

# Thermodynamics of Complexation of Cadmium(II) by Open-Chain N-Donor Ligands in Dimethyl Sulfoxide Solution

Clara Comuzzi,<sup>[a]</sup> Michela Grespan,<sup>[a]</sup> Andrea Melchior,<sup>[a]</sup> Roberto Portanova,<sup>[a]</sup> and Marilena Tolazzi\*<sup>[a]</sup>

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Thermodynamic parameters for the complexation of Cd<sup>II</sup> by the amines *n*-butylamine (*n*-but), ethylenediamine (en), *N,N'*-dimethylethylenediamine (dmen), *N,N,N'*-trimethylethylenediamine (trmen), *N,N,N',N'*-tetramethylethylenediamine (tmen), diethylenetriamine (dien), *N,N''*-dimethyldiethylenetriamine (dmdien), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien) have been determined in dimethyl sulfoxide (DMSO) solution by potentiometric and calorimetric techniques at 298 K and 0.1 mol dm<sup>-3</sup> ionic strength (NEt<sub>4</sub>ClO<sub>4</sub>). Only mononuclear complexes are

formed, in which the polyamines act predominantly as chelating agents. All the complexes are enthalpy-stabilized, whereas the entropy changes counteract the complexation. The steric requirements of the donors have a strong influence on the stoichiometry and nature of the Cd<sup>II</sup> complexes formed. Comparisons are made with data reported for some of these systems in water and with available data on silver(I) complexation by the same amines in DMSO, the latter showing that the selectivity of the ligands towards metal ions is also influenced by *N*-alkylation.

## Introduction

In the last few years, many papers have been published concerning the complexation of transition and f-block metal ions by a number of multidentate polyamines.<sup>[1–9]</sup> The aim of this work has been to improve knowledge on the coordination chemistry of hard and soft metal ions with N-donor ligands in aprotic solvents of varying donating ability, as well as to investigate the strong influence of the basicities and steric properties of the ligands on the thermodynamic stability and nature of the complexes formed. These studies have also attracted renewed interest as the coordination properties of open-chain polyamines towards different cations have been used as models allowing direct comparison with the corresponding macrocyclic systems.<sup>[10]</sup>

In particular, the papers published by our group concerning complexation of the transition metal ions silver(I) and cobalt(II)<sup>[3a–3f]</sup> have shown that the coordination properties of polyamines towards these ions may be modulated through adjustment of the alkyl chain length between the donor atoms or through nitrogen functionalization. Methylation of nitrogens leads to a decrease in the thermodynamic stability of the corresponding metal complexes due to the decreased  $\sigma$ -donor ability of *N*-methylated groups. Nitrogen functionalization may also lead to molecular crowding and to an increase in the radii of the complexes; such steric effects may strongly affect the selectivity pattern in metal coordination. As far as cobalt(II) complexes are concerned, different *N*-alkylation of polyamines has important effects on the dioxygen affinity of these complexes.<sup>[3f,10]</sup>

In this context, and as an extension of previous work, we have now undertaken an investigation on the complexation of Group 12 dications by a series of open-chain and cyclic polyamines in aprotic solvents. Especially interesting comparisons should be possible between the monovalent d<sup>10</sup> acceptor silver(I), with very soft character, and the divalent very soft Hg<sup>2+</sup> or moderately soft Cd<sup>2+</sup>. Moreover, despite the fact that complexation of Group 12 dications has been extensively studied in the past<sup>[11–14]</sup> and in more recent years,<sup>[15]</sup> scant thermodynamic data are available concerning their coordination by simple, open-chain N-donor ligands.<sup>[13h,14]</sup>


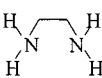
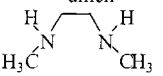
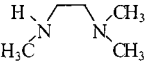
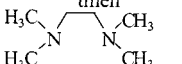
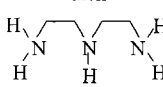
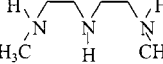
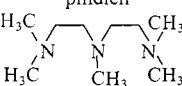
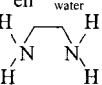
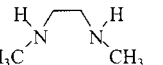
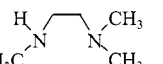
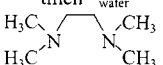
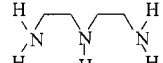
In this paper, we report the first results concerning the complexation of Cd<sup>II</sup> by the differently *N*-methylated mono- and polyamines *n*-butylamine (*n*-but), ethylenediamine (en), *N,N'*-dimethylethylenediamine (dmen), *N,N,N'*-trimethylethylenediamine (trmen), *N,N,N',N'*-tetramethylethylenediamine (tmen), diethylenetriamine (dien), *N,N''*-dimethyldiethylene triamine (dmdien), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien) in the aprotic solvent dimethyl sulfoxide (DMSO).

