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Standard enthalpy of formation of di-isobutyldithiocarbamate complexes of zinc-group elements and mean M–S bond-dissociation enthalpies

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Abstract

The standard enthalpies of formation of crystalline di-isobutyldithiocarbamate complexes of Zn, Cd and Hg(II) have been derived by solution calorimetry at 298.15 K, giving values −526.06 ± 3.30, −468.07 ± 3.23 and −310.15 ± 3.56 kJ mol^{-1}, respectively. The corresponding molar enthalpies of sublimation, 283 ± 2, 281 ± 2 and 247 ± 1 kJ mol^{-1}, were estimated by means of differential scanning calorimetry. From the standard molar enthalpies of formation of the gaseous chelates, −243 ± 4, −187 ± 4 and −63 ± 4 kJ mol^{-1}, the homolytic 137 ± 4, 118 ± 4 and 75 ± 4 kJ mol^{-1} and heterolytic 700 ± 4, 646 ± 4 and 682 ± 4 kJ mol^{-1} mean metal–sulphur bond enthalpies were calculated. The homolytic enthalpies decrease from zinc to mercury and depend on the nature of the radical attached to the nitrogen of the ligand.

INTRODUCTION

The main thrust of the field of investigation of dialkyldithiocarbamates was initially directed to the structural features of the complexes [1–3] and their large scale analytical applicability [4]. Today, thermochemical interest in these complexes has progressively increased. Reviews of the thermochemistry of dithiocarbamate complexes, including dithiocarbonates and dithiophosphates, have detailed such thermal properties as fusion, volatility, kinetics and mechanism of thermal decomposition, solution-reaction calorimetry and metal–sulphur bond dissociation enthalpy [5, 6].

The enthalpies of formation of chelates of di-*n*-propyl and di-*n*-butyldithiocarbamate of Zn(II), Cd(II) and Hg(II) in the solid state have

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been obtained by solution-reaction calorimetry [7,8]. From the thermochemical properties of these chelates in the gaseous phase, the enthapies of the metal–sulfur bonds have been derived [7,8].

This paper focuses on the thermochemical data for chelates of di-isobutyldithiocarbamate with a complete series of zinc-group elements. These results are compared with those for di-*n*-propyl and di-*n*-butyldithiocarbamate compounds [7,8] in order to help understand the effect of the length of the alkyl chain attached to the nitrogen of the ligand.

EXPERIMENTAL

Chemicals

Zinc(II), cadmium(II) and mercury(II) chlorides (Merck) were purified and dried in vacuo. Di-isobutylamine and carbon disulfide were purified and distilled at 412 and 319 K, respectively. The solvents used in all preparations were distilled and kept dry. Acetone was chosen as the calorimetric solvent due to its ability to dissolve the chlorides, salts and chelates.

Preparations

All operations involved in the preparations and purifications were carried out either in vacuo or in a dry-box in an atmosphere of dried nitrogen for air-sensitive compounds [7–9].

The salts of di-isobutylammonium chloride and di-isobutylammonium di-isobutyldithiocarbamate were synthesized. Their analyses and melting points were in complete agreement with their formulation and reported melting points [10,11].

Bis (di-isobutyldithiocarbamate) compounds of zinc, cadmium and mercury were prepared by slowly adding a solution of di-isobutylammonium di-isobutyldithiocarbamate in ethanol to a stirred solution of the metal chloride and ethanol in 1:2 molar proportions [12]. White (zinc and cadmium) and yellow (mercury) crystals were isolated, recrystallized from ethanol and dried in vacuo, with yields in the range 72–81%. Microanalyses for metal, carbon, hydrogen and nitrogen were within experimental error of the expected values from the established formulae.

