Metal-sulphur Bond Enthalpy Determination of Di-*n*-Butyldithiocarbamate Chelates of Zinc, Cadmium and Mercury

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The standard molar enthalpies of formation of crystalline $[M(S_2CNBu^n{}_2)_2]$ (M = Zn, Cd or Hg), determined through reaction-solution calorimetry at 298.15 K, were found to be -471.23 ± 3.90, -440.74 ± 3.79 and -319.29 ± 3.38 kJ mol^{-1}, respectively. The corresponding molar enthalpies of sublimation, 107 ± 3, 123 ± 3 and 195 ± 3 kJ mol^{-1}, were estimated by means of differential scanning calorimetry. From the standard molar enthalpies of formation of the gaseous chelates, -364 ± 5, 318 ± 5 and -124 ± 5 kJ mol^{-1}, the homolytic and heterolytic mean metal–sulphur bond enthalpies were calculated. The homolytic enthalpies decrease from zinc to mercury, while the heterolytic values are almost constant.

Much attention in the field of analytical chemistry[1] has been devoted to the study of dialkyldithiocarbamates and their respective complexes with a wide variety of cations as well as to their extensive applications as fungicides, pesticides, vulcanization accelerators, flotation agents and high-pressure lubricants.[2] Owing to the practical importance of these dithioacid ligands, a series of preparative methods were developed: (*a*) addition of carbon disulphide to a Grignard reagent, (*b*) base-catalysed condensation of carbon disulphide with compounds containing active hydrogen, (*c*) reaction of carbon disulphide with aryl compounds in the presence of aluminium chloride and (*d*) reaction of aromatic aldehydes with ammonium or hydrogen persulphides.[2]

Several publications have dealt with the structural features of a wide variety of dithiocarbamate metal-ion complexes, involving bidentate co-ordination by both sulphur atoms of the ligand.[2] However, thermochemical studies of chelates containing sulphur-bonded ligands are scarce. The thermal properties of some metal dithiocarbamate complexes[3–5] together with the determination of the standard molar enthalpies of formation of zinc, cadmium and lead chelates, through reaction-solution calorimetry, were used to estimate the homolytic and heterolytic metal–sulphur bond enthalpies. The standard molar enthalpy of formation of diethyldithiocarbamate complexes of iron,[6] nickel,[7] copper[8] and zinc[9] have been determined from reaction-solution calorimetry. Excluding the iron chelate, where the mean iron–sulphur bond enthalpy was not determined, the other complexes showed that this parameter correlated very well with the mean metal–sulphur bond distance observed in the solid compound.[4]

Recently, an extension of the thermochemical study to nickel and copper complexes with five distinct dialkyldithiocarbamate ligands showed that the mean sulphur–metal bond enthalpies have a parallel behaviour for both series of complexes, which depends on the alkyl group attached to the nitrogen of the ligand.[10,11]

The thermochemical results for tris chelates of the phosphorus to bismuth group with diethyl and di-*n*-butyldithiocarbamates showed a regular decrease of the mean element–sulphur bond enthalpy from the first to the last element of the group. However, the larger mean phosphorus–sulphur bond enthalpy was attributed to a better overlap of d orbitals to form a π bond. Plots of the mean element–sulphur bond enthalpy against the mean element–sulphur bond distance displayed similar behaviour for both series of complexes, where higher thermochemical values for di-*n*-butyldithiocarbamate ligand were observed.[12–14]

The purpose of this publication is to report thermochemical results obtained for a complete series of zinc group elements with di-*n*-butyldithiocarbamate as ligand.

Experimental

Chemicals.—Zinc(II), cadmium(II) and mercury(II) chlorides (Merck) were purified and dried. Di-*n*-butylamine (Merck) was dried and purified by distillation at 438 K. All solvents used in preparations were distilled and kept dry.

Preparations.—Di-*n*-butylammonium chloride was prepared under anhydrous conditions by bubbling a stream of hydrogen chloride into a solution of di-*n*-butylamine in acetone.[14] The white solid was filtered off and dried *in vacuo*. Di-*n*-butylammonium di-*n*-butyldithiocarbamate was obtained from the reaction between an excess of carbon disulphide and di-*n*-butylamine in acetone solution cooled in an ice–salt bath.[15] The product was recrystallized in a diethyl ether–acetone mixture and then dried *in vacuo* giving 83% yield.