In order to investigate both the influence of the solvent on Cd<sup>II</sup> complexation as well as the selectivity of these ligands toward metal ions, comparisons are made with available data for the same systems in water<sup>[14]</sup> and with previously obtained data concerning Ag<sup>I</sup> complexation by some of these polyamines.<sup>[3a–3e]</sup>

Potentiometric and calorimetric measurements have been used to obtain the free energies and enthalpies of the reactions, respectively. All measurements were performed at 298 K in an ionic medium adjusted to 0.1 mol dm<sup>-3</sup> with NEt<sub>4</sub>ClO<sub>4</sub> as the neutral salt. FT-IR spectroscopy has been used to provide insight into the coordination modes of the ligands.

<sup>[a]</sup> Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via Cotonificio 108, 33100 Udine, Italy  
Fax: (internat.) +39–0432–558803  
E-mail: tolazzi@dstc.uniud.it

Table 1. Overall stability constants and thermodynamic functions for the reaction  $\text{Cd}^{2+} + j\text{L} \rightleftharpoons \text{CdL}_j^{2+}$  in DMSO at 298 K and  $I = 0.1 \text{ mol dm}^{-3}$ , and for that in water;<sup>[14]</sup> the errors quoted correspond to three standard deviations

Ligand	Complex	$\log \beta_j$	$-\Delta G^\circ_{\beta_j}/\text{kJmol}^{-1}$	$-\Delta H^\circ_{\beta_j}/\text{kJmol}^{-1}$	$-T\Delta S^\circ_{\beta_j}/\text{kJmol}^{-1}$
n-but 	CdL	2.6(0.2)	14.8(1.2)	24.1(0.9)	9.3
	CdL <sub>2</sub>	4.2(0.2)	24.0(1.1)	58(3)	34
	CdL <sub>3</sub>	6.0(0.3)	34.2(1.7)	71(3)	36.8
en 	CdL	5.88(0.01)	33.62(0.02)	52.2(0.5)	19
	CdL <sub>2</sub>	11.40(0.02)	65.1(0.1)	96.9(0.4)	31.8
	CdL <sub>3</sub>	15.81(0.02)	90.2(0.1)	147.1(0.1)	56.9
dmen 	CdL	5.22(0.02)	29.8(0.1)	43.8(0.5)	14
	CdL <sub>2</sub>	9.61(0.01)	55.0(0.1)	90.0(0.5)	35
	CdL <sub>3</sub>	11.09(0.04)	63.3(0.2)	143.1(1.4)	79.8
trmen 	CdL	4.13(0.02)	23.6(0.1)	39.0(0.4)	15.4
	CdL <sub>2</sub>	6.39(0.02)	36.5(0.1)	78.6(0.3)	42.1
tmen 	CdL	3.1(0.03)	17.7(0.2)	35.7(0.9)	18
dien 	CdL	8.46(0.05)	48.3(0.3)	65.3(0.9)	17
	CdL <sub>2</sub>	17.18(0.08)	98.2(0.3)	137.2(0.8)	39
dmdien 	CdL	7.51(0.08)	42.8(0.5)	60.2(0.9)	17.4
	CdL <sub>2</sub>	13.42(0.09)	76.6(0.5)	109.7(0.9)	33.1
pmdien 	CdL	3.80(0.03)	21.7(0.2)	43.5(1.2)	21.8
en <sup>[a]</sup> water 	CdL	5.4	30.79	25	-5.79
	CdL <sub>2</sub>	9.87	56.28	55.6	-0.68
	CdL <sub>3</sub>	12.2	69.56	82.4	12.84
dmen <sup>[b]</sup> water 	CdL	5.28			
	CdL <sub>2</sub>	8.90			
	CdL <sub>3</sub>	10.8			
trmen <sup>[b]</sup> water 	CdL	4.56			
	CdL <sub>2</sub>	6.73			
	CdL <sub>3</sub>	7.7			
tmen <sup>[b]</sup> water 	CdL	3.97			
	CdL <sub>2</sub>	5.37			
dien <sup>[a]</sup> water 	CdL	8.3	47.33	41	-6.33
	CdL <sub>2</sub>	13.7	78.12		

<sup>[a]</sup>  $\mu = 0.1$ ,  $T = 298 \text{ K}$ ; <sup>[b]</sup>  $\mu = 1.0$ ,  $T = 298 \text{ K}$ .

## Results

Computer treatment of the potentiometric experimental data shows that for all the systems the best fit is obtained when the formation of successive mononuclear complexes is taken into account. The overall stability constants obtained

from the potentiometric data minimization procedures, with the corresponding error limits, are listed in Table 1 for the reactions  $\text{Cd}^{2+} + j\text{L} \rightleftharpoons \text{CdL}_j^{2+}$  ( $j = 1-3$  for  $\text{L} = n\text{-but}$ ,  $\text{en}$ ,  $\text{dmen}$ ;  $j = 1, 2$  for  $\text{L} = \text{trmen}$ ,  $\text{dien}$ ,  $\text{dmdien}$ ;  $j = 1$  for  $\text{L} = \text{tmen}$  and  $\text{pmdien}$ ).

