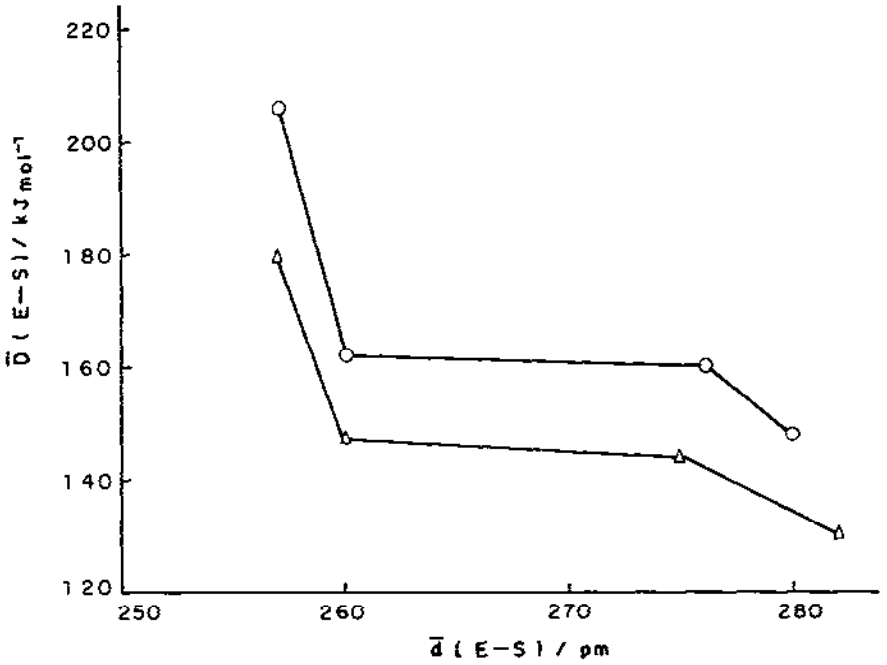

Fig. 4. A plot of the mean element–sulphur bond enthalpy $\bar{D}$(E–S) against mean element–sulphur distance for di-*n*-butyl (○) and diethyldithiocarbamato complexes (△). E = P, As, Sb, and Bi.

substitution of the normal chain from ethyl, *n*-propyl and *n*-butyl groups. This behaviour was interpreted as a mesomeric effect of the $-NR_2$ groups [93,94]. For copper and nickel diethyldithiocarbamate chelates, the $\bar{D}$(M–S) values are 187 ± 3 and 227 ± 2 kJ mol^{-1}, respectively. These values differ from the previous determinations, where a ligand-exchange procedure was used to determine $\Delta_r H^\circ_m$. In this kind of reaction [92], it is difficult to ensure a complete exchange and erroneous results can occur. In addition, this discrepancy is also affected by several quantities, including some estimated values.

$\bar{D}$(Ni–S) values are always higher than the corresponding copper values for both series of chelates. Taking into account the known metal–sulphur bond distance for diethyldithiocarbamate, 220 and 231 pm, for nickel and copper, respectively, the authors observed agreement between $\bar{D}$(M–S) and the respective bond distance [93,94]. This correlation was also previously observed for nickel, copper and zinc complexes [74] and also for phosphorus group elements [100].

G. HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

(i) Homogeneous systems

Complexes of lanthanide(III) perchlorate with the polar neutral molecule dma, $Ln(ClO_4)_3 \cdot n$dma ($n = 8$ for La to Nd, $n = 7$ for Sm to Er and $n = 6$ for Tm to Ln) [106] dissolve easily in the presence of excess ligand to form a homogeneous solution. Taking advantage of the high degree of solubility and the low coordinative power of this anion, the cations were titrated with other anions which were also dissolved in the same solvent. Cationic and neutral species were qualitatively detected through conductometric and spectrophotometric titrations, as expressed by the successive equilibria [107,108]

$$Ln^{3+} + X^- \rightleftharpoons LnX^{2+} \quad (1)$$

$$LnX^{2+} + X^- \rightleftharpoons LnX_2^+ \quad (2)$$

$$LnX_2^+ + X^- \rightleftharpoons LnX_3 \quad (3)$$

where $X^- = Cl$, Br, NO_3 and SCN.