Bis(di-*n*-butyldithiocarbamates) of zinc, cadmium and mercury were prepared by adding dropwise an ethanolic solution of di-*n*-butylammonium di-*n*-butyldithiocarbamate to a stirred solution of the metal chloride in ethanol in 1:2 mol proportion, under anhydrous conditions.[16] The solids were filtered off, washed with ethanol and dried *in vacuo*, with yields in the range 80–87%. Microanalyses for metal, carbon, hydrogen and nitrogen were within the experimental errors of the expected values from the established empirical formulas.

Calorimetric Measurements.—An LKB 8700-1 isoperibolic precision calorimeter system with a strip-chart recorder was used for all reaction-solution measurements.[14] The salts and chelates were rigorously dried *in vacuo* before preparing the ampoules, which were handled in a dry-box for air-sensitive compounds. Ampoules containing 6–82 mg of substrate were broken into a glass reaction vessel, charged with 0.10 dm^3 of a suitable calorimetric solvent at 298.15 ± 0.02 K. The enthalpy of fusion and heat capacities of the solid and liquid forms of the chelates were determined with a DuPont model 910 differential scanning calorimeter, purged with dry nitrogen. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

Other Measurements.—Thermogravimetric curves were ob-

Table 1 Mass percentage analyses (calculated values in parentheses), melting temperatures and C–N and C–S stretching wavenumbers (cm^{-1})

	Analysis							
Compound	M	C	H	N	Cl	T/K	ν(C–N)	ν(C–S)
$[NH_2Bu^n{}_2][S_2CNBu^n{}_2]$		61.3 (61.1)	11.3 (11.4)	8.4 (8.3)		321–323	1472	968
$[NH_2Bu^n{}_2]Cl$				8.4 (8.4)	21.0 (21.4)	543–546	—	—
$[Zn(S_2CNBu^n{}_2)_2]$	13.5 (13.7)	45.2 (45.6)	7.4 (7.6)	5.9 (5.9)	—	380–381	1495	958
$[Cd(S_2CNBu^n{}_2)_2]$	21.3 (21.6)	41.5 (41.5)	6.7 (6.9)	5.6 (5.4)	—	406–407	1490	955
$[Hg(S_2CNBu^n{}_2)_2]$	32.6 (32.9)	35.4 (35.5)	5.6 (5.9)	4.5 (4.6)	—	348–349	1485	952

tained in a dynamic atmosphere of nitrogen, using a DuPont model 1090 thermobalance, with a heating rate of 5 °C min^{-1}.

A DuPont model 910 differential scanning calorimeter coupled to the thermoanalyser and with a programmed heat flow was used. Infrared spectra were recorded as Nujol and Fluorolube mulls on a Perkin-Elmer 337 spectrophotometer. A Finnigan 1015 S/L spectrometer was used to obtain the mass spectra of the ligand and chelates. The melting points of the compounds were measured by a Quimis apparatus.

Results and Discussion

The microanalytical results for the ligand, $[NH_2Bu^n{}_2]Cl$ and chelates are listed in Table 1, together with the melting points of the complexes. Sharp melting intervals were observed for all compounds which are in agreement with those in the literature,[14,15,17] except for the mercury chelate which was not previously reported.

The main infrared bands associated with the NCS_2 moiety of the co-ordinated ligand are also listed in Table 1. Co-ordination of this ligand increases the CN double-bond character which results in a shift of the CN stretching mode to higher frequency and a decrease in the CS stretching frequency, as observed in Table 1. Usually, the CS stretching mode appears as a doublet, with separation less than 20 cm^{-1}, since the two sulphur atoms are bonded to the metal with different distances, as shown by X-ray structure determinations.[18–21] For the complexes studied here, CS stretching frequencies were not resolved and although the crystal structures are not available the characteristic shifts of CN and CS bands indicate sulphur-bonded chelates.