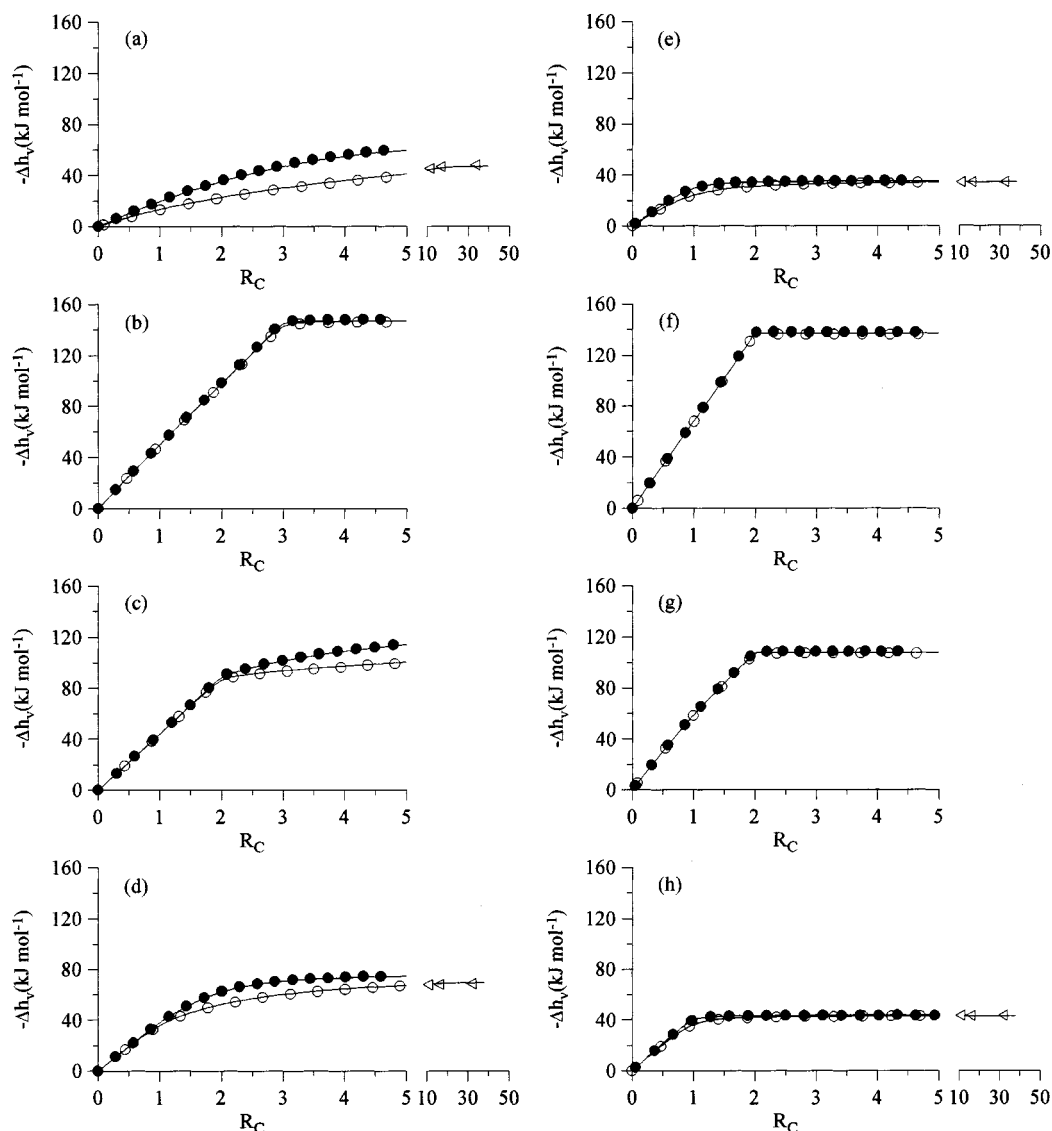


Figure 1. The total molar enthalpy changes,  $\Delta h_v$ , as a function of  $R_C = C_L/C_M$  for Cd<sup>II</sup>-polyamine systems in DMSO: (a) *n*-but (○) 5.05, (●) 19.90 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (b) en, (○) 5.05, (●) 19.90 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (c) dmen, (○) 5.10, (●) 19.98 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (d) trmen, (○) 5.10, (●) 19.98 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (e) tmen, (○) 5.05, (●) 19.90 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (f) dien, (○) 5.05, (●) 19.98 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (g) dmdien, (○) 5.10, (●) 20.05 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; (h) pmdien, (○) 5.05, (●) 20.05 mmol dm<sup>-3</sup> in Cd<sup>2+</sup>; the open triangles represent part of the "reverse" titrations; only some of the experimental points, chosen at random, have been plotted; the solid lines have been calculated from the values of  $\beta_j$  and  $\Delta H^\circ_{\beta_j}$  in Table 1

From an examination of the shape of the curves reproduced in Figure 1, some conclusions can be drawn about the coordinated species formed, which are fully consistent with the information obtained from analysis of the potentiometric data.