Chloride cationic species were detected by calorimetric titration of lanthanide(III) of all elements of the series. For these equilibria, K_1 and K_2 and the respective $\Delta_1 H^\circ$ and $\Delta_2 H^\circ$ values were calculated for eqns. (1) and (2), respectively [109]. The values show a break at gadolinium; the endothermic enthalpy change and the equilibrium constants presented a consistent behaviour for the first step of complexation, showing a tendency to decrease from lanthanum to gadolinium and after this point they increased until lutecium. The $P(M)$ function, which is related to the electronic configuration of the cations, correlates with both K and ΔH values for the

lanthanide series. The break at gadolinium in this system is better interpreted by means of $P(M)$ values [110,111].

The cationic species of lanthanum(III) and neodymium(III) with chloride, bromide and iodide show a different stability order for 1:1 species, being $Cl^- > Br^- > NO_3^-$ for La^{3+} and $Br^- > Cl^- > NO_3^-$ for Nd^{3+}. The order $NO_3^- > Br^- > Cl^-$ was observed for the respective variation of endothermic enthalpies for La^{3+} complexes (48.2 ± 0.2, 32.6 ± 0.2 and 26.1 ± 0.1 kJ mol^{-1}) and the order $Br^- > Cl^- > NO_3^-$ for Nd^{3+} species (33.6 ± 0.2, 24.1 ± 0.1 and 15.0 ± 0.1 kJ mol^{-1}) [112]. Based on the degree of solvation [113], calculations of other thermochemical values [114], Prue's model of ion-pair contact inner sphere model [115], the hypersensitive bands [116] and X-ray diffraction data for solution [117], it was proposed that the anions in solution complex the cations to form predominantly inner sphere species.

Another homogeneous system studied by calorimetric titration was a series of SbX_3 (X = Cl, Br, I) complexes in 1,2-dichloroethane, which is considered to be a poor solvating solvent [118]. The ligands dmf, dma and tmu were incrementally added to SbX_3 and the K and ΔH values for the mono and bis adducts equilibria were determined. In these reactions, the Lewis acid nature of the halides is reflected by the increase in coordination number of the metal through the formation of a σ ligand–metal bond. The strain caused by the lone pair on the metal results in a highly distorted geometry, which was confirmed by structural determinations of the isolated adducts [119,120].

Based on the exothermic $\Delta_f H^\circ$ values for tmu adducts, the acidity order is $SbCl_3 > SbBr_3 > SbI_3$ (-58.7 ± 0.1, -42.8 ± 0.2 and -33.5 ± 0.2 kJ mol^{-1}, respectively). Also, the basicity order tmu > dma > dmf is clearly represented by the adducts of $SbCl_3$: -58.7 ± 0.1, -36.4 ± 0.1 and -26.8 ± 0.1 kJ mol^{-1}, respectively. This sequence also correlates with the donor number of these bases [37].

(ii) Heterogeneous systems

In heterogeneous systems where at least one component is insoluble, the existence of a solid phase which participates in the reaction does not disturb the calorimetric titration. For example, insoluble silica gel in 1,2-dichloroethane was calorimetrically titrated with acetonitrile, acetone, dmf, dma and py [121]. During this process, the organic bases in solution were adsorbed on the solid/liquid interface. Thus, the bases displace the solvent on the surface and the silanol groups act as acid centres, forming typical hydrogen bonds [122] with the basic centres of the solute. This heterogeneous equilibrium can be written

$$\text{adsorbed} - \text{solvent} + \text{base} - \text{solvent} \rightleftharpoons \text{adsorbed} - \text{base} - \text{solvent} + \text{solvent}$$

To calculate the variation of enthalpy for the acid–base interaction from the net calorimetric curve, the amount of solute which was adsorbed on the surface was

determined by chromatography. The net isotherm was fitted to a modified Langmuir equation [123,124], and the enthalpy obtained by the expression

$$\frac{N}{Q} = \frac{1}{Q_m(K_e - 1)} + \frac{1}{Q_m}N$$

where N is the mole fraction of the solute in solution, Q is the enthalpy of adsorption per unit mass of adsorbed material, Q_m is the integral enthalpy of the adsorption of the solute in the monolayer of one gram of adsorbent and K_e is a proportionality factor. From K_e and ΔH, the other thermodynamic parameters, ΔG and ΔS, were also calculated. The ΔH and log K_e values displayed parallel behaviour and increased from acetonitrile to pyridine. The ΔH values represent the strength of acid–base interactions on formation of hydrogen bonds [125]. Taking silica gel as a standard acid, the sequence of bases (ΔH/kJ mol^{-1}) gives the basicity order, py (−7.09) > dma (−5.84) > dmf (−2.25) > acetone (−1.29) > acetonitrile (−1.28). The enthalpy data also correlate with the donor number of these bases [37].