The decomposition of the complexes above the melting temperatures was studied through thermogravimetry in the range 298–1073 K.[22] For the zinc compound, complete weight loss occurred in only one step in the range 493–622 K. This indicates that little decomposition took place in the final vaporization process. The cadmium chelate shows weight losses in two stages. In the first, 75% of its mass is lost in the range 543–638 K, which corresponds to $S_2CNBu^n{}_2$ plus $SCNBu^n{}_2$ fragments. In the second stage a loss of 5% in the range 938–1010 K is attributed to the loss of sulphur, leaving a stable residue of 22% of the corresponding metal up to 1013 K, in accord with the reaction $[Cd(S_2CNBu^n{}_2)_2] \longrightarrow CdS + Bu^n{}_2NC(S)S + Bu^n{}_2NCS$. A similar behaviour to that of the zinc chelate was observed for mercury where a mixture of fragments corresponding to 95% of the ligand was lost in the range 498–648 K.

All chelates showed the presence of the molecular parent ions[23] in the mass spectra, which were detected in relative intensities of 28.6, 4.4 and 1.8% for zinc, cadmium and mercury, respectively. Two other peaks involving the participation of metals, *i.e.* $[SMS_2CNBu^n{}_2]^{\bullet+}$ and $[MS_2CNBu^n{}_2]^{\bullet+}$ were also observed for all complexes. The general profiles of the fragments derived from the di-*n*-butyldithiocarbamate radical are the same for all chelates,[14] *i.e.* $[S_2CNBu^n{}_2]^{\bullet+}$, $[SCNBu^n{}_2]^{\bullet+}$, $[SCNBu^n{}_2]^{\bullet+}$, $[CNBu^n{}_2]^{\bullet+}$, $[NBu^n{}_2]^{\bullet+}$ and $[C_4H_9]^{\bullet+}$.

The standard molar enthalpies of formation of the crystalline chelates $[M(S_2CNBu^n{}_2)_2]$ (M = Zn, Cd or Hg) were determined by means of reaction (1).[12–14] The standard molar

$$MCl_2(cr) + 2[NH_2Bu^n{}_2][S_2CNBu^n{}_2](cr) \longrightarrow [M(S_2CNBu^n{}_2)_2](cr) + 2[NH_2Bu^n{}_2]Cl(cr);\ \Delta_r H_m^\circ \quad (1)$$

enthalpy of this reaction was obtained from the reaction-solution enthalpies, $\Delta_i H_m^\circ$, of each reagent and product dissolved sequentially in acetone as calorimetric solvent.

The standard molar enthalpy of reaction (1), $\Delta_r H_m^\circ$, can be obtained from the values collected in Table 2, since a rigorous control of the stoichiometry was maintained throughout each series of experiments in order that the final solutions, resulting from dissolution and reaction of reactants, were of the same composition as those from dissolution and reaction of the products.[12–14] The $\Delta_r H_m^\circ$ values derived from these experimental data are listed in Table 3. By applying these values in a convenient thermochemical cycle and by using the auxiliary data of Table 4, the enthalpy of formation, $\Delta_f H_m^\circ$, given in Table 3 for each chelate in crystalline form, was obtained by using expression (2).

$$\Delta_f H_m^\circ[M(S_2CNBu^n{}_2)_2, cr] = \Delta_r H_m^\circ - 2\Delta_f H_m^\circ[NH_2Bu^n{}_2Cl, cr] + \Delta_f H_m^\circ(MCl_2, cr) + 2\Delta_f H_m^\circ[NH_2Bu^n{}_2S_2CNBu^n{}_2, cr] \quad (2)$$

To determine the metal–sulphur bond enthalpy for these chelates, it is indispensable to have information about these compounds in the gas phase. For this purpose the standard molar enthalpy of sublimation, $\Delta_{cr}^{g} H_m^\circ$, was determined by means of differential scanning calorimetry (DSC) and estimative methods.[12–14]

The DSC curves for all chelates are very similar, exhibiting a sharp peak followed by a broad one. The former was attributed as a fusion at 382, 408 and 350 K for the zinc, cadmium and mercury compounds, respectively, from which were calculated the same standard molar enthalpies of fusion, $\Delta_{cr}^{l} H_m^\circ$. The second peaks showed a characteristic pseudo-vaporization profile. These peaks enabled the determination of the temperature of vaporization as 617, 591 and 551 K for the same sequence of compounds. From these temperatures the corresponding standard enthalpies were calculated by the methods of Giacolone,[26] Riedel–Planck–Miller [26] and Watson.[27] The heat capacities for the solid chelates in the temperature ranges 354–364, 405–415 and 363–373 K for zinc, cadmium and mercury, respectively, were determined. However, for the gas phase these quantities were estimated by means of the equation $C_{p,m}(g) = -0.082 + 1.983 \times 10^{-3}T - 1.065 \times 10^{-6}T^2$. All these values are listed in Table 3. From those data values of $\Delta_{cr}^{g} H_m^\circ$ were calculated for the complexes by means of expression (3), and

