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Thermodynamic study of Cd(II) complex formation with tripodal N-donor ligands in DMSO

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Abstract The complex formation of Cd(II) with N-donor ligands in dimethylsulfoxide (DMSO) is investigated by means of potentiometry and titration calorimetry. The ligands considered in this work are tripodal polyamines and polypyridines: 2,2′,2″-triaminotriethylamine (TREN), tris(2-(methylamino)ethyl)amine (Me_3TREN), tris(2-(dimethylamino)ethyl)amine (Me_6TREN), tris[(2-pyridyl)methyl] amine (TPA) and 6,6′-bis-[bis-(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine (BTPA). These ligands are characterized by a systematic modification of the donor groups to relate their structure to the thermodynamics of the complexes formed. The TREN and Me_3TREN ligands form highly stable species. The stability of the complex formed with the fully methylated Me_6TREN is much lower than with other polyamines and the enthalpic and entropic terms suggest an incomplete coordination to the metal ion. In general, the TPA ligand forms complexes less stable than TREN and Me_3TREN as a result of the combination of higher structural rigidity of TPA and lower basicity of pyridine moiety with respect to primary and secondary amines. Pyridine-containing ligands display, in general, a less unfavorable formation entropy than tripodal polyamines here considered. In particular, TPA forms a more stable 1:1 species with respect to Me_6TREN due to the entropic term, being the enthalpy less negative. The ligand BTPA is able to form only a monometallic complex, where the metal ion is likely to be encapsulated as indicated by the obtained thermodynamic parameters.

Keywords Cadmium (II) · Polyamines · Non-aqueous solution · Potentiometry · Calorimetry · Thermodynamics

Introduction

Interesting topics are provided in the field of coordination chemistry of polydentate amines and pyridines towards metal ions as a result of a wide range of applications of their complexes to prepare recognition and sensing molecular devices [1, 2] and develop receptors for metal ions of environmental importance, such as Cd(II), Hg(II) or Pb(II) [1, 3] lanthanides [4, 5] and anions [6].

The interest in the solution chemistry of cadmium and related compounds is due to the severe toxicity of this metal which is widely present in many industrial and mining activities. Its effect is tributable to interactions of this ion with proteins containing thiol-rich zinc-binding sites: the Cd(II) ion substitutes Zn(II) with a geometry different from the natural coordination and damages the protein function. For this reason, the removal of this toxic heavy metal contaminant, as well as others like Hg(II) and Pb(II), from industrial waste streams is currently an environmental issue of great importance. Many techniques are available to this purpose: precipitation, activated carbon absorption, bioremediation, reverse osmosis, electrolysis, cementation, irradiation, zeolite absorption, evaporation, membrane processes are some of the treatment methods used for heavy metal-containing waste remediation [7]. Liquid or supported membrane extraction [8] or functionalized materials [9] are important when high selectivity is required. For this reason, both the methods require the presence of an organic ligand able to strongly bind the heavy metal for its selective recovery.

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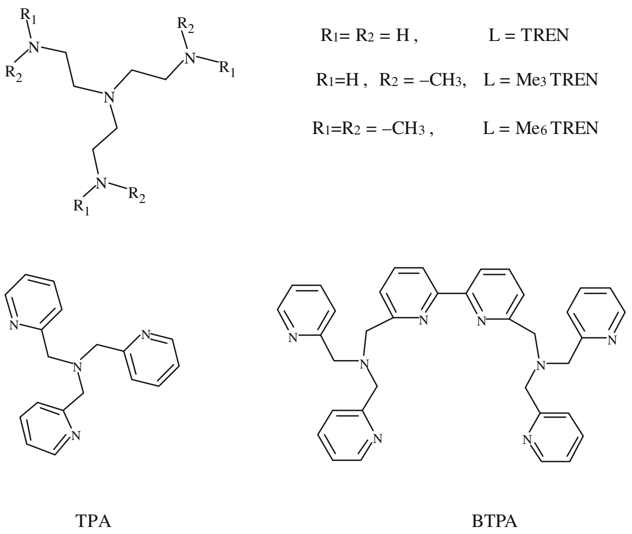

Scheme 1 Tripodal ligands studied in this work

Therefore, the determination of the thermodynamic parameters of complex formation with Cd(II) in water or organic solvent provide useful information for the designing of selective extraction and sensing systems [7]. Furthermore, their determination may be useful to get access to the formation constants of other ions, like Co(II), by means of competitive methods as previously reported [10, 11].

