Thermodynamics of Complex Formation of Silver(I), Cadmium(II) and Cobalt(II) with Open-Chain Polyamines in Dimethyl Sulfoxide and Molecular Dioxygen Binding to Cobalt(II) Complexes

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Ag^{I}, Cd^{II} and Co^{II} complex formation with the primary and tertiary tetraamines 1,4,7,10-tetraazadecane (trien) and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (hmtrien) has been studied at 298 K in the aprotic solvent dimethyl sulfoxide (DMSO) and in an ionic medium set to 0.1 mol·dm^{-3} with Et_4NClO_4 under anaerobic conditions. UV/Vis spectrophotometric and calorimetric measurements have been carried out to obtain the thermodynamic parameters for the systems investigated. Mononuclear 1:1 complexes are formed for all systems. In addition, trien also forms the ML_2 mononuclear complex and a polynuclear M_2L_3 species with M = Cd^{2+} and Co^{2+}. All the complexes are enthalpy stabilized, whereas the entropy changes counteract the complex formation. The results are discussed in terms of the different basicities, steric requirements and solvation both of the ligands and of the complexes formed. The influence of *N*-alkylation on the selectivity of the ligands towards metal ions is analysed. In the case of the Co^{II} complexes, their ability to take up dioxygen has also been studied by voltammetric and UV/Vis measurements and gasometric absorption.

Introduction

A comparison of the properties of transition-metal complexes with primary, secondary and tertiary amine ligands reveals several remarkable effects of *N*-alkylation of the ligands on the thermodynamics and kinetics[1−5] of complex formation and on ligand substitution reactions.

In a very recent work[3] it was shown that *N*-alkylation causes several contradictory effects: on one hand, the nitrogen atoms become better σ-donors as a consequence of the introduction of electron-donating substituents, which shifts the redox potential of the $M^{n+1}L_m/M^nL_m$ couples cathodically, while on the other hand, solvation and steric effects shift the potential anodically. As the solvation effects are larger, *N*-alkylation stabilizes low-valent transition metal complexes and the redox potentials of the couples are shifted anodically for L = tertiary amines.[1,3,5,6]

In addition, the stability constants of the complexes with the tertiary amines are smaller than those with primary and secondary amines,[3,5−9] this behaviour mainly being attributed to outer-sphere solvation effects and to ligand strain energy.[5c,5e,5g,5h]

In the last few years, a variety of polyamine structures have been investigated in water[9−18] and in non-aqueous solvents[8,19−25] with the aims both of improving knowledge of the coordination chemistry of soft and hard metal ions and of studying how basicities and steric effects may affect the selectivity pattern in metal coordination.

As examples of the great interest in these ligands and their application it should be remembered that they show potential for use as sequestering agents for metal ions of environmental importance,[18] both toxic and essentials, such as Cd^{II}, Pb^{II}, or Ca^{II}, Mg^{II}, Zn^{II}, Mn^{II}, Fe^{III}, Cu^{II}, and employment as models for carrier molecules,[6,15,18,26−31] such as in Cu^{I} or Co^{II} complexes.

In this context, the papers published by our group concerning the complexation of transition-metal ions such as Ag^{I}, Cd^{II} and Co^{II}[8,22a−22d] have shown that nitrogen functionalization strongly influences not only the stoichiometry and the nature of all the metal ion complexes formed, but also, very interestingly, the selectivity of these ligands towards metal ions.[8c] In fact, while − for example − dien shows a higher affinity for the borderline soft/hard divalent Cd^{II} than for the very soft univalent Ag^{I} ion, the opposite is true with regard to pmdien. As far as cobalt(II) complexes are concerned, different *N*-alkylation of polyamines also has important effects on the dioxygen affinity of these complexes:[6] electron transfer between the metal centre and di-

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oxygen should depend on the available electron density at the central metal ion, which is in turn greatly affected by the electron-donor properties of the ligands in the coordination sphere.[26,27]