$$\Delta_{cr}^{g} H_m^\circ(298\ K) = \int_{298}^{T_{fus}} C_p(cr)dT + \Delta_{cr}^{l} H_m^\circ(T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_p(l)dT + \Delta_{l}^{g} H_m^\circ(T_{vap}) - \int_{298\ K}^{T_{vap}} C_p(g)dT \quad (3)$$

consequently the standard molar enthalpies of formation[12–14] shown in Table 3 were calculated using auxiliary data[14,24,25] listed in Table 4.

Table 2 Standard molar enthalpies (kJ mol^{-1}) of solution and reaction at 298.15 K

Reactant	Solvent	Solution	No. of experiments	$\Delta_i H_m^\circ$
$ZnCl_2$(cr)	Acetone	A_1	5	-45.64 ± 1.36
$2[NH_2Bu^n{}_2][S_2CNBu^n{}_2]$(cr)	A_1	A_2	5	78.03 ± 1.00
$2[NH_2Bu^n{}_2]Cl$(cr)	Acetone	A_3	5	28.05 ± 0.46
$[Zn(S_2CNBu^n{}_2)_2]$(cr)	A_3	A_2	5	42.80 ± 1.12
$2[NH_2Bu^n{}_2][S_2CNBu^n{}_2]$(cr)	Acetone	B_1	5	76.89 ± 0.56
$CdCl_2$(cr)	B_1	B_2	5	-63.63 ± 1.66
$2[NH_2Bu^n{}_2]Cl$(cr)	Acetone	B_3	5	28.05 ± 0.46
$[Cd(S_2CNBu^n{}_2)_2]$(cr)	B_3	B_2	5	16.73 ± 0.46
$HgCl_2$(cr)	Acetone	C_1	5	6.24 ± 0.13
$2[NH_2Bu^n{}_2][S_2CNBu^n{}_2]$(cr)	C_1	C_2	5	-14.03 ± 1.87
$2[NH_2Bu^n{}_2]Cl$(cr)	Acetone	C_3	5	28.05 ± 0.46
$[Hg(S_2CNBu^n{}_2)_2]$(cr)	C_3	C_2	5	41.43 ± 0.65

Table 3 Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ K^{-1} mol^{-1}) and temperatures (K) for the chelates

	$[Zn(S_2CNBu^n{}_2)_2]$	$[Cd(S_2CNBu^n{}_2)_2]$	$[Hg(S_2CNBu^n{}_2)_2]$
$\Delta_r H_m^\circ$	-38.46 ± 2.08	-31.52 ± 1.87	-77.27 ± 2.04
$\Delta_f H_m^\circ$(cr)	-471.23 ± 3.90	-440.74 ± 3.79	-319.29 ± 3.88
$\Delta_{cr}^{l} H_m^\circ$	37.48 ± 1.04	20.05 ± 0.62	28.32 ± 1.55
$\Delta_l^g H_m^\circ$	65.65 ± 2.72	64.52 ± 2.22	63.75 ± 2.38
T_{fus}	382 ± 1	408 ± 1	350 ± 1
T_{vap}	671 ± 1	591 ± 1	551 ± 1
$C_{p,m}$(cr)	0.27 ± 0.03	0.67 ± 0.02	0.54 ± 0.07
$C_{p,m}$(l)	0.95 ± 0.01	0.99 ± 0.03	1.29 ± 0.05
$C_{p,m}$(g)	0.76 ± 0.33	0.74 ± 0.23	0.73 ± 0.59
$\Delta_{cr}^{g} H_m^\circ$	107 ± 3	123 ± 3	195 ± 3
$\Delta_f H_m^\circ$(g)	-364 ± 5	-318 ± 5	-124 ± 5
$\Delta_{ho} H_m^\circ$	-731 ± 12	-677 ± 12	-421 ± 12
$\Delta_{he} H_m^\circ$	-2982 ± 12	-2777 ± 12	-2849 ± 12
$\langle D\rangle$(M–S)	183 ± 3	168 ± 3	105 ± 3
$\langle D'\rangle$(M–S)	746 ± 3	694 ± 3	712 ± 3