The reaction of surface silanols of silica gel with active molecules leads to a new surface with covalently attached organofunctional groups [126–129], as shown in Fig. 5. The immobilized molecules completely change the original characteristics of the surface and have properties of interest in various fields of research [126–129]. From the point of view of coordination, this surface is prone to extract cations from solutions, depending on the basic centre of the anchored groups [130–133]. The complexing agent property of many surfaces has been used in analytical applications [134–137], and an interesting application is related to the removal, separation and cation-binding properties of silica gel-bonded macrocycle system [138–142].

The nitrogen bases, ethylenediamine (en) [143], *ortho*- (opy) [144], *meta*- (mpy) [145] and *para*-aminopyridine (ppy) [145] and acetylhydrazine (acy) [146] (see Fig. 5), covalently bonded to silica gel, can extract divalent cations of the first transition series from acetone and ethanol solutions. Taking advantage of this behavi-

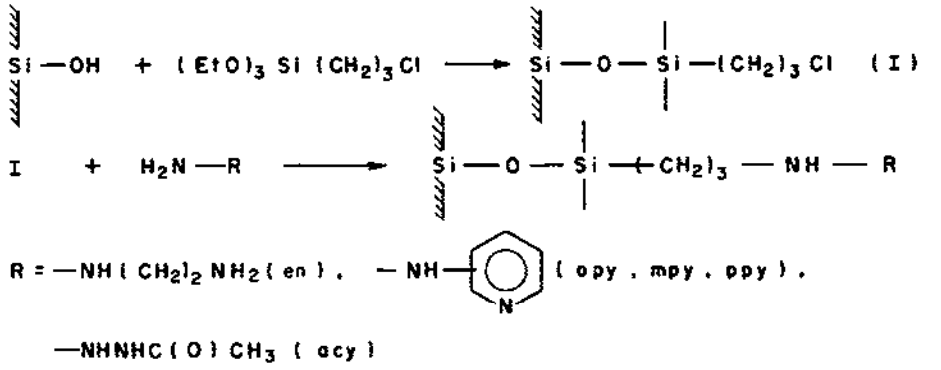

Fig. 5. Reaction of surface silanols of silica gel-bound ethylenediamine (en), *orthyo*- (opy), *meta*- (mpy), *para*-aminopyridine (ppy) and acethylhydrazine (acy).

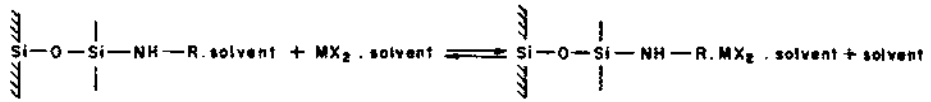

Fig. 6. A general representation of cation adsorption in solution.

our, a suspension of these surfaces was calorimetrically titrated in both solvents with cations dissolved in the same solvent as the adsorbate [121]. A general equilibrium representation for this adsorption is schematized in Fig. 6.

The results of calorimetric determinations are summarized in Table 10.

Based on the few systems studied and others in progress, some general considerations can be inferred. The K_e values and the calculated ΔG data give evidence of a favourable complexation reaction in both media and the variation of enthalpy seems to be a good thermochemical datum to express the energetics of these interactions. ΔH values are always exothermic in ethanol. With Zn(II) well-established behaviour was observed in enthanol solution with a pronounced exothermicity, which changed to an endothermic process in acetone medium. ΔH values in ethanol are always