In this article, we report the results of study of the complex formation in the organic solvent dimethylsulfoxide (DMSO) between Cd(II) ion and the tripodal ligands shown in Scheme 1: 2,2′,2″-triaminoethylamine (TREN), tris(2-(methylamino)ethyl)amine (Me_3TREN), tris(2-dimethylamino)ethyl)amine (Me_6TREN), tris[(2-pyridil)methyl]amine (TPA). Furthermore, the study has been extended to the complexes formed with 6,6-bis-bis-(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine (BTPA), which is essentially a TPA dimer, potentially able to host two metal ions [12]. The stability constants of Cd(II) with the same ligands were obtained by potentiometry using an ion selective electrode and the corresponding reaction enthalpy values were determined by titration calorimetry.

Experimental

Materials

$Cd(DMSO)_6(ClO_4)_2$ was prepared as previously described [10, 11]. Tetraethylammonium perchlorate (TEAP) (Aldrich >97%) was recrystallized from methanol and then dried under vacuum at 110 °C. The ligands TREN and Me_3TREN (Aldrich) were purified by distillation. The ligands Me_6TREN, TPA and BTPA were prepared according to literature procedures [13–15], and their purity checked by LC-MS and NMR analysis.

Dimethylsulfoxide (Aldrich 99%) was purified by distillation and stored under nitrogen with molecular sieves. Perchlorate stock solutions of Cd(II) ion were prepared by dissolving in anhydrous degassed DMSO weighed amounts of the adducts and their concentrations were checked by titration with EDTA.

Solutions of the ligands were prepared by dissolving weighted amounts in DMSO and standardized by thermometric titration with standard $HClO_4$ solutions. All standard solutions were prepared and stored in a glove box under a controlled atmosphere containing less than 1 ppm of water and less than 1 ppm of oxygen. The water content in the solutions, typically 10 ÷ 20 ppm, was determined by a Metrohm Karl Fischer Coulometer.

Potentiometric measurements

All measurements were carried out in the glove box in a thermostated cell maintained at 25.0 °C. The free concentrations of cadmium ion were obtained from the e.m.f. data of a galvanic cell measured by means of an Amel 338 pHmeter equipped with a Cd ion selective electrode (Weiss Research) and a Methrom Ag/AgCl reference. Aliquots of ligand solutions of known concentrations were added to solutions of Cd(II) perchlorate only ($1.00 < C^{\circ}_{\mathrm{Cd}} < 10.00$ mmol dm^{-3}) of known concentration and the free metal concentration was measured. Equilibrium was reached typically in 2–3 min. The computer program Hyperquad [16] was used for the calculation of the stability constants.

Calorimetric titrations

A Tronac model 87-558 precision calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water and used to measure the reaction heats. The experimental value of the heat of neutralization of tham was found to be $\Delta H^{\circ} = -47.58$ kJ mol^{-1}, in good agreement with the accepted value [17] of -47.53 ± 0.13 kJ mol^{-1}.

The calorimetric titrations were performed at 25.00 ± 0.02 °C by adding known volumes of ligand solutions ($30 < C^{\circ}_{\mathrm{polyamines}} < 250$ mmol dm^{-3}) to 20 mL of metal solutions ($3.00 < C^{\circ}_{\mathrm{Metal}} < 16.0$ mmol dm^{-3}). The measured heats were corrected for the dilution heat of the ligands. In the case of BTPA, 20 mL of ligand solutions ($0.7 < C^{\circ}_{\mathrm{BTPA}} < 1.5$ mmol dm^{-3}) were titrated with solutions of the metal ($8 < C^{\circ}_{\mathrm{Metal}} < 10$ mmol dm^{-3}). This was done for the low solubility of BTPA in DMSO

(<2 mmol dm^{-3}). The computer program HyperDeltaH [18] was used for the calculation of the enthalpy changes.

FT-IR spectroscopy

The FT-IR spectra were obtained using a Bruker Vector 22 spectrometer using a cell with barium fluoride windows. The cells were filled and closed in glove box and quickly transferred to the spectrometer. The C^{2+}_{Cd} was about 50 mmol dm^{-3}, and $C^{\circ}_{\mathrm{TREN}}$ was varied from 50 to 150 mmol dm^{-3}.

Results and discussion

The stability constants and reaction enthalpy values best fitting the experimental potentiometric and calorimetric data are reported in Table 1 along with the calculated entropic terms with the corresponding limits of error. Also, the available data in water are reported [19, 20].