For the diamine en, the shape of the thermogram is consistent with the formation of three successive complexes of high stability. For the dmen system, the calorimetric curves indicate the formation of a third complex of lower stability in addition to two highly stable mononuclear species. The overlapping of the complexation curves up to  $R_C = 2$  for the triamines dien and dmdien is indicative of the formation of two successive complexes of high stabilities and the lack of heat evolution at  $R_C > 2$  clearly indicates that no more

complexes are formed beyond the second one. The fit between the experimental and calculated curves is quite good.

Figure 2 depicts the FT-IR spectra of a series of solutions containing the same concentration (about 50 mmol dm<sup>-3</sup>) of Cd<sup>2+</sup> and different ligand-to-metal ratios  $R_C$  for the Cd<sup>II</sup>-dmen system, chosen as a representative example.

Figure 3 shows  $\log \beta_{jCd}$  plotted as a function of  $\log \beta_{jAg}$  to allow better visualization of the comparison between the behaviour of the two ions.

## Discussion

All the complexation reactions are strongly exothermic whereas the entropy terms oppose the reactions (Table 1).

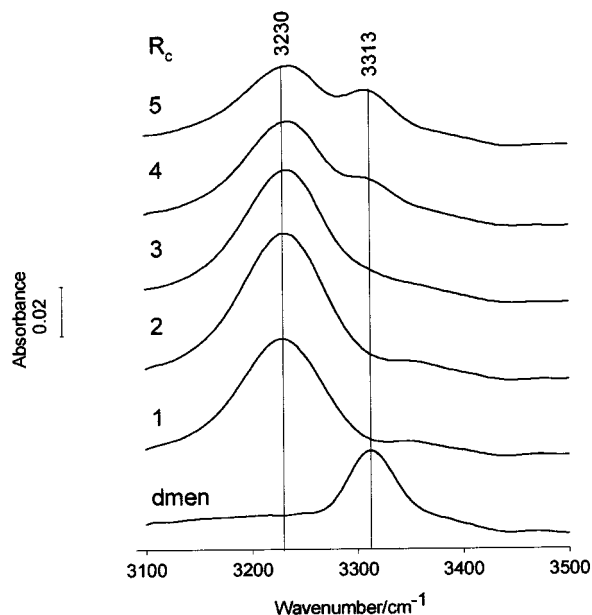


Figure 2. FT-IR spectra of solutions containing 50 mmol dm<sup>-3</sup> cadmium(II) and different dmen/metal ratios,  $R_c$

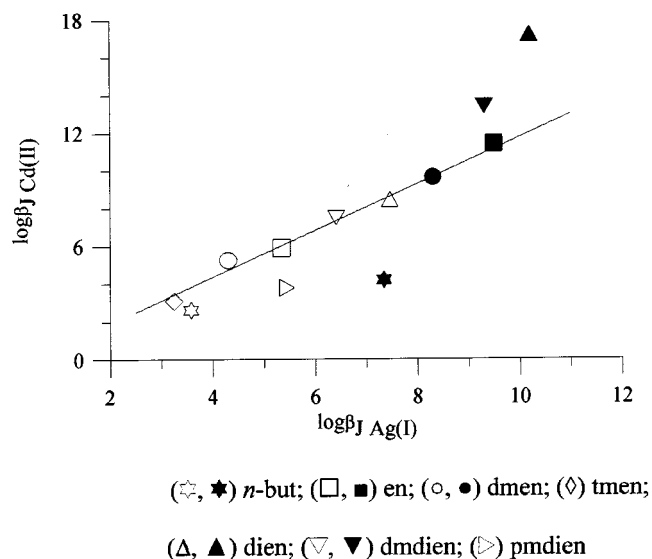


Figure 3. The  $\log \beta_j$  relationship of the complexation of cadmium(II)- and silver(I)-amines; open symbols refer to ML, filled symbols to ML<sub>2</sub> species

The negative enthalpy values are typical of reactions involving the complexation of metal ions by neutral ligands in aprotic solvents.<sup>[3,5]</sup> The negative entropy values are in line with the fact that the release of solvent molecules from the coordination sphere of the metal ions does not compensate the decrease in internal entropy of the ligand and the negative entropy change due to the loss of translational entropy of the reagents upon complexation.<sup>[16]</sup> Data are available for a few of these species in aqueous solution.<sup>[14]</sup> Cd<sup>2+</sup> is hexasolvated in both DMSO and water with the solvent molecules in a regular octahedral arrangement.<sup>[16]</sup>

The complexes are characterized by lower stabilities in water than in DMSO when primary and secondary amines are involved. Moreover, the complexes are always more enthalpy-stabilized in DMSO than in water, while in the latter solvent the entropy terms are favourable or, when negative, much less unfavourable. This trend is at variance with what might be expected on the basis of the thermodynamic parameters for the transfer of Cd<sup>2+</sup> from water to DMSO ( $\Delta G^\circ_{\text{transfer water} \rightarrow \text{DMSO}} = -60.4 \text{ kJ mol}^{-1}$  [17]) and may be attributed to a greater solvation, through hydrogen bonding, of amines in water than in DMSO.<sup>[16]</sup> For the complexes with the tertiary amines trmen and tmen the opposite is observed as they are more stable in water than in DMSO; hydrogen bonds are only formed to a limited extent (for trmen) or not at all (for tmen) and therefore the greater solvation of the metal ion in DMSO prevails in governing the trend in the stabilities.