Calorimetric measurements

An LKB 8700-1 isoperibolic precision calorimeter system with a strip-chart recorder was used for all solution-reaction measurements. Details of the operational procedure, calculation method and accuracy of the instrument are as described before [7, 13]. The air-sensitive compounds were handled in dried nitrogen to prepare the ampoules. The enthalpies of fusion, and the heat capacities of the solid and liquid forms of the chelates were determined in a Perkin-Elmer differential scanning calorimeter model DSC-7, purged with dry nitrogen [14]. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

Other measurements

The melting temperatures for all compounds were determined by means of a Quimis model 340 apparatus. Thermogravimetric curves were obtained using a Perkin-Elmer model TGA-7 thermobalance, at a heating rate of $10\,\mathrm{K\,min^{-1}}$ in a dry nitrogen stream in the temperature range 373–618 K. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer model 467 spectrophotometer, and mass spectra of the ligand and chelates on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV (about 1.12×10^{-17} J).

RESULTS AND DISCUSSION

The chelates of Zn, Cd and Hg showed narrow melting ranges, (389–391, 451–453 and 363–367 K, respectively), in good agreement with those reported [15–17]. The mode of co-ordination of the dialkyldithocarbamate and the small intervals of melting suggest the existence of very stable compounds. However, on cooling the melting sample and heating again the previous melting-point interval was not reproduced. Microanalytical data for ligand, chloride and chelates are listed in Table 1.

The main infrared bands associated with the NCS_2 moiety of the

TABLE 1

Mass percentage analyses (calculated values in parentheses) and C–N and C–S stretching wavenumbers (in $\mathrm{cm^{-1}}$)

Compound	M	C	H	N	ν(C–N)	ν(C–S)
$Zn(S_2CNBu^i_2)_2$	13.5 (13.7)	46.2 (45.5)	7.4 (7.6)	5.9 (5.9)	1487	972
$Cd(S_2CNBu^i_2)_2$	21.2 (21.5)	41.7 (41.5)	6.6 (6.9)	5.4 (5.4)	1471	978
$Hg(S_2CNBu^i_2)_2$		35.3 (35.4)	5.4 (5.9)	4.7 (4.6)	1469	971
$NH_2Bu^i_2S_2CNBu^i_2$		61.2 (61.0)	11.1 (11.4)	8.3 (8.3)	1455	969
$(NH_2Bu^i_2)Cl$ [a]				8.4 (8.4)		

[a] Cl, 21.0 (21.3)%.

co-ordination ligand are also listed in Table 1. The CN band assumes a double-band character which is reflected in the appearance of a stretching band shifted to higher frequency. For all complexes this band frequency is higher than that of the respective ligand. However, a decrease in the Cs stretching band is observed and an isolated band near $1000\,\mathrm{cm}^{-1}$ indicates that the ligand is bonded in a bidentate manner to the metal [18–21].

The mass spectra of dialkyldithiocarbamate complexes revealed the presence of the parent ions [22], which were observed for di-isobutyldithiocarbamate compounds with intensities of 24, 20 and 0.8% for zinc, cadmium and mercury, respectively. The cations (M) appeared in two other peaks for all chelates: $\mathrm{SMS_2CNBu^i_2}$ and $\mathrm{MS_2CNBu^i_2}$. The other peaks were derived from the ligand fragmentation, i.e. m/z 204 ($\mathrm{S_2CNBu^i_2}$), 172 ($\mathrm{SCNBu^i_2}$), 116 ($\mathrm{SCHNBu^i}$), 115 ($\mathrm{SCNBu^i}$) 84 ($\mathrm{CHNBu^i}$), 76 ($\mathrm{S_2C}$) 60 ($\mathrm{SCNH_2}$) and 57 ($\mathrm{Bu^i}$).

The thermogravimetric curves showed loss of mass after the melting temperature for all chelates [12]. With the exception of the residues left by the cadmium, the thermogravimetric curves resemble those of the ligand, which lost all mass in only one stage. This implies that the decomposition of the chelate occurred to a small extent in the final vaporization process. For zinc and mercury complexes, complete mass loss occurred in only one step in the ranges 493–603 and 508–558 K, respectively. The cadmium complex shows loss of all ligands plus a percentage of cadmium $[2(\mathrm{S_2CNBu^i_2}) + 0.5\mathrm{Cd}]$, which corresponds to 89% in the range 518–618 K, leaving a stable residue of 11% of the corresponding metal up to 618 K.