As an extension of previous works we report here on results concerning the complex formation of Ag^{I}, Cd^{II} and Co^{II} with the differently *N*-methylated polyamines 1,4,7,10-tetraazadecane (trien) and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (hmtrien) in the aprotic solvent dimethyl sulfoxide (DMSO). For silver(I), data relating to trien complexation in DMSO had been published previously.[22d]

Especially interesting comparisons between the monovalent d^{10} acceptor silver(I), of very soft character, and the divalent and mildly soft Cd^{2+} should be possible. In addition, although the complex formation of Cd^{II} has been extensively studied in the past[32–34] and in more recent[7,17,33] years, nevertheless few thermodynamic data concerning its ability to coordinate simple open-chain N-donor ligands are available.[7,8c,34f,35] Moreover, Co^{II} model compounds are of great interest since they may provide a better understanding of biological molecules and assist in the study of new homogeneous catalysts for selective oxidations under mild conditions.[26–31]

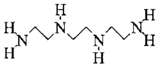
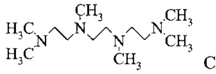
The values of the stability constants of the various systems investigated were determined by different techniques. Direct potentiometric techniques were used for Ag^{I} and Cd^{II} (see Exp. Sect., potentiometric measurements), whereas for the Co^{II}/polyamine systems, UV/Vis spectroscopic measurements were employed, with the use of Cd^{II} as auxiliary metal ion[36] for reasons discussed in a previous paper.[8b] The enthalpy values were obtained by direct calorimetric titrations. In the case of the Co^{II} complexes, their ability to take up dioxygen was also studied by voltammetric and UV/Vis measurements and by gasometric absorption. All measurements were performed at 298 K and in an ionic medium adjusted to 0.1 mol·dm^{-3} with Et_4NClO_4 as neutral salt.

Results

Computer treatment of the potentiometric experimental data shows that the best fit is obtained when the polynuclear species M_2L_3 (M = Cd, Co) is considered in addition to ML and ML_2 mononuclear ones for metal(II)/trien systems, whereas the ML species is the only one formed in all other cases. The overall stability constants obtained from the potentiometric data minimization procedures, with the corresponding limits of error, are listed in Table 1 for the reactions $i\,M^{n+} + j\,L \rightleftarrows M_iL_j^{\,n+}$ (M = Ag^{I}, Cd^{II}, Co^{II}, L = trien and hmtrien). Figure 1 gives the distributions of Cd^{2+} and Co^{2+} among the various species. Figure 2 gives Δh_v, the total molar enthalpy change, as a function of $R_c = c_L/c_M$ (total ligand/total metal concentration) for the Cd^{2+}/trien and Co^{2+}/trien systems.

Some conclusions about the prevalent coordinated species formed can be drawn from examination of the shapes of the curves, which are fully consistent with the information obtained from analysis of the potentiometric data.

Table 1. Overall stability constants and thermodynamic functions for the reaction reactions $i\,M^{n+} + j\,L \rightleftarrows M_iL_j^{\,n+}$ (M = Ag^{I}, Cd^{II}, Co^{II}, L = trien and hmtrien) in DMSO at 298 K and I = 0.1 mol·dm^{-3} and in water;[7,15] the errors quoted correspond to three standard deviations

Ligand	Complex	$\log\beta_{ij}$	$-\Delta G°_{\beta ij}$ [kJmol^{-1}]	$-\Delta H°_{\beta ij}$ [kJmol^{-1}]	$-T\Delta S°_{\beta ij}$ [kJmol^{-1}]
	AgL[a]	10.32	58.91	91.5	32.6
	AgL(water)[b]	7.7	43.9	–	–
	CdL	11.81(0.04)	67.4(0.2)	79(2)	11.6
trien	Cd_2L_3	30.9(0.1)	176.4(0.7)	249(7)	72.6
	CdL_2	17.00(0.08)	97.0(0.5)	138(3)	41
	CdL(water)[b]	11.12	63.5	41	–22.5
	CoL	12.50(0.06)	71.3(0.3)	86(1)	14.7
	Co_2L_3	33.2 (0.3)	189(2)	273(9)	84
	CoL_2	18.2(0.3)	104(2)	149(4)	45
	CoL(water)[b]	11.31	64.5	44.3	–20.3
hmtrien	AgL	7.82(0.04)	44.6(0.2)	69.3(0.6)	24.7
	CdL	6.30(0.02)	36.0(0.1)	68(4)	32
	CoL	4.0(0.2)	23(1)	42(4)	19
	CoL(water)[c]	8±1			