Table 4 Auxiliary quantities (kJ mol^{-1})

Substance	$\Delta_f H_m^\circ$	Ref.
$ZnCl_2$(cr)	-415.05 ± 0.02	24
$CdCl_2$(cr)	-391.50 ± 0.22	24
$HgCl_2$(cr)	-224.30 ± 0.13	24
$[NH_2Bu^n{}_2][S_2CNBu^n{}_2]$(cr)	-461.3 ± 1.6	25
$[NH_2Bu^n{}_2]Cl$(cr)	-452.44 ± 0.39	14
Zn(g)	130.73 ± 0.01	24
Cd(g)	120.01 ± 0.01	24
Hg(g)	61.30 ± 0.01	24
Zn^{2+}(g)	2782.78 ± 0.03	24
Cd^{2+}(g)	2623.54 ± 0.02	24
Hg^{2+}(g)	2890.47 ± 0.03	24
$Bu^n{}_2NCS_2{}^\bullet$(g)	117.9 ± 5.5	*
$Bu^n{}_2NCS_2{}^-$(g)	82.5 ± 5.5	*

* This work (see text).

From $\Delta_f H_m^\circ(HS_2CNEt_{2,g}) = 33.2 \pm 3.8$ kJ mol^{-1},[28] the standard molar enthalpy of di-*n*-butyldithiocarbamic acid was recalculated as -49.1 ± 3.8 kJ mol^{-1}, by using a previous procedure.[14] Thus, the standard enthalpies of formation of the radical and anion (Table 4) were calculated by means of the auxiliary data $D(S\text{–}H) = 385 \pm 4$,[10] $\Delta_f H_m^\circ(H,g) = 218.00 \pm 0.001$[9] and the electron affinity of a sulphur atom -200.42 ± 0.05 kJ mol^{-1}.[9]

The homolytic and heterolytic quantities needed to characterize the metal–sulphur bond can be derived from the gas-phase data,[12–14] defined by expressions (4) and (5), respectively.

$$M(g) + 2Bu^n{}_2NCS_2{}^\bullet(g) \longrightarrow [M(S_2CNBu^n{}_2)_2](g);\ \Delta_{ho}H_m^\circ \quad (4)$$

$$M^{2+}(g) + 2Bu^n{}_2NCS_2{}^-(g) \longrightarrow [M(S_2CNBu^n{}_2)_2](g);\ \Delta_{he}H_m^\circ \quad (5)$$

Since the vibrational results are consistent with the di-*n*-butyldithiocarbamate being bonded to the metal in a bidentate manner *via* the sulphur atoms, the mean metal–sulphur bond enthalpies for homolytic $\langle D\rangle(M\text{–}S) = -\Delta_{ho}H_m^\circ/4$ and heterolytic $\langle D'\rangle(M\text{–}S) = -\Delta_{he}H_m^\circ/4$ can be calculated by using the auxiliary data of Table 4. In these determinations the reorganization energy associated with the ligand upon complexation is neglected and an equivalence of all metal–sulphur bonds is assumed, even though for these complexes the metallic atoms are expected to be anisobidentately bonded by the sulphur atoms.[20,29]

The mean metal–sulphur bond enthalpies decrease from zinc to mercury for $\langle D\rangle$(M–S) and are almost constant for $\langle D'\rangle$(M–S). In the absence of structural parameters it is not possible to confirm the correlation between $\langle D\rangle$(M–S) and the mean metal–sulphur bond distance, as observed for the same ligand with phosphorus group chelates which also showed a decrease in the mean element–sulphur bond enthalpy from phosphorus to bismuth.[12–14] A decrease in the mean metal–ligand bond enthalpy is observed for several adducts containing oxygen[30] and nitrogen[31] donor ligands for zinc group elements. However, for two other series of thiourea adducts, $\langle D\rangle$(M–S) was 117, 127 and 93 kJ mol^{-1} and 148, 142 and 104 kJ mol^{-1} for the tetra[32] and bis adducts[33] of zinc, cadmium and mercury, respectively. Also, $\langle D\rangle$(Zn–S) for the diethyldithiocarbamate[9] chelate was 170 ± 3 kJ mol^{-1}. An inspection of our results, 183 ± 3, 168 ± 3 and 105 ± 3 kJ mol^{-1} (Table 3), shows a higher value for the zinc chelate which is also higher than for the equivalent thiourea adducts. As observed before, the *n*-butyl alkyl group causes higher $\langle D\rangle$(M–S) values for the carbamate chelates.[11,14]

The scarce thermochemical results seem to indicate a high tendency of the zinc group elements to bond to sulphur donor atoms to form complexes, being very favourable for chelates. However, additional data will be needed to confirm this behaviour.