**Cd<sup>II</sup>-*n*-but System:** The upper limit of Cd<sup>II</sup> complexation is the fourth complex in both water and aprotic solvents when charged halides and thiocyanate ligands are involved.<sup>[15c,16]</sup> With these ligands, the behaviour of which has been extensively studied, a switch from an octahedral to a tetrahedral configuration has been shown to take place in DMSO as well as in water, which occurs at the second or third step of complexation, respectively.<sup>[16]</sup> The only data available in the literature for Cd<sup>II</sup> monoamine systems in water relate to methylamine<sup>[14]</sup> and show that four successive mononuclear complexes are also formed in this case. In DMSO, only three successive mononuclear complexes are detected for the Cd<sup>II</sup>-*n*-but system, despite the fact that the mildly soft character of Cd<sup>II</sup> becomes hard in DMSO<sup>[16]</sup> and its affinity towards the hard N-atom is enhanced accordingly. Evidently, the steric requirements of this bulky ligand prevent the monodentate *n*-but from forming higher Cd<sup>II</sup> complexes.

The only available data concerning Cd<sup>II</sup> complexation by uncharged amines in DMSO do not allow suitable comparisons as they refer to the very bulky tri-*N*-butylamine,<sup>[13]</sup> which is only able to form one mononuclear complex, whereas data relating to secondary monoamines show that they are able to form three successive complexes with the Group 12 dication Hg<sup>II</sup> in DMSO.<sup>[13]</sup> Interesting features emerge on analyzing the values of the thermodynamic functions. The more exothermic stepwise enthalpy value of the second complexation step,  $\Delta H(K_2)$ , as compared with  $\Delta H(K_1)$ , is probably due to the occurrence of particularly extensive desolvation in the first step of complexation: the enthalpy needed for desolvation causes  $\Delta H(K_1)$  to be less exothermic than  $\Delta H(K_2)$  in spite of the greater exothermicity associated with Cd<sup>II</sup>-amine bond formation in the first step.

A switch in the coordination seems to take place at the third complexation step; indeed, the rupture of the solvate shell generally results in the liberation of more solvent molecules than would occur in the case of a simple substitution. Consequently, this step will be characterized by an abnormally large entropy gain while, on the other hand, the

extensive desolvation will absorb extra energy thereby resulting in an abnormally unfavourable enthalpy change.<sup>[16]</sup>

The low enthalpy gain and the slight counteracting effect of the entropy term associated with the third complexation step are consistent with this hypothesis.

**Cd<sup>II</sup>-diamine Systems:** The [CdL]<sup>2+</sup> complexes of the various primary, secondary, and tertiary diamines are all more stable than the corresponding *n*-but complex. Furthermore, their enthalpies and entropies of formation are more exothermic and more negative, respectively, than the corresponding  $\Delta H^\circ_1$  and  $\Delta S^\circ_1$  values with the unidentate amine. This indicates the formation of chelate complexes with all the investigated diamines.

It can be seen in Table 1 that the  $\log \beta_1$  values decrease smoothly as the number of methyl groups is increased on going from primary to secondary diamines (and triamines; see below), while the decrease in both stability and exothermicity is much more evident when tertiary groups are present. Evidently, for primary and secondary diamines, the decrease in stability is primarily due to the different basicities of the N-atoms, which decrease in the order  $\text{NH}_2 > \text{-NHR} > \text{-NR}_2$ .<sup>[18]</sup> The huge decrease in the thermodynamic stability and exothermicity shown by Cd<sup>II</sup>-trmen and, in particular, -tmen systems can readily be explained in terms of the greater steric crowding resulting from complete *N*-methylation leading to decreased strength and marked elongation of the M–N bonds.<sup>[19]</sup> The steric requirements of the ligands evidently play an important role in determining the nature and stoichiometry of the complexes formed; this is even more clearly evidenced by the absence of higher complexes beyond the first one using the bulky tmen (or pmdien when triamines are considered).

The stability constants available in the literature relating to Cd<sup>II</sup> complexation by dmen, trmen, and tmen in water at  $\mu = 1.0$ <sup>[14]</sup> are listed in Table 1. It should be noted that steric requirements also strongly influence the stoichiometry of the species formed in water as dmen and trmen form three successive mononuclear complexes while only two species are formed by the bulkier tmen.