The standard molar enthalpy of reaction, $\Delta_r H_m^\ominus$, was obtained, at 298.15 K, from the reaction-solution enthalpies, $\Delta_i H_m^\ominus$, of each reagent and product dissolved sequentially in acetone as calorimetric solvent (Table 2) for the reaction [7, 8]

$$\mathrm{MCl_2(cf)} + 2(\mathrm{NH_2Bu^i_2})(\mathrm{S_2CNBu^i_2})(\mathrm{cr}) \rightarrow \mathrm{M(S_2CNBu^i_2)_2(cr)} + 2(\mathrm{NH_2Bu^i_2})\mathrm{Cl(cr)} \qquad \Delta_r H_m^\ominus \tag{1}$$

The $\Delta_r H_m^\ominus$ values were derived from these tabulated values by applying a convenient thermochemical cycle, the relevant data being listed in Table 3.

The standard molar enthalpies of formation of the crystalline chelates (Table 3) were determined from $\Delta_r H_m^\ominus$ and the standard molar enthalpies of formation of the metal chlorides [23], ligand [24] and ammonium chloride [10], using expression (2), for which data are listed in Table 4.

$$\Delta_f H_m^\ominus[\mathrm{M(S_2CNBu^i_2)_2(cr)}] = \Delta_r H_m^\ominus - 2\Delta_f \mathrm{H}_m^\ominus[(\mathrm{NH_2Bu^i_2})\mathrm{Cl(cr)}] + \Delta_f H_m^\ominus[\mathrm{MCl_2(cr)}] + 2\Delta_f H_m^\ominus[(\mathrm{NH_2Bu^i_2})(\mathrm{S_2CNBu^i_2})(\mathrm{cr})] \tag{2}$$

To determine the metal–sulfur bond enthalpy for these chelates, it is indispensable to have information about these complexes in the gas phase.

TABLE 2

Standard molar enthalpies (in kJ mol^{-1}) of solution and reaction at 298.15 K

i	Reactant	Solvent	Solution	Number of expts.	$\Delta_i H^\ominus_m$
01	$ZnCl_2(cr)$	Acetone	A_1	5	−53.69 ± 0.66
02	$2(NH_2Bu^i_2)(S_2CNBu^i_2)(cr)$	A_1	A_2	5	16.23 ± 0.59
03	$2(NH_2Bu^i_2)Cl(cr)$	Acetone	A_3	5	17.23 ± 0.76
04	$Zn(S_2CNBu^i_2)_2(cr)$	A_3	A_2	5	51.22 ± 0.83
05	$2(NH_2Bu^i_2)(S_2CNBu^i_2)(cr)$	Acetone	B_1	5	45.31 ± 0.50
06	$CdCl_2(cr)$	B_1	B_2	5	−84.45 ± 0.77
07	$2(NH_2Bu^i_2)Cl(cr)$	Acetone	B_3	5	16.43 ± 0.58
08	$Cd(S_2CNBu^i_2)_2(cr)$	B_3	B_2	5	15.90 ± 0.61
09	$HgCl_2(cr)$	Acetone	C_1	5	5.22 ± 0.01
10	$2(NH_2Bu^i_2)(S_2CNBu^i_2)(cr)$	C_1	C_2	5	−17.74 ± 0.54
11	$2(NH_2Bu^i_2)Cl(cr)$	Acetone	C_3	5	16.41 ± 1.02
12	$Hg(S_2CNBu^i_2)_2(cr)$	C_3	C_2	5	51.82 ± 1.60

All attempts to measure directly the thermochemical parameters for the compounds in the gaseous phase were unsuccessful due to the difficulty in subliming the chelates. For this purpose the standard molar enthalpies of sublimation, $\Delta^g_{cr}H^\ominus_m$, were determined by means of differential scanning calorimetry (DSC) and estimative methods [7, 8, 14, 25, 26]. The molar

TABLE 3

Standard molar enthalpies (in kJ mol^{-1}), heat capacities (in kJ mol^{-1} K^{-1}) and temperatures (in K) for the chelates

