Standard enthalpies of formation of crystalline dimethylammoniumdimethyldithiocarbamate and of dimethyldithiocarbamate complexes of copper(II) and nickel(II). The mean Cu–S and Ni–S bond-dissociation enthalpies

Manuel A. V. Ribeiro da Silva, Ana M. M. V. Reis, and Rita I. M. C. P. Faria

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, P-4050 Porto, Portugal

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The standard $(p^{\circ} = 0.1 \text{ MPa})$ enthalpies of formation of crystalline dimethylammoniumdimethyldithiocarbamate and of the dimethyldithiocarbamate complexes of Ni(II) and Cu(II) were determined, at the temperature 298.15 K, by solution-reaction calorimetry. The enthalpy of "decomposition" of the dimethylammoniumdimethyldithiocarbamate salt and the enthalpies of sublimation of the metal complexes were measured by high-temperature microcalorimetry. From these values, the mean molar bond-dissociation enthalpies $\langle D_m \rangle$ (M–S) were derived.

 $\Delta_{\rm f} H^{\circ}_{\rm m}({
m cr})/({
m kJ}\cdot{
m mol}^{-1})$

 -144.0 ± 6.4

 -146.1 ± 10.9

 -85.5 ± 11.0

 $\begin{array}{l} (CH_3)_2 NH_2 S_2 CN(CH_3)_2 \\ Ni \{S_2 CN(CH_3)_2\}_2 \\ Cu \{S_2 CN(CH_3)_2\}_2 \\ (0) 1995 \ Academic \ Press \ Limited \end{array}$

1. Introduction

The last three decades have witnessed a progressive development of the thermochemistry of metal dithiocarbamates due to their important applications in many areas. Most of this thermochemical work has been subject of three major literature reviews,⁽¹⁻³⁾ although a critical assessment of the experimental results is still missing. In previous papers, we reported thermochemical studies of complexes of copper(II),⁽⁴⁾ nickel(II),⁽⁵⁾ iron(III),⁽⁶⁾ cobalt(III),⁽⁶⁾ chromium(III),⁽⁶⁾ and manganese(III),⁽⁶⁾ with five different dialkyldithiocarbamates: M(S₂CNR₂)₂ (R = C₂H₅, CH₃CH₂CH₂, (CH₃)₂CH, CH₃(CH₂)₂CH₂, and CH₃CH(CH₃)CH₂). In order to have more thermochemical information on this type of complex and to investigate the effect of the different alkyl groups in these complexes upon the mean metal–sulfur molar bond-dissociation enthalpies, $\langle D_m \rangle$ (M–S), thermochemical studies of

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 $\langle D_{\rm m} \rangle (M-S)/(kJ \cdot mol^{-1})$

 222 ± 4

 183 ± 4

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dimethylammoniumdimethyldithiocarbamate, and the standard molar enthalpies of formation and of sublimation of the dimethyldithiocarbamate complexes of copper(II) and nickel(II) are reported.

2. Experimental

The dimethylammoniumdimethyldithiocarbamate, $(CH_3)_2NH_2S_2CN(CH_3)_2$, was prepared as reported by Cavell *et al.*,⁽⁷⁾ by adding to a certain volume of an aqueous solution containing 40 per cent by volume of dimethylamine (Merck, p.a.) an equal volume of acetone (Merck, p.a.) followed by the addition of an excess of CS₂ (Aldrich Chemical Co., >99 moles per cent), holding the reaction mixture at a temperature lower than 283 K, by means of an ice-bath. The solid product was recrystallized from light petroleum, dried *in vacuo*, and stored in the dark.

The dimethyldithiocarbamate complexes Ni{S₂CN(CH₃)₂}₂ and Cu{S₂CN(CH₃)₂}₂, of nickel(II) and copper(II), were prepared by adding an aqueous solution of the appropriate AnalaR metal salt: Ni(NO₃)₂·6H₂O or CuSO₄·5H₂O (50 cm³ containing 0.014 mol), to an aqueous solution containing an excess of (CH₃)₂NH₂S₂CN(CH₃)₂ (in a mole ratio r = 3). The resulting precipitates of metal complexes were filtered, washed several times with hot water, recrystallized from trichloromethane, and dried over phosphorus pentoxide.