TABLE 10

Thermodynamic values for cation–surface interactions at 298 K

Metal(II)	Anchored molecule	Solvent	ln K_e	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Co	en	Acetone	14.4	-6.1 ± 0.1	-35.7 ± 0.8	99 ± 3
	opy	Acetone	11.3	-29.4 ± 0.6	-28.0 ± 0.6	-5 ± 1
	opy	Ethanol	10.1	-33.7 ± 0.7	-25.0 ± 0.5	-29 ± 1
	mpy	Ethanol	11.1	$-10.3 + 0.2$	-21.8 ± 0.4	39 ± 1
	ppy	Acetone	10.2	-8.1 ± 0.2	-25.3 ± 0.5	58 ± 1
	ppy	Ethanol	11.6	-13.2 ± 0.3	-28.7 ± 0.6	52 ± 1
	acy	Acetone	15.0	5.4 ± 0.2	-37.1 ± 0.6	142 ± 1
Ni	ppy	Ethanol	9.8	-15.8 ± 0.3	-24.3 ± 0.5	29 ± 1
Cu	en	Acetone	12.4	-49.8 ± 1.0	-30.7 ± 0.6	-64 ± 5
	en	Ethanol	10.7	-35.7 ± 0.7	-26.5 ± 0.5	-30 ± 4
	mpy	Acetone	11.1	2.4 ± 0.1	-27.5 ± 0.6	100 ± 1
	mpy	Ethanol	10.9	-32.6 ± 0.7	-27.1 ± 0.5	-18 ± 1
	ppy	Acetone	10.9	7.5 ± 0.2	-27.0 ± 0.5	116 ± 1
	ppy	Ethanol	11.7	-50.5 ± 1.0	-29.0 ± 6.6	-72 ± 1
	acy	Acetone	14.5	-6.2 ± 0.3	-35.9 ± 0.6	100 ± 1
Zn	en	Acetone	12.3	8.8 ± 0.1	-30.5 ± 0.6	132 ± 2
	opy	Ethanol	8.3	-25.1 ± 0.5	-20.6 ± 0.4	-15 ± 1
	mpy	Ethanol	11.2	-40.9 ± 0.1	-27.8 ± 0.6	-44 ± 1
	ppy	Acetone	11.1	11.3 ± 0.2	-27.5 ± 0.1	130 ± 1
	ppy	Ethanol	11.1	-9.7 ± 0.2	-27.5 ± 0.1	60 ± 1
	acy	Acetone	13.4	6.2 ± 0.2	-33.2 ± 0.2	132 ± 1

larger than the corresponding enthalpy values in acetone for a given cation-anchored support interaction. The only exception is the copper(II)-anchored ethylenediamine system [143].

With the exception of a missing mpy [145] result with Co(II) in acetone, the ΔH values for the other two immobilized aminopyridine isomers [144,145] with Co(II) and zinc(II) have been determined in ethanol. From these data, the opy enthalpy [144] change is clearly favourable for cobalt(II) as is mpy [145] for zinc(II). Although the lack of a complete series of values for copper(II) makes comparison difficult, this cation normally displays large exothermic ΔH values. Nevertheless, other features related to the surface could be considered. The tendency to retain the cation follows the sequence ppy > mpy > opy, which is the same order as the degree of functionalization [144]. The molecular density of the immobilized opy groups is nearly one fourth of that of ppy. During the interactive process involving the cation–base centres, the former surface is extremely favourable. For example, copper(II) in ethanol gave -33.7 ± 0.7 and -13.2 ± 0.3 kJ mol^{-1} for opy and ppy, respectively [144,145]. This behaviour is reasonable since both basic centres are available to coordinate the cations in the opy surface, while only the heterocyclic nitrogen is available in the ppy surface.

The solvated cation releases solvent molecules into solution on binding to the anchored molecules and an entropic factor should make a significant contribution to the metal–ligand bond formation on the surface. In this process, the cation desolvation disturbs the structured solvent around it, causing an entropic enhancement. ΔS values are more favourable in acetone than in the more polar ethanol, for the same cation and surface, which denotes that ethanol solvates the cations more strongly than acetone [145]. For example, copper(II) interacts with immobilized mpy giving ΔH values of $+2.4 \pm 0.1$ and -32.6 ± 0.7 kJ mol^{-1}; nevertheless, an inverse behaviour takes place with ΔS values: 100 ± 1 and -18 ± 1 J mol^{-1} K^{-1} for acetone and ethanol, respectively. These data indicate that the reaction is entropically favourable in the less solvating acetone.

In order to obtain data to support the hypothesis $\Delta_c^g H_m^\circ(\text{adduct}) = \Delta_{cd}^g H_m^\circ$ (ligand) [4], some thermochemical data were obtained in heterogeneous systems using classical and titrimetric calorimetry. The system chosen was the well-studied adducts formed between zinc chloride and dma [20] in 1,2-dichlorethane. Some reasonable assumptions suggest that the formation of adduct in poorly solvating solvents such as 1,2-dichloroethane, carbon tetrachloride, benzene, cyclohexane, etc., yields a variation in donor–acceptor enthalpy which could be close to that obtained in the gaseous phase [37,125,147,148]. In these interaction processes, the solvation enthalpy contributions should be minimized due to the compensation between products and reagent enthalpies of solvation.