[a] Ref.[22d] [b] Ref.[7], I = 1.00 mol·dm^{-3}. [c] Ref.[15], estimated value, medium unknown.

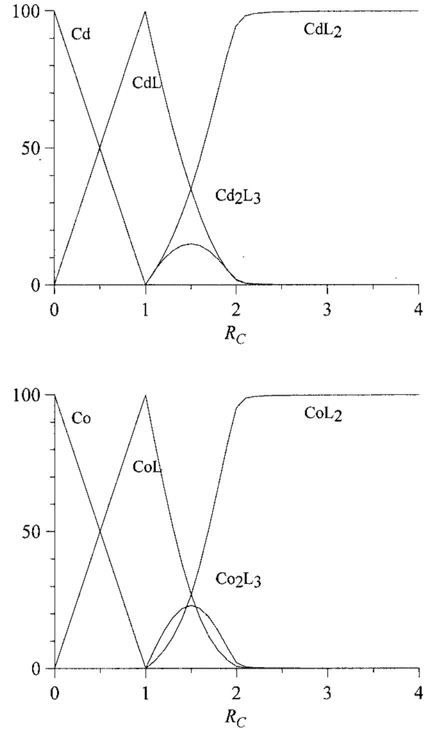


Figure 1. The percent distribution of the species in the Cd^{II}/trien and Co^{II}/trien systems in DMSO at c_M = 10 mmol·dm^{-3}

The slope change at R_c = 1 is connected with the formation of the very stable mononuclear ML complex. As c_L increases, a slope change is observed at R_c = 1.5, a separation of the curves at various concentrations is then shown until R_c = 2, and then no heat is released. This agrees with the formation of a very stable M_2L_3 and a subsequent, less

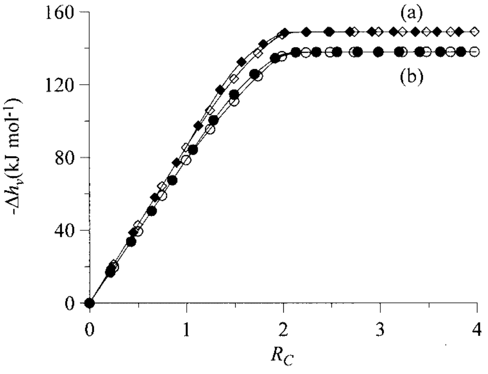


Figure 2. The total molar enthalpy changes, Δh_v, as a function of $R_c = c_L/c_M$ for Cd^{II}/trien and Co^{II}/trien systems in DMSO: (a) 5.05 (open circles), 19.91 (filled circles) mmol·dm^{-3} in Cd^{2+}; (b) 5.04 (open squares), 20.01 (filled squares) mmol·dm^{-3} in Co^{2+}; the solid lines have been calculated from the values of β_{ij} and $\Delta H°_{\beta ij}$ in Table 1

stable, ML_2 complex according to the reaction steps in Equations (1) and (2).

$$2\,ML + L \rightleftharpoons M_2L_3 \tag{1}$$

log β = 7.28 and 8.2, $\Delta H° = -91$ and -101, $T\Delta S° = -49.4$ and -54.6 kJ·mol^{-1} for M = Cd and Co, respectively

$$M_2L_3 + L \rightleftharpoons 2\,ML_2 \tag{2}$$

log β = 3.1 and 3.2, $\Delta H° = -27$ and -25, $T\Delta S° = -9.4$ and -6 kJ·mol^{-1} for M = Cd and Co

No more complexes are formed beyond ML_2. The fit between experimentally determined and calculated curves (full lines in Figure 2) is quite good.