The purities of the "ligand" and of the complexes were checked by elementary analyses. The mass-fraction *w* analyses were as follows:

	$10^2 \cdot w(C)$	$10^2 \cdot w(H)$ Expected	$10^2 \cdot w(\mathbf{N})$	$10^2 \cdot w(C)$	$10^2 \cdot w(H)$ Found	$10^2 \cdot w(\mathbf{N})$
$(CH_3)_2NH_2S_2CN(CH_3)_2 \\ Cu\{S_2CN(CH_3)_2\}_2 \\ Ni\{S_2CN(CH_3)_2\}_2 \\$	36.11	8.48	16.84	36.11	8.38	16.86
	23.71	3.98	9.22	23.75	4.01	9.25
	24.09	4.04	9.36	24.12	4.10	9.44

From an aqueous solution containing 40 per cent of volume (Merck, p.a.), an aqueous solution of molality 1 mol·kg⁻¹ was prepared, by dilution with water, and potentiometrically titrated with a standard solution of $HCl(c=0.1 \text{ mol·dm}^{-3})$; the density of the solution was measured and found to be 0.9839 g·cm⁻³, leading to the composition (CH₃)₂NH·63.39H₂O. AnalaR nickel(II) chloride hydrate was powdered and dried over sodium hydroxide pellets and its composition determined by means of nickel(II) analyses and found to be NiCl₂·6.00H₂O; copper sulphate pentahydrate (Merck, p.a.) was dried over silica gel and its composition was confirmed by means of copper analyses and found to be CuSO₄·5.00H₂O; CS₂ (Aldrich Chemical Co., >99 moles per cent) and dimethylformamide (Merck, p.a.) were used as supplied.

A glass Dewar calorimeter containing 120 cm³ of solvent, previously described,⁽⁸⁾ was used. The samples were sealed in thin glass ampoules which were broken into the appropriate solvent by compression between two glass rings. The calorimeter temperature changes were measured to 10^{-4} K, at time intervals of 20 s, using a quartz

thermometer (Hewlett Packard HP 2804A) and recorded by a thermal printer (HP 5150A). The adiabatic temperature change was calculated using the equal-area method.⁽⁹⁾ The calorimeter was calibrated electrically for each experiment. The accuracy and performance of the calorimeter were tested by measuring the molar enthalpy of solution of tris(hydroxymethyl)aminomethane, $C(CH_2OH)_3NH_2$ (THAM, N.B.S. reference sample 724) in HCl(aq, $c = 0.100 \cdot \text{mol} \cdot \text{dm}^{-3}$) at T = 298.15 K. The value obtained: $\Delta_{sol}H^{\circ}_{m}(cr) = -(29.736 \pm 0.016)$ kJ·mol⁻¹ (mean of five experiments) was in agreement with the literature value of Kilday and Prosen: $-(29.770 \pm 0.032)$ kJ·mol⁻¹.⁽¹⁰⁾

The enthalpy of decomposition of (CH₃)₂NH₂S₂CN(CH₃)₂(cr) and the enthalpies of sublimation of the Ni(II) and Cu(II) complexes were measured by the "vacuum sublimation" drop-microcalorimetric method.⁽¹¹⁾ Samples (of mass about 4 mg) of each compound, contained in a small thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter, held at constant temperature, and then removed from the hot zone by applying a vacuum. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were made as small as possible by dropping tubes of nearly equal mass, to within $\pm 10 \,\mu$ g, into the twin calorimeter cells. The calorimeter was calibrated *in situ* by making use of the reported enthalpy of sublimation of napththalene.⁽¹²⁾ The quantity measured in the calorimeter: $\{H_{\rm m}^{\circ}({\rm g},T) - H_{\rm m}^{\circ}({\rm cr},298.15 \,{\rm K})\}\$ was corrected to $T = 298.15 \,{\rm K}$, using $\Delta_{298.15 \,{\rm K}}^{T} H_{\rm m}^{\circ}({\rm g})$; for $(CH_3)_2NH_2S_2CH(CH_3)_2(cr)$, the correction term was calculated assuming the gas to be a mixture of equal amounts of substances of (CH₃)₂NH and HS₂CN(CH₃)₂. The $\Delta_{79815K}^{T} H_{m}^{\circ}(g)$ values for the decomposition and also for the sublimation of the complexes, were estimated by means of a group-additivity method, as previously reported,⁽¹³⁾ using values reported by Stull et al.⁽¹²⁾

The molar masses used for the elements were those recommended by the IUPAC Commission;⁽¹⁴⁾ each uncertainty interval quoted is twice the standard deviation of the mean.