Tripodal polyamines

Selected potentiometric data points are plotted in Fig. 1 in terms of Δe.m.f. (the difference between e.m.f. at a given concentration of added ligand and without ligand) versus $R_c = C_L/C_M$ (total ligand/total metal concentration) for the Cd–TREN system, together with the percent distribution diagram. The formation of two well-distinct CdL_j^{2+} ($j = 1, 2$) species is clearly evident. In Fig. 2, the Δh_v (total molar enthalpy change per mole of metal ion) as a function of R_c is reported for the titration of Cd with all tripodal polyamines. From the sharp change of slope of the curve relative to Cd(II)–TREN titration the formation of two CdL and CdL_2 species of high stability is clearly confirmed.

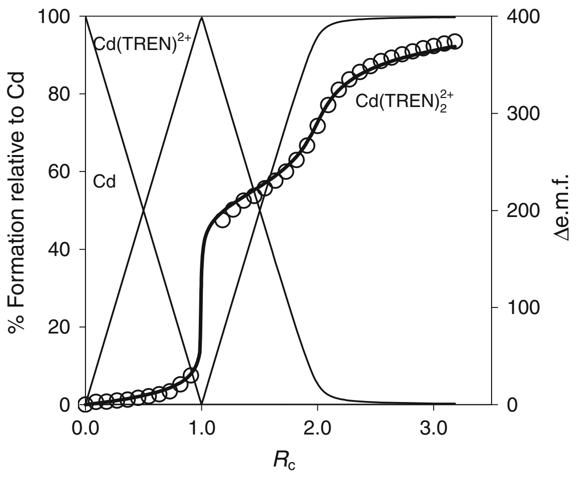

Fig. 1 Experimental (open *circle*) and calculated (*line*) Δe.m.f. values for the titration of Cd^{2+} with TREN. The percent species distribution is also reported

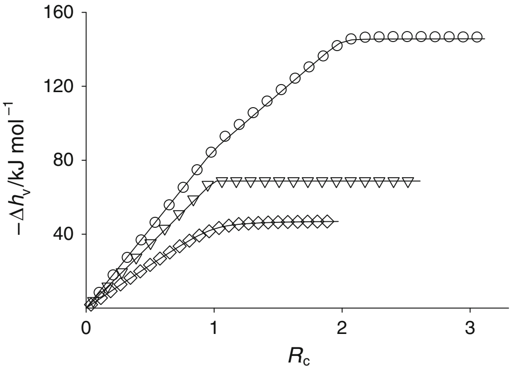

Fig. 2 Total molar enthalpy changes per mole of metal, Δh_v, as a function of the ligand to metal ratio $R_c = C_L/C_{\mathrm{Cd}}$ in DMSO for: (*open circle*) L = TREN, $C^{\circ}_{\mathrm{Cd}} = 10.8$ mmol dm^{-3}; (*inverted open triangle*) L = Me$_3$TREN, $C^{\circ}_{\mathrm{Cd}} = 16.1$ mmol dm^{-3}; (*open diamond*) L = Me$_6$TREN, $C^{\circ}_{\mathrm{Cd}} = 7.0$ mmol dm^{-3}. Only some experimental points are plotted

Table 1 Overall stability constants and thermodynamic functions for the reactions $\mathrm{Cd}^{2+} + j\mathrm{L} \rightleftharpoons \mathrm{CdL}_j^{2+}$ (L = tripodal polyamine) in DMSO (NEt$_4$ClO$_4$ 0.1 mol dm^{-3}, 25 °C). The errors quoted correspond to three standard deviations

DMSO	ML$_j$	log β_j	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1}	$-\Delta S°$/J mol^{-1} K^{-1}
TREN[a]	CdL	12.32 ± 0.05	70.2 ± 0.3	86 ± 2	53.0
	CdL$_2$	17.39 ± 0.07	99.1 ± 0.4	146 ± 3	157.3
Me$_3$TREN	CdL	9.87 ± 0.01	56.36 ± 0.06	69 ± 3	42.4
Me$_6$TREN[b]	CdL	4.18 ± 0.02	23.9 ± 0.1	47 ±1	77.5
TPA[c]	CdL	6.29 ± 0.01	35.9 ± 0.1	42.2 ± 1	21.1
	CdL$_2$	8.91 ± 0.04	50.8 ± 0.2	82.8 ± 3	107.3
BTPA	CdL	10.52 ± 0.04	60.0 ± 0.2	61 ± 3	3.4