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References

1 R. J. Magee and J. O. Hill, *Rev. Anal. Chem.*, 1985, **8**, 5.
2 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.
3 M. A. Bernard and M. Borel, *Bull. Soc. Chim. Fr.*, 1964, 3064.
4 J. O. Hill and R. J. Magee, *Rev. Inorg. Chem.*, 1981, **3**, 141.
5 P. M. Burkinshaw and C. T. Mortimer, *Coord. Chem. Rev.*, 1983, **48**, 101.
6 B. Annuar, J. O. Hill, D. J. McIvor and R. J. Magee, *Thermochim. Acta*, 1974, **9**, 143.
7 K. J. Cavell, J. O. Hill and R. J. Magee, *J. Chem. Soc., Dalton Trans.*, 1980, 763.
8 K. J. Cavell, J. O. Hill and R. J. Magee, *J. Chem. Soc., Dalton Trans.*, 1980, 1638.
9 C. Airoldi, *J. Chem. Soc., Dalton Trans.*, 1985, 369.
10 M. A. V. R. da Silva and A. M. M. V. Reis, *J. Chem. Thermodyn.*, 1989, **21**, 167.
11 M. A. V. R. da Silva and A. M. M. V. Reis, *J. Chem. Thermodyn.*, 1989, **21**, 423.
12 C. Airoldi and A. G. de Souza, *J. Chem. Soc., Dalton Trans.*, 1987, 2955.
13 A. G. de Souza and C. Airoldi, *Thermochim. Acta*, 1988, **130**, 95.
14 C. Airoldi and A. G. de Souza, *J. Chem. Thermodyn.*, 1989, **21**, 283.
15 K. J. Cavell, J. O. Hill and R. J. Magee, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1277.
16 M. L. Riekkola, *Mikrochim. Acta*, 1982, **1**, 327.
17 M. L. Riekkola, *Ann. Acad. Sci. Fenn., Ser. A*, 1983, **199**, 1.
18 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 1967, **10**, 257.
19 R. Kellner, *Inorg. Chim. Acta*, 1984, **84**, 233.
20 C. P. Sharma, N. Kumar, M. C. Khandpal, S. Chandra and V. G. Bhide, *J. Inorg. Nucl. Chem.*, 1981, **43**, 923.
21 C. Petri, G. Tosim and P. Zannini, *J. Mol. Struct.*, 1979, **53**, 35.
22 M. L. Kantouri and G. E. Manoussakis, *J. Therm. Anal.*, 1984, **29**, 1151.
23 M. L. Riekkola, *Acta Chem. Scand., Ser. A*, 1983, **37**, 691.
24 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*, 1982, **11**, suppl. 2.
25 M. A. V. Ribeiro da Silva, A. M. V. Reis and G. Pilcher, *J. Chem. Thermodyn.*, 1987, **19**, 837.
26 R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd edn., McGraw-Hill, New York, 1968.
27 G. J. Janz, *Thermodynamic Properties of Organic Compounds*, Revised edn., Academic Press, New York, 1968.
28 M. A. V. Ribeiro da Silva, A. M. V. Reis and G. Pilcher, *Thermochim. Acta*, 1988, **124**, 139.
29 M. Colapietro, A. Domenicano, L. Scaramuzza and A. Vaciago, *Chem. Commun.*, 1968, 302.
30 M. R. M. C. Santos and C. Airoldi, *Thermochim. Acta*, 1988, **125**, 295.
31 M. L. C. P. da Silva, A. P. Chagas and C. Airoldi, *J. Chem. Soc., Dalton Trans.*, 1988, 2113.
32 S. J. Ashcroft, *J. Chem. Soc. A*, 1970, 1020.
33 S. J. Ashcroft, *J. Chem. Eng. Data*, 1988, **33**, 73.

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