The standard molar enthalpies of formation of the crystalline compound $(CH_3)_2NH_2S_2CN(CH_3)_2$ and of the complexes of Ni(II) and Cu(II) were determined by solution and reaction calorimetry, using the thermochemical reactions:

 $CS_2(l) + 2(CH_3)_2NH \cdot 63.39H_2O(l) = 126.78H_2O(l) +$

 $(CH_3)_2 NH_2 S_2 CN(CH_3)_2(cr),$ (1)

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$$174.00H_{2}O(l) + NiCl_{2} \cdot 6H_{2}O(cr) + 2(CH_{3})_{2}NH_{2}S_{2}CN(CH_{3})_{2}(cr) = [Ni\{S_{2}CN(CH_{3})_{2}\}_{2}](cr) + 2(CH_{3})_{2}NH \cdot 63.39H_{2}O(l) + 2HCl \cdot 26 \cdot 61H_{2}O(l), (2) 175.32H_{2}O(l) + CuSO_{4} \cdot 5H_{2}O(cr) + 2(CH_{3})_{2}NH_{2}S_{2}CN(CH_{3})_{2}(cr) = [Cu\{S_{2}CN(CH_{3})_{2}\}_{2}](cr) + 2(CH_{3})_{2}NH \cdot 63.39H_{2}O(l) + H_{2}SO_{4} \cdot 53.54H_{2}O(l), (3)$$

which were carried out in dimethylformamide (120 cm^3) as calorimetric solvent. In all the cases, ampoules containing the reactants were added consecutively, in the order

i	Reactant	Solvent	Solution	$\Delta_i H_{\rm m}/({\rm kJ}\cdot{\rm mol}^{-1})$
1	$CS_{2}(1)$	DMF	А	$+3.66\pm0.04$
2	(CH ₃) ₂ NH·63.39H ₂ O(1)	Α	F	-257.4 ± 1.7
3	$H_2O(1)$	DMF	В	-3.43 ± 0.04
4	$(CH_3)_2NH_2S_2CN(CH_3)_2(cr)$	В	F	$+16.11\pm0.12$

TABLE1.Molarenthalpiesofsolutionandreaction,atT = 298.15 K,fordimethylammoniumdimethylammoniumdimethyldimethylamdimethylamdimethylam

TABLE 2. Molar enthalpies of solution and reaction, at T = 298.15 K, for the nickel(II) complex

i	Reactant	Solvent	Solution	$\Delta_i H_{ m m}/({ m kJ}{ m \cdot mol^{-1}})$
1	$H_2O(1)$	DMF	A_1	-3.45 ± 0.03
2	$NiCl_2 \cdot 6.00H_2O(cr)$	A_1	A_2	-34.86 ± 0.21
3	$(CH_3)_2NH_2S_2CN(CH_3)_2(cr)$	A_2	A_3	$+7.19\pm0.24$
4	$Ni{S_2CN(CH_3)_2}_2(cr)$	DMF	\mathbf{B}_1	$+15.53\pm0.34$
5	$(CH_3)_2 NH \cdot 63.39 H_2 O(1)$	\mathbf{B}_1	\mathbf{B}_2	-190.43 ± 0.47
6	$HCl \cdot 26.61 H_2O(l)$	\mathbf{B}_2	A_3	-157.71 ± 0.75

they are written in the equations, to the solvent, and the corresponding $\Delta_r H_m^{\circ}$ values were measured. To a second portion of the same solvent, were also added consecutively, ampoules containing the products, and the corresponding $\Delta_r H_m^{\circ}$ values were measured. A rigorous control of the stoichiometry was maintained throughout each series of experiments to ensure that the final solutions resulting from the dissolution and reactions were of the same composition as those from the dissolution and reaction of the products. This was verified by breaking ampoules of the solution