The high values of the stability constants relating to the formation of the second complex and the high exothermicities of the reactions  $\text{ML} + \text{L} \rightleftharpoons \text{ML}_2$  suggest that both ligands are bidentate in these complexes. A reasonable question about this assumption may be raised in view of the high  $K_1/K_2$  value associated with the Cd<sup>II</sup>-trmen system. The highly exothermic value of the stepwise  $\Delta H(K_2)$  favours chelation; in fact, if rough values of  $-22 \text{ kJ mol}^{-1}$  and  $-18 \text{ kJ mol}^{-1}$ , respectively, are calculated for the formation of one Cd<sup>II</sup>–NHR and one Cd<sup>II</sup>–NR<sub>2</sub> bond of a diamine chelate (on the basis of the mean enthalpy values relating to Cd<sup>II</sup>-dmen and Cd<sup>II</sup>-tmen complex formation), then the stepwise value of  $\Delta H(K_2) = -39.6 \text{ kJ mol}^{-1}$  found for the Cd<sup>II</sup>-trmen system [calculated:  $-22 + (-18) = -40 \text{ kJ mol}^{-1}$ ] is wholly consistent with the hypothesis that both the –NR<sub>2</sub> and –NHR groups coordinate to the metal ion in the formation of the [Cd(trmen)]<sup>2+</sup> complex.

Chelation is certainly also achieved when the [Cd(en)<sub>3</sub>]<sup>2+</sup> complex is formed. For the [Cd(dmen)<sub>3</sub>]<sup>2+</sup> system, the abrupt decrease in  $K_3$  might be viewed as an indication of a possible rearrangement of the ligands in this third complexation step. In reality, this is an example illustrating the fact that a determination of the complete thermodynamics of complexation is necessary in order to ensure a reliable interpretation of the reactions involved; the values of the enthalpy and entropy terms are, in fact, in line with a bidentate behaviour of dmen in the [Cd(dmen)<sub>3</sub>]<sup>2+</sup> complex.

Independent FT-IR spectroscopic measurements were carried out in order to corroborate the conclusions drawn from thermodynamic data. The interactions of the amino groups with the metal ions were studied by observing the bathochromic shift of the NH stretching modes of primary (at 3360 and 3300 cm<sup>-1</sup>) and secondary (at 3313 cm<sup>-1</sup>) groups in DMSO when Cd<sup>II</sup> ions were added to amine solutions.<sup>[3g]</sup> Figure 2 shows the spectra of a series of solutions containing Cd<sup>II</sup> and different dmen-to-metal ratios,  $R_c$ . It can be seen that up to  $R_c = 3$  only the band due to the bonded amine (at 3230 cm<sup>-1</sup>) is present, while the band due to the free amino group is present only when  $R_c > 3.0$ , clearly indicating that all the –NH groups are coordinated to the Cd<sup>II</sup> ion in each of the complexation steps. Similar measurements were also carried out for the other diamine (and triamine, see below) systems and confirmed the hypotheses suggested on the basis of the thermodynamic data.

**Cd<sup>II</sup>-triamine Systems:** The higher values of the stability constants and the higher exothermicities associated with the formation of the [CdL]<sup>2+</sup> complexes of the triamines dien and dmdien, compared with those of the corresponding diamines, indicate that these ligands are tridentate, forming two fused five-membered chelate rings. The same arguments discussed in detail for the Cd<sup>II</sup>-diamine systems can also be applied to the Cd<sup>II</sup>-triamine systems to account for the decrease in stability and exothermicity observed on going from primary to tertiary triamines. In particular, it should be stressed that in this case as well, and to an even greater extent, the values of the stability constants and enthalpy gains for Cd<sup>II</sup>-pmdien differ greatly from the values found for the secondary dmdien, further supporting the statement that, in addition to the decreased basicity of the amino groups, steric crowding plays a very important role in determining the coordinating abilities of the amines. The thermodynamic parameters for the Cd<sup>II</sup>-pmdien system show better agreement with a bidentate coordination for this ligand; no additional information could be obtained by independent spectroscopic measurements.

The Cd<sup>II</sup> ion is certainly hexacoordinated ion in the ML<sub>2</sub> complexes with the other triamines. This is unequivocally indicated by the thermodynamic parameters and was confirmed by independent FT-IR measurements run on the Cd<sup>II</sup>-dien and -dmdien systems, which did not show the presence of uncoordinated amino groups up to  $R_c > 2$  (see above for details). Evidently, a certain “preorganization” of the diamines and triamines is responsible for their ability to saturate the coordination sphere of the Cd<sup>II</sup> ion, which is not achieved using monoamines.

It should be noted that  $[\text{Cd}(\text{dien})_2]^{2+}$  is formed alongside  $[\text{Cd}(\text{dien})]^{2+}$  as a result of the higher stability constant relating to the second complexation step ( $\log K_2 = 8.74$ ), which is not seen in water. This result may be explained by considering that in  $\text{Cd}^{\text{II}}$  complexation by dien the desolvation of the species involved occurs mainly in the first step of complexation; this is confirmed by the lower enthalpy gain and the unfavourable entropy term associated with the formation of the ML complex as compared to the stepwise terms relating to the formation of the  $\text{ML}_2$  species [ $\Delta H(K_2) = -72$ ,  $T\Delta S(K_2) = -22.3 \text{ kJ mol}^{-1}$ ].