Figure 3 (a) shows the spectral changes observed during reactions between Co^{2+} and trien, in the presence of Cd^{2+} as competitor, in terms of absorbances vs. wavelengths. Figure 3 (b) also shows (inserted) the spectral modification due to dioxygen uptake for the [Co(trien)]$^{2+}$ species. Figure 4 shows log β_{1Cd} plotted as a function of log β_{1Co} to provide a better illustration of the behaviour of the two ions.

The O_2 absorption by the [Co(trien)]$^{2+}$ adduct was measured at constant pressure by use of a standard apparatus containing a thermostatted gas burette in order to determine the stoichiometry of the dioxygenated complex. Figure 5 gives the dioxygen binding curve, $R_{O2} = n_{O_2}/n_{[Co(trien)]^{2+}}$ vs. time.

Discussion

All the complexes are formed in strongly exothermic reactions, whereas the entropy terms oppose the reactions (Table 1). The negative enthalpy and entropy values are typical of reactions involving complexation of metal ions by neutral ligands in aprotic solvents.[3,6,19] Data in water solutions are also available for all the trien systems,[7] whereas analogous data for the Co^{II}/hmtrien system are reported only as estimated values. It should be remembered that Cd^{2+} and Co^{2+} are hexasolvated in both solvents, with the solvent molecules in a regular octahedral arrangement,

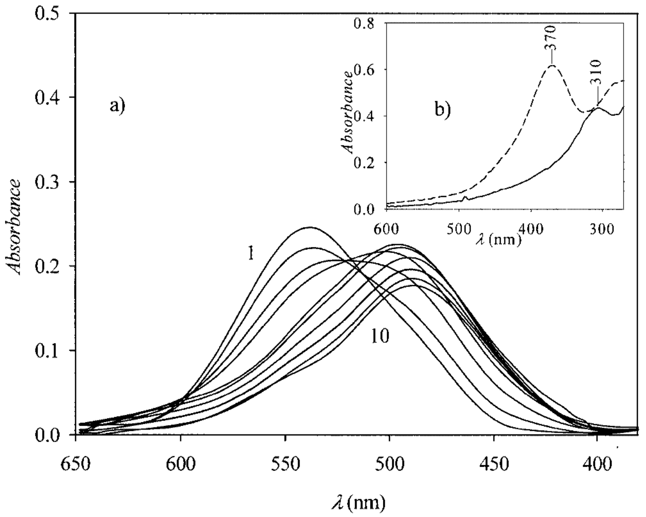


Figure 3. (a) Spectral changes observed during the reaction between Co^{2+} and trien in DMSO: calcd. $c°_{Co}$ = 21.8 mmol·dm^{-3}, $c°_{Cd}$ = 21.6 mmol·dm^{-3} (spectrum 1); $c°_{trien}$ varied from 0 (spectrum 1) to 54.5 (spectrum 10) mmol·dm^{-3}; (b) UV/Vis spectrum of a solution of [Co(trien)$^{2+}$] = 0.2 mmol·dm^{-3} under nitrogen with 4% O_2 after 9 s of exposure and after 30 min of exposure (dotted line); the spectrum remains unchanged after 6−8 h of exposure