TABLE 3. Molar enthalpies of solution and reaction, at T = 298.15 K, for the copper(II) complex

i	Reactant	Solvent	Solution	$\Delta_i H_{\rm m}/({\rm kJ}\cdot{ m mol}^{-1})$
1	$H_2O(1)$	DMF	A_1	-3.45 ± 0.03
2	$CuSO_4 \cdot 5.00H_2O(1)$	A_1	A_2	$+15.16\pm0.58$
3	$(CH_3)_2NH_2S_2CN(CH_3)_2(cr)$	A_2	A_3	-13.80 ± 0.37
4	$Cu{S_2CN(CH_3)_2}_2(cr)$	DMF	\mathbf{B}_1	$+18.32\pm0.29$
5	$(CH_3)_2 NH \cdot 63.39 H_2 O(1)$	\mathbf{B}_1	\mathbf{B}_2	-189.46 ± 0.96
6	$H_2SO_4 \cdot 53.54H_2O(l)$	\mathbf{B}_2	A_3	-281.62 ± 0.46

TABLE 4. Standard molar enthalpies of reaction and formation, at T = 298.15 K

	$\frac{\Delta_{\rm r} H_{\rm m}^{\circ}}{\rm kJ{\cdot}mol^{-1}}$	$rac{\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}}{\mathrm{kJ}\cdot\mathrm{mol}^{-1}}$
$\begin{array}{l} (CH_3)_2 NH_2 S_2 CN(CH_3)_2(cr) \\ [Ni \{S_2 CN(CH_3)_2\}2](cr) \\ [Cu \{S_2 CN(CH_3)_2\}_2](cr) \end{array}$	$-92.4 \pm 2.4 + 60.0 \pm 1.4 + 24.9 \pm 1.7$	$\begin{array}{c} -144.0\pm \ 6.4\\ -146.1\pm 10.1\\ -85.5\pm 11.0\end{array}$

Compound	$\Delta_{\rm f} H_{ m m}^{\circ}/({ m kJ}{ m \cdot}{ m mol}^{-1})$
$\begin{array}{c} H_2O(1) \\ CS_2(l) \\ (CH_3)_2NH\cdot 63.39H_2O(l) \\ HCl\cdot 26.61H_2O(l) \\ H_2SO_4\cdot 53.54H_2O(l) \\ NiCl_2\cdot 6.00H_2O(cr) \\ CuSO_4\cdot 500H_2O(cr) \\ CuSO_4\cdot 500H_2O(cr) \\ \end{array}$	$\begin{array}{r} -285.83 \pm 0.04 {}^{(15)} \\ +89.7 \ \pm 0.7 {}^{(15)} \\ -70.6 \ \pm 4.2 {}^{(16)} \\ -164.44 \ \pm 0.01 {}^{(15)} \\ -886.87 \pm 0.30 {}^{(15)} \\ -2103.17 \pm 0.21 {}^{(15)} \\ -2279 65 \pm 0.21 {}^{(15)} \end{array}$
(CH ₃) ₂ NH(g)	$-18.46 \pm 0.80^{(16)}$

TABLE 5. Standard molar enthalpies of formation at T = 298.15 K

resulting from the dissolution of the reactants into that resulting from the dissolution of the products, in the calorimeter, where no enthalpy change was detected.

3. Results

Tables 1 to 3 list the average values of at least five independent determinations of the molar enthalpies of solution and reaction for the $(CH_3)_2NH_2S_2CN(CH_3)_2$ compound and for the nickel(II) and copper(II) complexes, respectively, from which the standard molar enthalpies of the thermochemical reactions, listed in table 4, were derived by means of the equations:

$$\Delta_{\rm r} H_{\rm m}^{\circ} \{ ({\rm CH}_3)_2 {\rm NH}_2 {\rm S}_2 {\rm CN} ({\rm CH}_3)_2 \} = \Delta_1 H_{\rm m} + 2\Delta_2 H_{\rm m} - 126.78\Delta_3 H_{\rm m} - \Delta_4 H_{\rm m}, \tag{4}$$

 $\Delta_{\rm r} H_{\rm m}^{\circ} [\operatorname{Ni} \{ S_2 CN(CH_3)_2 \}_2] =$

$$174.00\Delta_1 H_{\rm m} + \Delta_2 H_{\rm m} + 2\Delta_3 H_{\rm m} - \Delta_4 H_{\rm m} - 2\Delta_5 H_{\rm m} - 2\Delta_6 H_{\rm m},$$
 (5)

 $\Delta_{\rm r} H_{\rm m}^{\circ} [{\rm Cu} \{ {\rm S}_2 {\rm CN} ({\rm CH}_3)_2 \}_2] =$

$$175.32\Delta_1 H_{\rm m} + \Delta_2 H_{\rm m} + 2\Delta_3 H_{\rm m} - \Delta_4 H_{\rm m} - 2\Delta_5 H_{\rm m} - \Delta_6 H_{\rm m}.$$
 (6)

The standard molar enthalpies of formation of the crystalline compounds were derived, with the auxiliary quantities listed in table 5.