**$\text{Cd}^{\text{II}}$ - vs.  $\text{Ag}^{\text{I}}$ -amines Complexation:** In Figure 3, the stabilities of the 1:1 and 1:2  $\text{Cd}^{\text{II}}$ -amine complexes are plotted against the corresponding stabilities of the  $[\text{AgL}]^+$  and  $[\text{AgL}_2]^+$  species<sup>[3a–3e]</sup> in DMSO. The positive slope (1.2) of the line, calculated by taking into account the  $\log \beta_1$  values for all the amines except *n*-but and pmdien (for the reasons discussed below), indicates that the stabilities of the 1:1  $\text{Cd}^{\text{II}}$ -amine complexes are invariably greater than those of the corresponding  $\text{Ag}^{\text{I}}$  complexes (although almost of the same order of magnitude in the case of tmen); this probably reflects the higher affinity of the N atom for the soft-hard borderline divalent acceptor  $\text{Cd}^{\text{II}}$  than for the very soft univalent  $\text{Ag}^{\text{I}}$  ion. The linearity evident in Figure 3 seems to indicate that the different coordination structures of the two metal ions in DMSO, octahedral for  $\text{Cd}^{\text{II}}$  and tetrahedral for  $\text{Ag}^{\text{I}}$ <sup>[16]</sup> does not play a significant role in the ML complexation by the polyamines en, dmen, tmen, dien, and dmdien.

In the case of the bulkier *n*-but and pmdien, however, the selectivity of the ligands changes and  $\text{Ag}^{\text{I}}$  complexation becomes more favourable than  $\text{Cd}^{\text{II}}$  complexation. The steric hindrance of the ligands, together with the different structures of the metal ion solvates, is likely to be responsible for this behaviour. In fact, the environment of a tetrahedrally coordinated metal ion is less crowded compared with an octahedral structure<sup>[15c]</sup> and may allow enough space for the steric bulk of the *n*-but or pmdien molecules to no longer be significant.

In line with this hypothesis is the fact that pmdien is able to act as a terdentate ligand in the  $[\text{AgL}]^+$  complex,<sup>[3e]</sup> while bidentate ligation is more reasonable in the  $[\text{CdL}]^{2+}$  species (see the above discussion).

Furthermore, the  $\log \beta_2$  values for the dmen and en systems fall on the line shown in Figure 3, indicating that the same arguments invoked to explain the trends observed for their ML ( $M = \text{Cd}, \text{Ag}$ ) species can also be applied in rationalizing the behaviour of their  $\text{ML}_2$  complexes.

Considering the dien and dmdien  $\text{ML}_2$  compounds, the huge increase in stability of the  $\text{Cd}^{\text{II}}$  complexes with respect to their  $\text{Ag}^{\text{I}}$  counterparts certainly stems from the fact that terdentation is also achieved in the second complexation step using  $\text{Cd}^{\text{II}}$ . This is not possible in the case of  $[\text{AgL}_2]^+$  as the maximum coordination number of silver(I) in solution is usually four.<sup>[20]</sup>

## Conclusions

$\text{Cd}^{\text{II}}$  complexes with open-chain N-donors in DMSO have been shown to be stable. Hexacoordination of the metal ion is achieved with primary and secondary polyamines. Complexation by primary and secondary amines is favoured in DMSO compared to that in water due to the less extensive hydrogen bonding of the amines in the aprotic solvent. The greater solvation of the metal ion in DMSO prevails in governing the stability trend in the case of the  $\text{Cd}^{\text{II}}$ -trmen and -tmen systems, the complexes being more stable in water than in DMSO.

The *N*-functionalization of the ligands has a strong influence not only on the stoichiometry and the nature of the  $\text{Cd}^{\text{II}}$  complexes formed but, very interestingly, on the selectivity of the ligands towards metal ions as well, as shown by a comparison with the available data on silver(I) complexation by the same amines.

## Experimental Section

**Warning!** Although metal perchlorates solvated by DMSO are generally explosive under certain conditions,<sup>[11,21]</sup> no problems were encountered when handling  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ . Nevertheless, as a precaution, the salt should only be prepared in small quantities. Great caution has been exercised when handling DMSO solutions of poisonous cadmium salts, since they are easily carried through the skin by DMSO, which penetrates lipid tissues at an astonishing rate. Moreover, DMSO dissolves many natural and synthetic polymers.<sup>[11,21]</sup> These solvent properties were, of course, taken into account when designing the apparatus (e.g. the ion-selective cadmium electrode was externally covered by Teflon), particularly so as to ensure good personal and environmental protection.