	$Zn(S_2CNBu^i_2)_2$	$Cd(S_2CNBu^i_2)_2$	$Hg(S_2CNBu^i_2)_2$
$\Delta_r H^\ominus_m$	−105.91 ± 1.43	−71.47 ± 1.24	80.75 ± 1.97
$\Delta_f H^\ominus_m(cr)$	−526.06 ± 3.30	−468.07 ± 3.23	−310.15 ± 3.56
$\Delta^l_{cr} H^\ominus_m$	33.69 ± 0.07	32.17 ± 0.79	29.48 ± 0.57
$\Delta^g_l H^\ominus_m$	59.44 ± 1.51	61.78 ± 1.18	62.10 ± 1.08
T_{fus}	385 ± 1	441 ± 1	364 ± 1
T_{vap}	577 ± 1	575 ± 1	541 ± 1
$C_{p,m}(cr)$	0.84 ± 0.03	1.01 ± 0.04	0.90 ± 0.01
$C_{p,m}(l)$	1.72 ± 0.02	1.90 ± 0.02	1.60 ± 0.01
$C_{p,m}(g)$	1.29 ± 0.21	1.24 ± 0.23	1.25 ± 0.21
$\Delta^g_{cr} H^\ominus_m$	283 ± 2	281 ± 2	247 ± 1
$\Delta_f H^\ominus_m(g)$	−243 ± 4	−187 ± 4	−63 ± 4
$\Delta_{ho} H^\ominus_m$	−549 ± 16	−474 ± 16	−299 ± 16
$\Delta_{he} H^\ominus_m$	−2800 ± 16	−2585 ± 16	−2728 ± 16
$\langle D \rangle$(M–S)	137 ± 4	118 ± 4	75 ± 4
$\langle D' \rangle$(M–S)	700 ± 4	646 ± 4	682 ± 4

TABLE 4

Auxiliary data (in kJ mol^{-1})

Compound	$\Delta_f H_m^\ominus$	Ref.
$ZnCl_2$(cr)	-415.05 ± 0.02	23
$CdCl_2$(cr)	-391.50 ± 0.22	23
$HgCl_2$(cr)	-224.30 ± 0.13	23
$(NH_2Bu^i_2)(S_2CNBu^i_2)$(cr)	-463.80 ± 1.40	24
$(NH_2Bu^i_2)Cl$(cr)	-461.07 ± 0.50	25
Zn(g)	130.73 ± 0.01	23
Cd(g)	120.01 ± 0.01	23
Hg(g)	61.30 ± 0.01	23
$Zn^{\pm2}$(g)	2782.78 ± 0.03	23
$Cd^{\pm2}$(g)	2623.54 ± 0.02	23
$Hg^{\pm2}$(g)	2890.47 ± 0.03	23
$^{\bullet}S_2CNBu^i_2$(g)	87.50 ± 7.60	30
$^{-}S_2CNBu^i_2$(g)	-112.9 ± 7.6	[a]

[a] This work (see text).

standard enthalpies of fusion, $\Delta_{cr}^{l} H_m^\ominus$, were obtained from the sharp peaks at 385, 441 and 364 K for zinc, cadmium and mercury chelates, respectively (Table 3). In these thermograms, the peaks due to vaporization at 577, 575 and 541 K for the same sequence of complexes were used to estimate these enthalpies, by means of the Giacolone [27], Riedel–Planck–Miller [27] and Watson [28] methods. Table 3 lists the mean value obtained for the three estimative methods. The heat capacities for the solid complexes in the temperature ranges 355–365, 365–375 and 345–355 K for zinc, cadmium and mercury, respectively, were determined [7, 8, 14, 25, 26]. However, for the gas phase these quantities were estimated by means of the eqn. (3) [28]

$$C_{p,m}(g) = -0.082 + 2.356 \times 10^{-3} T - 0.860 \times 10^{-6} T^2 \text{ (kJ mol}^{-1}) \qquad (3)$$