[a] $\log\beta_1 = 12.35$

[b] $\log\beta_1 = 7.32$ in water (25 °C, $I = 1.0$ M) [19]

[c] $\log\beta_1 = 9.9$, $\Delta H_1° = -58.6$; $\log\beta_2 = 14.3$, $\Delta H_2° = -74.5$ kJ mol^{-1} in water (20 °C, $I = 0.1$ M) [20]

The FT-IR spectrum on Cd–TREN solutions where $R_c = 1$ is consistent with a complete coordination of the tripodal polyamine to the metal ion, as evident from the absence of free –NH$_2$ group band (Fig. 3). In this case, the Cd(TREN)$^{2+}$ complex could be 5- or 6-coordinated: spectroscopic evidences for Co(TREN)$^{2+}$ in water [21] and the very negative entropy associated to the second coordination step, indicate that desolvation occurred mainly in the formation of the 1:1 complex. Therefore, a tripod bipyramid structure for Cd(TREN)$^{2+}$ is likely to be the correct one, with one axial solvent molecule coordinated.

When the stability of the 1:1 complex formed is compared with available data in DMSO for other linear polyamines it emerges that the complexes with TRIEN are slightly less stable ($\log \beta_{1\ \mathrm{TRIEN}} = 11.81$, $\Delta H^\circ_{1\,\mathrm{TRIEN}} = -79$ kJ mol^{-1}) [22] than those formed with TREN suggesting a slight preference for the tripodal ligand. In the second complexation step, a species having the same order of stepwise stability as that found for the octahedral 1:2 Cd–TREN system (stepwise $\log K_{2\ \mathrm{TREN}} = 5.2$, $\Delta H^\circ_{\mathrm{K_2\,TRIEN}} = -63$ kJ mol^{-1}) [22] is formed. This indicates that the initial five-coordinate complex is converted into a octahedral 1:2 species. From FT-IR at $R_c = 2$ (Fig. 3), it is evident that free –NH$_2$ groups are certainly present, but it is difficult to safely draw conclusions about the coordination of this second ligand. However, two hypothesis seem acceptable: (i) two primary –NH$_2$ groups of the second entering TREN ligand are bonded to Cd(II) and form a large eight-membered ring; (ii) a five-membered chelate ring is formed, involving one tertiary and one primary amino group. Hypothesis (i) implies a coordination similar to that observed in an octahedral solid structure of a polymeric species formed by Cd(II) [23], where one TREN ligand is wrapped around a Cd(II) ion and other two TREN are able to fully coordinate Cd(II) ion with two –NH$_2$ terminal groups and form a large ring with a second Cd(II) ion. Hypothesis (ii) is reasonable as well, since the stepwise constant ($\log K_2$) is intermediate between those found for the 1:1 Cd complex with *N*,*N*,*N*′-trimethylethylenediamine (TRMEN) ($\log K_1 = 4.28$) and ethylenediamine (EN) ($\log K_1 = 5.88$), both forming five-membered chelate ring [11].

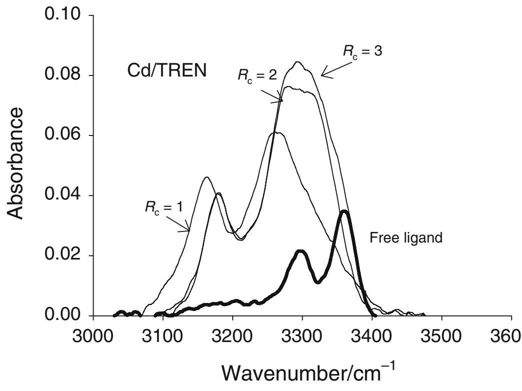

Fig. 3 FT-IR spectra of Cd^{2+}/TREN solution ($R_c = 1$–3, $C_{\mathrm{Cd^{2+}}} = 50$ mM) and of free TREN (*bold line*)