**General Remarks:**  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$  was prepared by precipitation from an almost saturated solution of the hydrated salt (Aldrich; 98%) in dimethyl sulfoxide by the addition of diethyl ether. It was collected by filtration and dried in vacuo for several days at 50 °C. The compound was characterized as  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$  by elemental analysis and by titration of  $\text{Cd}^{\text{II}}$  with EDTA<sup>[22]</sup> using Eriochrome Black T as indicator. The molar conductivity of a 1.00 mmol  $\text{dm}^{-3}$  solution of  $\text{Cd}(\text{ClO}_4)_2$  in DMSO (about 75  $\Omega^{-1} \text{ m}^{-1} \text{ cm}^2$ ) was measured with a Metrohm 712 conductometer and was found to be in good agreement with the accepted value for 1:2 electrolytes in DMSO.<sup>[23]</sup> Dimethyl sulfoxide (Fluka, > 99%) was purified by distillation according to the described procedure<sup>[3a]</sup> and stored over 4 Å molecular sieves. The ligands *n*-but, en, dmen, trmen, tmen, dien, and pmdien (Aldrich, >97%) were purified by fractional distillation.<sup>[24]</sup> The ligand dmdien was synthesized and purified as described previously.<sup>[25,26]</sup> Its purity (> 99%) was checked by GC mass spectrometry and <sup>1</sup>H NMR measurements.  $\text{Cd}^{\text{II}}$  perchlorate stock solutions were prepared by dissolving weighed amounts of the adducts in anhydrous DMSO and their concentrations were checked by titration with EDTA.<sup>[22]</sup> The supporting salt  $\text{NEt}_4\text{ClO}_4$  was recrystallized twice from methanol and dried at 110 °C. The solutions of the ligands were prepared by dissolving weighed amounts in DMSO and were standardized by thermometric titration with standard  $\text{HClO}_4$  solutions. All standard solutions were prepared and stored in an MB Braun 150 glove box under a controlled atmosphere containing less than 1 ppm of

water. The water content in the solutions, typically 10–20 ppm, was determined using a Metrohm 684 KF coulometer.

**Potentiometric Measurements:** All measurements were carried out in the aforementioned MB Braun 150 glove box in a thermostatted cell maintained at  $298.0 \pm 0.1$  K. The experimental data required for the determination of the stability constants of the Cd<sup>II</sup>-polyamine complexes were the equilibrium concentrations of the cadmium ion, which were obtained from the e.m.f. data of a galvanic cell. For this purpose, a Weiss WCDIOOI Cd ion selective electrode with a Teflon body was used as the working electrode and a Metrohm 6.0718.000 silver electrode was used as the reference. To Cd<sup>II</sup> solutions in the concentration range  $2.00 < c_{\text{Cd}}^0 < 20.00$  mmol dm<sup>-3</sup>, ligand solutions of known concentration were added and the free cadmium(II) concentration was measured after each addition of titrant. Some titrations were carried out in duplicate to verify the reproducibility of the systems. Equilibrium was typically reached in 2–5 minutes. The Nernstian response of the Cd electrode was checked in the range  $10^{-2} < [\text{Cd}^{\text{II}}] < 10^{-6}$  mmol dm<sup>-3</sup>. The computer program Hyperquad<sup>[27]</sup> was used to calculate the stability constants.

**Calorimetric Measurements:** A Tronac model 87–558 precision calorimeter was employed to measure the heats of reaction. The calorimeter was calibrated by titrating tris(hydroxymethyl)amino-methane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be  $\Delta H^\circ = -47.59$  kJ mol<sup>-1</sup>, in good agreement with the accepted value of  $-47.53 \pm 0.13$  kJ mol<sup>-1</sup>.<sup>[14]</sup>

The calorimetric titrations were performed at  $298.00 \pm 0.02$  K by adding known volumes of ligand solutions ( $50 < c_{\text{L}}^0 < 200$  mmol dm<sup>-3</sup>) to 20 mL of cadmium(II) solution ( $2.00 < c_{\text{Cd}}^0 < 20.0$  mmol dm<sup>-3</sup>). In order to reach higher ligand-to-metal ratios so as to confirm that no higher complexes beyond the reported ones were formed by *n*-but, trmen, tmen, and pmdien, “reverse” calorimetric titrations were carried out for the relevant systems. In these titrations, Cd<sup>II</sup> ion solutions (100 mmol dm<sup>-3</sup>) were added to solutions of ligand ( $\approx 30$  mmol dm<sup>-3</sup>).

For each titration run, *n* experimental values of the total heat produced in the reaction vessel ( $Q_{\text{ex},j}$ ,  $j = 1$  to  $n$ ) were calculated as a function of the amount of titrant added. These values were only corrected for the heat of dilution of the titrant ( $Q_{\text{dil},j}$ ), which was determined separately. The heat of dilution of the titrate was found to be negligible in the metal ion concentration range used. The net heat of reaction at the *j*th point ( $Q_{\text{r},j}$ ) was obtained from the difference  $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$ .

The quantity  $\Delta h_{\text{v}}$ , the total heat per mol of metal ion, was defined and calculated by dividing the net heat of reaction by the number of mol of metal ion in the calorimetric vessel. The enthalpy and entropy changes of the identified complexes were calculated using a Fortran program, MQ90,<sup>[28]</sup> with  $q_{\text{r},j}$  ( $= Q_{\text{r},j} - Q_{\text{r},j-1}$ ) or  $\Delta h_{\text{v}}$  as the error-carrying variables.

**FT-IR Measurements:** The FT-IR measurements were made using a Bio-Rad FTS40 spectrometer (maximum resolution 4 cm<sup>-1</sup>; 16 scans). A cell with barium fluoride windows (thickness of 32 μm) was used. The cell was filled and sealed in a glove box and then transferred to the spectrometer.

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