The molar enthalpies of "apparent sublimation" of $(CH_3)_2NH_2S_2CN(CH_3)_2$ are listed in table 6. Tables 7 and 8 list, respectively, the observed measurements for

$\frac{T}{K}$	$\frac{m}{mg}$	$\frac{\Delta_{\rm dec}H^{\circ}_{\rm m}(T)}{\rm kJ{\cdot}mol^{-1}}$	$\frac{\Delta_{298.15 \text{ K}}^{T} H_{\text{m}}^{\circ}}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{dec}H^\circ_m(298.15~\text{K})}{kJ\cdot\text{mol}^{-1}}$
412	2.631	214.4	24.2	190.2
412	3.723	212.5	24.2	188.3
412	3.532	214.8	24.2	190.6
412	3.419	213.4	24.2	189.2
412	2.249	214.9	24.2	190.7
			$\langle \Delta_{ m dec} angle$	$H_{\rm m}^{\circ}(298.15 \text{ K})\rangle = (189.8 \pm 0.91) \text{ kJ} \cdot \text{mol}^{-1}$

TABLE 6. Enthalpy of "apparent sublimation" of a mass *m* of (CH₃)₂NH₂S₂CN(CH₃)₂

$\frac{T}{K}$	$\frac{\Delta_{\mathrm{cr,298.15K}}^{\mathrm{g,T}}H_{\mathrm{m}}}{\mathrm{kJ}{\cdot}\mathrm{mol}^{-1}}$	$\frac{\Delta_{298.15 \text{ K}}^{T} H_{\text{m}}^{\circ}}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{cr}^{\epsilon}H_{m}^{\circ}(298.15~\mathrm{K})}{\mathrm{kJ}\cdot\mathrm{mol}^{-1}}$
519	222.0	71.6	150.4
519	222.9	71.6	151.3
519	221.4	71.6	149.8
519	222.4	71.6	150.8
519	221.3	71.6	149.7
		$\langle \Delta^{ m g}_{ m cr} H angle$	$_{\rm m}^{\circ}(298.15 \text{ K})\rangle = (150.4 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$

TABLE 7. Standard molar enthalpies of sublimation of [Ni{S₂CN(CH₃)₂}₂](cr)

the standard molar enthalpies of sublimation of the complexes of Ni(II) and Cu(II) and the corrections to T = 298.15 K. The standard molar enthalpies of formation of the complexes in the gaseous state, at T = 298.15 K, were derived: $\Delta_{\rm f} H^{\circ}_{\rm m} [\text{Ni} \{\text{S}_2 \text{CN}(\text{CH}_3)_2\}_2, g] = (4.3 \pm 20.9) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\rm f} H^{\circ}_{\rm m} [\text{Cu} \{\text{S}_2 \text{CN}(\text{CH}_3)_2\}_2, g] = (70.5 \pm 11.0) \text{ kJ} \cdot \text{mol}^{-1}$.

4. Discussion

The enthalpy of "apparent sublimation" is the enthalpy of the decomposition reaction represented by

$$(CH_3)_2 NH_2 S_2 CN(CH_3)_2 (cr) = (CH_3)_2 NH(g) + HS_2 CN(CH_3)_2(g),$$
(7)

from which the value of $\Delta_{f}H_{m}^{\circ}$ {HS₂CN(CH₃)₂,g} = (64.3 ± 2.7) kJ·mol⁻¹ was derived. No experimental values are available for the molar enthalpies of dissociation of the (S–H) bond in this type of compound. Benson⁽¹⁷⁾ proposed a constant value of 385 kJ·mol⁻¹ for D_{m} (S–H) in a wide variety of compounds such as H₂S, CH₃SH, C₂H₅SH, and in general C_vH_{2v+1}SH; so, in the absence of an experimental value, we have used, as in previous papers^(4,5) D_{m} (S–H) = (385±4) kJ·mol⁻¹, to derive $\Delta_{f}H_{m}^{\circ}$ {S₂CN(CH₃)₂,g} = (231.3 ± 7.5) kJ·mol⁻¹. The mean metal–sulfur bond-dissociation enthalpies, $\langle D_{m} \rangle$ (M–S), in M{S₂CN(CH₃)₂}₂ complexes may be