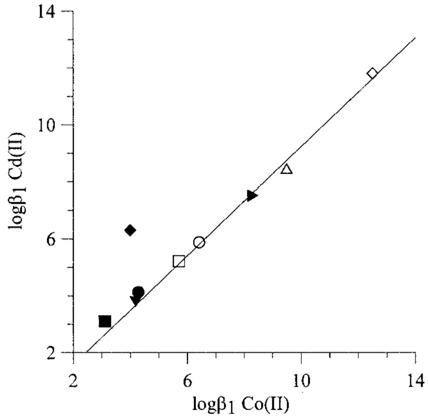


Figure 4. log β_{1Cd} as a function of logβ_{1Co} for ethylenediamine (en; open circle); *N,N'*-dimethylenediamine (dmen; open square); *N,N,N'*-trimethylenediamine (trmen; filled circle); *N,N,N'N'*-tetramethylenediamine (tmen; filled square); diethylenetriamine (dien; open triangle); *N,N''*-dimethyldiethylenetriamine (dmdien; filled triangle); *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien; filled triangle next to filled circle); 1,4,7,10-tetraazadecane (trien; open diamond), 1,1,4,7,10,10-hexamethyltriethylenetetraamine (hmtrien; filled diamond)

whereas silver(I) is tetrahedrally solvated both in DMSO and in water.[8b,19]

The complexes are characterized by lower stabilities in water than in DMSO. In addition, they are always more enthalpy-stabilized in DMSO than in water, while in the latter solvent the entropy terms are favourable. It has already been found that this trend is inconsistent with what would be expected on the basis of the thermodynamic parameters of transfer of the metal ions investigated here from water to DMSO,[6,37] and should be associated with greater solvation, through hydrogen bonding, of primary and secondary amines in water than in DMSO.[38] This was also

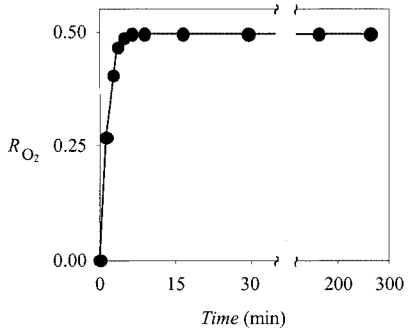


Figure 5. Plot of the ratio R_{O2} = moles O_2/moles complex vs. time measured for a 30 mM solution of $[Co(trien)]^{2+}$ complex in pure oxygen

confirmed by the fact that the opposite has been observed for the complexes with tertiary amines, as these are more stable in water than in DMSO,[6,8b,8c] *N*-methylation inhibiting the formation of hydrogen bonds of the type M−*N*−H···O with the solvent and the higher solvation of the metal ion in DMSO therefore prevailing in governing the trend of the stabilities.

Silver(I)/hmtrien System

A comparison with the thermodynamic functions previously determined for the Ag^I/trien system[22d] (also shown in Table 1), in which the ligand was shown to behave as tetradentate ligand, shows that hmtrien is also able to tetracoordinate Ag^I, forming three fused five-membered chelate rings.

The drop in $\log\beta_1$, of about two orders of magnitude, on going from primary to tertiary amino groups should be associated with: (i) the different basicities of the amino groups, which decrease in the order $-NH_2 > -NHR > -NR_2$ in DMSO,[38] (ii) steric hindrance, which results in elongation of the metal−nitrogen bonds,[1,3,5c,5e,5g,5h] and (iii) the absence of M−*N*−H···O hydrogen bonds, which are responsible for a decrease in outer-sphere solvation energy, thus increasing the hydrophobic nature of the complexes,[16] and of a decrease in the nitrogen σ-donating properties, which reverses the trend found in the gas phase, in which it has been shown that tertiary amine ligands are better σ-donors.[3] Effects (i) and (ii) in particular are also responsible for the decreased enthalpy gain for hmtrien complexation. Effect (iii) transforms the central cation into a harder acid.[3] As far as point (ii) is concerned, some authors have recently proposed, on the basis of X-ray results and molecular-mechanics calculations (MM), that nonbonded repulsions between the *N*-methyl groups are the primary cause of the observed elongation of the M−N bonds.[5c,5e,5g,5h]

Cd^{II}/Tetraamine Systems

Trien certainly behaves as tetradentate ligand in the CdL complex, as shown by the trend in the thermodynamic functions in relation to those of the $[Cd(dien)]^{2+}$ system [diethylenetriamine (dien), $\log\beta_1 = 8.46$, $\Delta H^\circ_1 = -65.3$, $T\Delta S^\circ_1 = -17$ kJ·mol^{-1} [8c]], in which dien is known to act as terdentate ligand; this was confirmed by independent FT-IR measurements run on a 1:1 Cd/trien solution, in which the bands due to free secondary (at 3313 cm^{-1}) and primary (at 3360 and 3300 cm^{-1}) amino groups were not present.