The values obtained are listed in Table 3, together with the standard molar enthalpies of sublimation, which were calculated by applying all these auxiliary data in the expression (4) [7, 8, 14, 25, 26]; consequently the standard molar enthalpies of formation in the gas phase, listed in Table 3, were calculated.

$$\Delta_{cr}^{g} H_m^\ominus(298\text{ K}) = \int_{298\text{ K}}^{T_{fus}} C_{p,m}(cr)\,dT + \Delta_{cr}^{l} H_m^\ominus(T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_{p,m}(l)\,dT + \Delta_{l}^{g} H_m^\ominus(T_{vap}) + \int_{298\text{ K}}^{T_{fus}} C_{p,m}(g)\,dT \qquad (4)$$

Assuming that the metal is co-ordinated in a bidentate manner by each ligand, the mean bond-dissociation enthalpies of the chelates are related to one fourth of the standard molar enthalpy of disruption in homolytic, $\Delta_{\mathrm{ho}}H_{\mathrm{m}}^{\ominus}$, or heterolytic, $\Delta_{\mathrm{he}}H_{\mathrm{m}}^{\ominus}$, reactions [7, 8, 14, 25, 26]; see eqns. (5) and (6), respectively.

$$\mathrm{M(g)} + 2{}^{\bullet}\mathrm{S_2CNBu^i_2(g)} \rightarrow \mathrm{M(S_2CNBu^i_2)_2(g)} \qquad \Delta_{\mathrm{ho}}H_{\mathrm{m}}^{\ominus} \tag{5}$$

$$\mathrm{M^{2+}(g)} + 2{}^{-}\mathrm{S_2CNBu^i_2(g)} \rightarrow \mathrm{M(S_2CNBu^i_2)_2(g)} \qquad \Delta_{\mathrm{he}}H_{\mathrm{m}}^{\ominus} \tag{6}$$

From the auxiliary data listed in Table 4, one can calculate the mean enthalpy of the metal–sulfur bond for homolytic, $\langle D\rangle(\mathrm{M{-}S}) = -\Delta_{\mathrm{ho}}H_{\mathrm{m}}^{\ominus}/4$ and for heterolytic, $\langle D'\rangle(\mathrm{M{-}S}) = -\Delta_{\mathrm{he}}H_{\mathrm{m}}^{\ominus}/4$ reactions. In these determinations the reorganization energy associated with the ligand upon complexation is neglected and an equivalence of all metal–sulfur bonds is assumed, even though, for these complexes, the metallic atoms are expected to be anisobidentately bonded by the sulfur atoms [19, 29].

The standard enthalpy of formation of the anion, $\mathrm{S_2CNBu^i_2(g)}$ (Table 4) was estimated by means of

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}[{}^{-}\mathrm{S_2CNBu^i_2(g)}] = E_{\mathrm{L}} + \Delta_f H_{\mathrm{m}}^{\ominus}(\mathrm{e^-}) + \Delta_f H_{\mathrm{m}}^{\ominus}[{}^{\bullet}\mathrm{S_2CNBu^i_2(g)}] \tag{7}$$

using auxiliary data of electron affinity (E_{L}) of a sulfur atom $-200.42 \pm 0.05\ \mathrm{kJ\ mol^{-1}}$ [9] and standard enthalpy of formation of the radical ${}^{\bullet}\mathrm{S_2CNBu^i_2(g)}$ [30] (Table 4).

The homolytic and heterolytic mean metal–sulfur bond enthalpies presented in Table 3 show that $\langle D\rangle(\mathrm{M{-}S})$ decreases from zinc to mercury while $\langle D'\rangle(\mathrm{M{-}S})$ remains almost constant, as observed before with chelates of di-*n*-propyl and di-*n*-butyldithiocarbamates [7, 8].

The series of thermochemical data for dialkyldithiocarbamates showed the $\langle D\rangle(\mathrm{M{-}S})$ values 182 ± 3, 154 ± 3 and $102 \pm 3\ \mathrm{kJ\ mol^{-1}}$ for di-*n*-propyl and 183 ± 3, 168 ± 3 and $105 \pm 3\ \mathrm{kJ\ mol^{-1}}$ for di-*n*-butyldithiocarbamates of zinc, cadmium and mercury, respectively [7, 8], are somewhat higher than the corresponding values for the di-isobutyldithiocarbamates. In the present case, the small values for the di-isobutyldithiocarbamates might be associated with the larger steric effect of the iso-butyl radicals.