$\frac{T}{K}$	$\frac{\Delta_{\mathrm{cr,298 K}}^{\mathrm{g,T}}H_{\mathrm{m}}}{\mathrm{kJ}{\cdot}\mathrm{mol}^{-1}}$	$\frac{\Delta_{298.15 \text{ K}}^T H_{\text{m}}^{\circ}}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(298.15~{\rm K})}{{\rm kJ}\cdot{\rm mol}^{-1}}$
497	219.8	64.1	155.7
497	220.3	64.1	156.2
497	220.0	64.1	155.9
497	220.5	64.1	156.4
497	219.7	64.1	155.6
		$\langle \Delta^{ m g}_{ m cr} H^{\circ}_{ m m}$	$(298.15 \text{ K})\rangle = (156.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$

TABLE 8. Standard molar enthalpies of sublimation of $[Cu{S_2CN(CH_3)_2}_2](cr)$

defined as one quarter of the standard molar enthalpy of dissociation of the hypothetical gaseous reaction:

$$M\{S_{2}CN(CH_{3})_{2}\}_{2}(g) = M(g) + 2S_{2}CN(CH_{3})_{2}(g)$$
(8)

for which

$$4\langle D_{m}\rangle(M-S) = \Delta_{diss}H_{m}^{\circ} = \Delta_{f}H_{m}^{\circ}(M,g) + 2\Delta_{f}H_{m}^{\circ}\{HS_{2}CN(CH_{3})_{2},g\} - 2\Delta_{f}H_{m}^{\circ}(H,g) - \Delta_{f}H_{m}^{\circ}[M\{S_{2}CN(CH_{3})_{2}\}_{2},g] + 2D_{m}(H-S).$$
(9)

With the auxiliary values: $\Delta_{f}H_{m}^{\circ}(H,g) = (218.00 \pm 0.01) \text{ kJ} \cdot \text{mol}^{-1}$,⁽¹⁸⁾ $\Delta_{f}H_{m}^{\circ}(\text{Ni},g) = (429.7 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$,⁽¹⁵⁾ and $\Delta_{f}H_{m}^{\circ}(\text{Cu},g) = (338.3 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$,⁽¹⁵⁾ values of $\Delta_{diss}H_{m}^{\circ}$ and $\langle D_{m} \rangle (M-S)$ were then calculated: $\Delta_{diss}H_{m}^{\circ}[\text{Ni}\{S_{2}\text{CN}(\text{CH}_{3})_{2}\}_{2},g] = (888 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}$ and $\langle D_{m} \rangle (\text{Ni}-\text{S}) = (222 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta_{diss}H_{m}^{\circ}[\text{Cu}\{S_{2}\text{CN}(\text{CH}_{3})_{2}\}_{2},g] = (730 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}$ and $\langle D_{m} \rangle (\text{Cu}-\text{S}) = (183 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$.

In previous papers^(4, 5) we have shown that there is a trend of variation of $\langle D_m \rangle$ (M–S), M = Cu, Ni with the number of carbon atoms of the alkyl groups of the metal dithiocarbamates, M{S₂CN(CH₃)₂}, R = C₂H₅, CH₃CH₂CH₂, (CH₃)₂CH, CH₃(CH₂)₂CH₂, and CH₃CH(CH₃)CH₂, and now it is clear that the effect of the CH₃ follows the same trend:

$$D_{\rm m}({\rm M-S})_{\rm Me} < D_{\rm m}({\rm M-S})_{\rm Et} < D_{\rm m}({\rm M-S})_{\rm Pr} < D_{\rm m}({\rm M-S})_{\rm Bu}$$

as can be seen from figure 1.



FIGURE 1. Variation of $\langle D_m \rangle$ (M–S) for M = Cu(II) or Ni(II) with the alkyl group R in $\{M(S_2CNR_2)_2\}$ complexes.

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