From the solubility, $5.14 \pm 0.04 \times 10^{-4}$ mol dm^{-3}, and enthalpy of dissolution, -38.1 ± 6.8 kJ mol^{-1} of $ZnCl_2$ in dce, other thermochemical quantities were calcu-

TABLE 11

Enthalpy (kJ mol^{-1}), free energy (kJ mol^{-1}) and entropy (J K^{-1} mol^{-1}) calculated for the $ZnCl_2$–dma–dce system at 298.15 K

Process	ΔH_m°	ΔG_m°	ΔS_m°
$ZnCl_2(s) + dce(l) = ZnCl_2(sln)$	-38.1 ± 6.8	19.3	−193
$ZnCl_2(sln) + dma(sln) = ZnCl_2 \cdot dma(sln)$	11.7 ± 6.8	−19	100
$ZnCl_2(sln) + 2dma(sln) = ZnCl_2 \cdot 2dma(sln)$	-26.3 ± 1.0	–	–

lated for chloride and dma interactions in this solvent [149] based on eqns. (4) and (5) and the results are shown in Table 11.

$$ZnCl_2(sln) + dma(sln) \rightleftharpoons ZnCl_2 \cdot dma(sln) \quad (4)$$

$$ZnCl_2(sln) + 2dma(sln) \rightleftharpoons ZnCl_2 \cdot 2dma(sln) \quad (5)$$

The large exothermic enthalpy value for the halide dissolution indicated that 1,2-dichlorethane is not a poor solvating solvent for $ZnCl_2$. This enthalpic value is opposite to that obtained for $HgCl_2$ (13.4 kJ mol^{-1} [4]) under the same conditions, even though this chloride is much more soluble than zinc chloride. Furthermore, the large negative entropy of -193 J K^{-1} mol^{-1} indicates a strong solvation in this non-ionized solvent; in comparison, the entropy of dissolution of molecular iodine in the same solvent is -15.2 J K^{-1} mol^{-1} [150].

From the variation in enthalpies for donor–acceptor interactions displayed by eqn. (4) (11.7 ± 6.8 kJ mol^{-1}) and eqn. (5) (-26.3 ± 1.0 kJ mol^{-1}), it is easy to conclude that these values are not comparable with the equivalent enthalpies in gaseous phase processes. For example, the ΔH value for eqn. (5) differs strongly from the same process in the gaseous phase, calculated as -278 kJ mol^{-1} [20].

Another heterogeneous system studied is α-titanium hydrogen phosphate, which is composed of layered sheets of tetrahedral phosphate with 756 pm separation, and which undergoes insertion of neutral polar molecules by the spreading apart of the layers to accommodate the guest molecules [151,152]. The *n*-alkylamines intercalate into this crystalline compound as double-packed layers with two moles of amine per molecule of exchanger. The intercalated solid shows remarkable stability on heating and washing with water or other polar solvents [152].

The intercalation of primary amines (C_1 to C_4) into this lamellar compound was studied in water and in 1,2-dichloroethane (dce). The thermal effects and sheet separation caused by the entrance of the amines into the lamellae were followed by incremental calorimetric titrimetry and X-ray diffraction, respectively [153]. A proposed mechanism of intercalation is based on protonation of the amines (RNH_2), with the NH_2 groups interacting with the O_3P–OH groups of the matrix. The standard enthalpy of reaction for the following process was determined in the condensed phase:

$$O_3P{-}OH(c) + RNH_2(l) = O_3P{-}O^{-}{}^{+}H_3NR(c) \qquad \Delta_r H^\circ_m$$

This enthalpy value decreases in water and increases in dce with the number of carbons (n) of the amine with a very good correlation (r is the coefficient of correlation).

$$\Delta_r H^\circ_m = 2.551n - 52.66\ (H_2O) \qquad r = 0.9979$$

$$\Delta_r H^\circ_m = -2.479n - 53.14\ (\text{dce}) \qquad r = 0.9947$$

The same behaviour was also observed for the interlayer distance (d/pm) after n-alkylamine intercalation, which correlates with the number of carbon atoms present in the alkyl chain.

$$\Delta_r H^\circ_m = 1.302 \times 10^{-2} d - 66.78\ (H_2O) \qquad r = 0.9992$$

$$\Delta_r H^\circ_m = -1.233 \times 10^{-2} d - 39.99\ (\text{dce}) \qquad r = 0.9977$$

From the enthalpy data for this system, the contribution to the enthalpy change for each CH_2 group of the n-alkylamine chain and also the interlamellar distance in dce and water were found to be -2.67 and $+2.5\ kJ\ mol^{-1}$ or -1.24 and $+1.20\ kJ\ mol^{-1}/10^2$ pm, respectively. These data suggest a general behaviour which may be used to extrapolate $\Delta_r H^\circ_m$ values for n-alkylamines containing more than four carbon atoms [153].

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