The huge drop in stability and exothermicity observed on going from trien to hmtrien was similarly observed for other analogous primary and tertiary polyamines; from the thermodynamic values it therefore seems reasonable to suppose that hmtrien also acts as tetradentate ligand, the trend in the data being greatly influenced, as in the case of the silver(I) system, by the different basicities and steric requirements of the ligands.

The Cd^{II} ion is certainly hexacoordinate in the ML_2 complex with trien, according to its tendency to bind polyamines, exhausting all coordinative positions.[8c,39] This is clearly indicated by the values of the thermodynamic functions for the stepwise reaction according to Equation (3), which are of the same order of magnitude as those found for the CdL complex formation with the diamine ethylenediamine (en) ($\log\beta_1 = 5.88$, $\Delta H^\circ_1 = -52.2$, $T\Delta S^\circ_1 = -19$ kJ·mol^{-1} [8c]).

$$CdL + L \rightleftharpoons CdL_2 \qquad (3)$$
$$\log K_2 = 5.19,\ \Delta H_{K_2} = -59,\ T\Delta S_{K_2} = -29.4\ \text{kJ·mol}^{-1}$$

The more favourable enthalpy gain (with respect to that of the 1:1 Cd/en system) reported for Equation (3), despite one of the nitrogen atoms of the second entering trien being secondary, is due to the observed fact[8c] that in Cd^{II} − as well as in Co^{II} − complexation with polyamines, the desolvation of the species involved occurs mainly in the first step of complexation.[6,8b,8c] This is also confirmed by the less favourable entropy term.

A real novelty for the Cd^{II} system is the formation of an appreciable amount of a Cd_2L_3 species (Table 1 and Figure 1), which is formed despite the dielectric constant of DMSO (46.4[19]) and enhances the importance of electrostatic repulsion in the case of polynuclear species formation. The high stability of this complex is due to the enthalpic factors, as the entropy value strongly counteracts the complex formation. Unfortunately, it was not possible to obtain unambiguous information about the number of coordinated amino groups by spectroscopic (NMR, FT-IR or UV/Vis) measurements, as Cd_2L_3 (and also Co_2L_3, see below) is present in solution together with both the mononuclear CdL and, even worse, the CdL_2 species. Nevertheless, two reasonable coordination modes may be hypothesized: (i) that in which the exhaustive hexacoordination of the metal ions is achieved, and (ii) that in which two ML tetracoordinate complexes are bridged by another trien ligand, which coordinates only with the two primary amino groups. As a large number of thermodynamic data relating to complex formation of Cd^{II} with differently methylated mono-, di- and triamines are available,[8c] an attempt to draw some conclusions about the coordination mode described above has been made by use of a chemometric approach based on a multiple linear least-squares regression. The contribution of each bonded nitrogen atom to the total value of the thermodynamic functions has therefore been calculated.

The calculated values of $\Delta G°$ and $\Delta H°$ (and their errors) expected for the coordination of one single primary and secondary N groups in chain (not methylated) are, respectively:
$\Delta G_{Cd} = -15.7(0.6)$ and $-14.6(1.0)$;
$\Delta H_{Cd} = -25.1(0.7)$ and $-15.7(1.1)$ kJ·mol^{-1}
[for Co^{II} the calculated values are, respectively, $\Delta G_{Co} = -16.6(0.6)$ and $-15.0(1.0)$; $\Delta H_{Co} = -27.5(1.0)$ and $-17.9(1.5)$ kJ·mol^{-1} [6,8b]]