The 1:1 complex of Cd(II) with Me$_3$TREN is less stable and exothermic than with TREN and this can be ascribed to the lower stabilization of the complex, due to the minor extent of hydrogen bonds formed with the solvent, which are known to increase the electron donation to the metal ion [24]. Furthermore, the introduction of methyl groups increases the steric strain of the structure of the complex. These effects are even more evident when the complex with the fully methylated Me$_6$TREN ligand is formed as a marked drop in stability and less negative enthalpy with respect to Me$_3$TREN is observed ($\Delta\log\beta_1$ (Me$_3$TREN − Me$_6$TREN) = 5.6, $\Delta(\Delta H_1) = -22$ kJ mol^{-1}). In both the cases, no evidence of a 1:2 species is observed from calorimetric (Fig. 2) and potentiometric measurements. When the Me$_6$TREN is compared with other fully methylated linear polyamines it can be observed that the complex formed is more stable than that formed with the triamine *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDIEN, $\log\beta_1 = 3.8$ $\Delta H_1 = -43.5$ kJ mol^{-1} [11]) but much less than that for the linear tertiary tetramine 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTRIEN, $\log\beta_1 = 6.3$ $\Delta H_1 = -68$ kJ mol^{-1}) [22]. This result suggests an incomplete coordination of Me$_6$TREN to Cd(II) ion which seems the result of a solvent effect rather than of a structural feature of the ligand, since in water a much higher stability constant is found ($\log\beta_1 = 7.32$) [19]. This could be explained by the fact that DMSO is a much stronger solvating agent for Cd(II) than water, as evident from transfer Gibbs free energy($\Delta G_{\mathrm{transfer}}$ water → DMSO = −55.9 kJ mol^{-1} [25], and thus a better competitor for the tertiary amine.

Tripodal polypyridines

From the analysis of the calorimetric data for Cd(II)–TPA and –BTPA systems (Fig. 4), it is well clear that an enthalpy stabilized 1:1 species is formed.

Polypyridine and aminopyridine complexes with some transition metals are characterized by higher stabilities in water than in DMSO as found in previous works [10, 11]. Differently from ligands containing primary or secondary amine groups, for which the greater solvation of ligands in water overcomes the greater solvation of metal ions in DMSO [10], for pyridinic ligands the stability constants in these two solvents follow the trend expected on the basis of metal ion solvation [26]. In agreement with these observations, we find here that Cd(II)–TPA system forms the same species and in water [20] and in DMSO (Table 1),

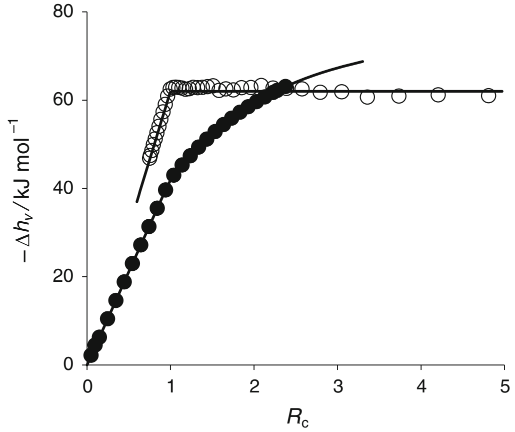

Fig. 4 Total molar enthalpy changes per mole of metal, Δh_v, as a function of the ligand to metal ratio $R_c = C_L/C_M$ in DMSO for: (*filled circle*) L = TPA, $C_{Cd}° = 3.5$ mmol dm^{-3}; (*open circle*) L = BTPA (ligand in the cell), $C^{\circ}_{Cd} = 8.1$ mmol dm^{-3}

but less stable and with less negative enthalpy in the latter medium. The TPA ligand is likely to be completely coordinated to Cd in the 1:1 species, given the values of the thermodynamic parameters found. Also the 1:2 species is formed with a large enthalpy gain, whereas the entropic term is largely opposing the reaction. Our results can be explained by admitting that the Cd(II) ion is able to expand its coordination number when coordinating a second TPA unit, as found in the solid state for $[Cd(TPA)_2](ClO_4)_2]$ complex [27], where this cation is octa-coordinated.

The stability of the $Cd(BTPA)^{2+}$ complex is higher and the enthalpy more negative than that found for $Cd(TPA)^{2+}$ indicating that more donor groups are coordinated in this case. This is also in agreement with the entropy value (Table 1) which reflects the extensive desolvation accompanying the 1:1 complex formation (i.e. more solvent molecules removed). Not much can be said about the structure in solution of $Cd(BTPA)^{2+}$ but it was already reported [28] that BTPA was not able to fully coordinate Zn(II), Fe(II) and Ru(II), leaving two pyridinic nitrogens unbound. However, this result is also in agreement with the above mentioned possibility of Cd(II) to bind more than six N-donor groups.

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