In the absence of structural parameters it is not possible to confirm the correlation between $\langle D\rangle(\mathrm{M{-}S})$ and the mean-sulfur bond distance, as observed for the any dialkyldithiocarbamates of the phosphorus group chelates which also showed a decrease in the mean element–sulfur bond enthalpy from phosphorus to bismuth [14, 25, 26].

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REFERENCES

1 D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 233.
2 D. Coucouvanis, Prog. Inorg. Chem., 26 (1979) 301.
3 R. Eisenberg, Prog. Inorg. Chem., 12 (1970) 295.
4 R.J. Magee and J.O. Hill, Anal. Chem., 8 (1985) 5.
5 J.O. Hill and R. J. Magee, Rev. Inorg. Chem., 3 (1981) 141.
6 C. Airoldi and A.P. Chagas, Coord. Chem. Rev., 119 (1992) 29.
7 A.G. de Souza, J.H. Souza and C. Airoldi, J. Chem. Soc. Dalton Trans., (1991) 1751.
8 M.A.R.P. Carvalho, A.G. de Souza and C. Airoldi, J. Chem. Soc. Dalton Trans., (1992) 1235.
9 C. Airoldi, J. Chem. Soc. Dalton Trans., (1985) 369.
10 A.G. de Souza, C.D. Pinheiro and C. Airoldi, Polyhedron, 11 (1992) 371.
11 K.J. Cavell, J.O. Hill and R.J. Magee, J. Inorg. Nucl. Chem., 41 (1980) 1277.
12 M.L. Riekkola, Mikrochim. Acta, 1 (1982) 327.
13 R.A. Jorge, C. Airoldi and A.P. Chagas, J. Chem. Soc. Dalton Trans., (1978) 1102.
14 C. Airoldi and A.G. de Souza, J. Chem. Soc. Dalton Trans., (1987) 2955.
15 V. Gemmer-Colos and R. Neeb, Fresenius' Z. Anal. Chem., 293 (1978) 290.
16 A. Tavlaridis and R. Neeb, Fresenius' Z. Anal. Chem., 293 (1978) 211.
17 M.L. Riekkola and O.J. Makitie, J. Therm. Anal., 25 (1982) 89.
18 F. Bonati and R. Ugo, J. Organomet. Chem., 10 (1967) 257.
19 C.P. Sharma, N. Kumar, M.C. Khandpal, S. Chandra and V.G. Bhide, J. Inorg. Nucl. Chem., 43 (1981) 923.
20 C. Petri, G. Tosi and P. Zannini, J. Mol. Struct., 53 (1979) 35.
21 R. Kellner, G.S. Nikolov and N. Trendafilova, Inorg. Chim. Acta, 84 (1984) 233.
22 M.L. Riekkola, Acta Chem. Scand. Ser. A, 37 (1983) 691.
23 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.W. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
24 M.A.V. Ribeiro da Silva and A.M.V. Reis and G. Pilcher, J. Chem. Thermodyn., 19 (1987) 837.
25 A.G. de Souza and C. Airoldi, Thermochim. Acta, 130 (1988) 95.
26 C. Airoldi and A.G. de Souza, J. Chem. Thermodyn., 21 (1989) 283.
27 R.C. Reid and T.K. Sherwood, The Properties of Gases and Liquids, 2nd edn., McGraw-Hill, New York, 1968.
28 G.J. Janz, Thermodynamic Properties Organic Compounds, revised edn., Academic Press, New York, 1968.
29 M. Colapietro, A. Domenicano, L. Scaramuzza and A. Vaciago, J. Chem. Soc. Chem. Commun., (1968) 302.
30 M.A.V.R. da Silva, A.M.V. Reis and G. Pilcher, Thermochim. Acta, 124 (1988) 319.