According to the $\Delta G°$ and $\Delta H°$ values calculated above, expected values for Cd_2L_3 should be:
$\Delta G_{Cd} = -182.1(8.7)$ (logβ = 31.9) and
$\Delta H_{Cd} = -245(9.5)$ in the case of formation of species (i) and
$\Delta G_{Cd} = 152.8(8.1)$ (logβ= 26.7) and
$\Delta H_{Cd} = -213.4(8.9)$ kJ·mol^{-1} for the species (ii)

From comparison with the experimental results in Table 1, one can suggest that hypothesis (i) seems to be more reasonable**.**

The 1:1 complex stability with trien is greater than that of the corresponding Ag^{I} complex and reflects the higher affinity of the N atom for the borderline soft/hard divalent acceptor Cd^{II} than for the very soft univalent Ag^{I} ion. As far as hmtrien is concerned, the selectivity towards the metal ions is reversed. This agrees with other experimental evidence[8c] explained in terms of the more difficult arrangement that a bulky ligand may suffer when octahedrally rather than tetrahedrally coordinated.[8c,35b] The decreasing hard nature of the ligand[1] is also responsible for this behaviour.

Co^{II}/Tetraamine System

Co^{II} forms the same complexes as Cd^{II} with trien; the trend in the thermodynamic functions, together with analysis of the data obtained previously for other di- and triamines,[6,8b] suggest conclusions very similar to those reported here for the Cd^{II}/trien system (see above).

Better, comparison between the two systems shows that a higher stability (and exothermicity) is associated with Co^{II}/trien complex formation than that of the analogous situation with Cd^{II}, and this was also observed for other primary and secondary polyamines (see Figure 4, in which, for the sake of simplicity, only the logβ_1 values for CdL polyamine systems are reported as a function of the logβ_1 values for the analogous Co^{II} complexes). The harder Co^{II} is in fact characterized by stronger affinity than the medium/soft Cd^{II} towards the $-NH_2$ and $-NHR$ groups.

In addition, in the polynuclear M_2L_3 complex, it is likely that the larger Cd^{II} ions may be closer to each other than Co^{II} ions, and its stability should therefore be more dependent on electrostatic repulsions (see Table 1 for comparison).

With regard to *N*-alkylated hmtrien, the trend is completely reversed, the value of the stability constant being about two orders of magnitude less than the value found for the analogous Cd^{II}/hmtrien and much of the same order of magnitude as found for the Co^{II}/bidentate pmdien (pmdien = *N,N,N′,N′′,N′′*-diethylenetriamine) system.

This value was surprisingly low in comparison with that, though uncertain, available for the same Co^{II}/hmtrien system in water (Table 1). Unfortunately, data on hmtrien coordination to Cd^{II} in water are not known and so no comparison between the Δlogβ_1 values of Cd^{II}/- and Co^{II}/primary and tertiary tetraamine complexes in water is possible. On the other hand, a considerable drop in stability is also seen when considering the complex formation of the borderline[19] Cu^{II} ion, the chemical behaviour of which is, in certain aspects, similar to that of Co^{II} with trien and hmtrien in water (from 20.1 to 12.60[16]).

Other experimental techniques − direct UV/Vis titration of Co^{II} solutions and potentiometric titrations with Ag^{I} as competitor ion − were therefore also performed on the Co/hmtrien system, and the value reported in Table 1 was fully confirmed.

An analysis of all data so far reported for the two Cd^{II}/- and Co^{II}/polyamine systems in DMSO may provide an explanation for this behaviour. From Figure 4 it can be inferred that: (i) the drop in complex stability on *N*-methylation is more evident for Co^{II} than for Cd^{II}, and (ii) this drop, especially for Co^{II}, is more important on going from secondary to tertiary N groups. This can probably be explained by taking into account that: (i) large metal ions such as Cd^{II} can better minimize steric hindrances when bulky $-N(CH_3)_2$ moieties are involved in complex formation,[8c] and (ii) the increasingly soft nature of the nitrogen donors accounts for the difficulty encountered by tertiary amines in exhausting the coordination sites in Co^{II} complexation, whereas they are able to do it when the Cd^{II} ion is involved. This is confirmed in particular by analysis of the data in Figure 4 for the amines containing tertiary amino groups; they show similar stabilities with Co^{II}, whereas their CdL complex stabilities increase gradually with the increase in the number of probably coordinated nitrogen atoms. With Co^{II} a maximum of two nitrogen atoms are found to be able to coordinate the hard central ion, when tertiary polyamines are considered. As far as this last point is concerned, it has already been shown that the severe steric strain present in tertiary *N*-methylated amines, also confirmed by MM calculations, does not allow formation of a hexaamine complex when all N donors are tertiary, whereas this does occur when the degree of *N*-methylation is decreased.[5c,5g,5h]

The electron densities on the metal ions in the complexes, and therefore their dioxygen affinities, would be expected to be significantly lowered when the Co^{II}/hmtrien complex is formed, in relation to its Co^{II}/trien analogue.

With the aim of improving knowledge of correlation between electrochemical properties of the complexes and their dioxygen affinities, voltammetric measurements were carried out on both 1:1 Co^{II}/trien and Co^{II}/hmtrien systems.

The results obtained showed that the signals relative to the Co^{II}L$_j$/Co^{III}L$_j$ couples, and therefore to the reaction according to Equation (4) were not visible for the two systems investigated, probably for the reasons explained previously.[6]

$$Co^{II}L_j \rightarrow Co^{III}L_j + e \qquad (4)$$

The values of E_{pc}, the cathodic potential at maximum diffusion current, for the reaction according to Equation (5) are, on the other hand, easily evaluated for the two systems investigated and are -1.65 and $-$ 1.50 V for the trien and hmtrien system, respectively.

$$Co^{II}L_j + 2e \rightarrow Co(0) + jL \qquad (5)$$

By taking into account that the dioxygen uptake by a given complex represents the formation of a charge-transfer complex, a correlation between E_{pc} and Co^{II} charge density and therefore $Co^{II}L_j$ dioxygen affinity, should be observed. The higher the charge density, the more difficult the reduction process to Co^0 should be, and the more negative the E_{pc} value;[6] the E_{pc} value for the tertiary amine is in fact shifted anodically. That confirms how steric aspects of ligand design might be used to produce desired redox properties.[40]

It is of interest to note that the critical value of -1.54 V proposed in ref.[6] is not reached by the Co^{II}/hmtrien complex and that therefore, on the basis of the correlation between electrochemical properties and $Co^{II}L$ dioxygen affinity (see ref.[6] for details), we should predict that this adduct should not be able to bind dioxygen.

This is confirmed by the fact that no changes are observed in the spectra of deaerated and aerated solutions of the Co^{II}/hmtrien system, whereas for the Co^{II}/trien 1:1 species the aerated spectrum shows the very rapid (Figure 3, b) appearance of a charge-transfer band at 310 nm, to which a second band at 370 nm is added within a few minutes. The intensity of the latter band increased for about 60 min when the O_2 concentration was 4%, the kinetic behaviour being dependent on the initial dioxygen concentration. This band then remained constant for at least 6 h. This development seems to be consistent with the formation of two different dioxygenated species formed by different kinetic and thermodynamic pathways; the thermodynamically stable species seems not to undergo autoxidation, at least within the first 6 h. In addition, the dioxygen uptake is likely to be irreversible, as the UV absorption did not decrease with N_2 bubbling

A confirmation of this qualitative interpretation, together with an indication of the stoichiometry of the CoL/O_2 species, is provided by the O_2 absorption, which shows a quick uptake of dioxygen and then a plateau reached at $R_{O2} = 0.5$ (Figure 5), suggesting the formation of a μ-peroxo complex in which the dioxygen molecule bridges two metal ions; the dinuclear μ-superoxo complex is not considered, as the maximum of the charge-transfer band is located here at 325 nm, whereas normally the electronic spectrum of the green μ-superoxo adduct shows an additional band around 710 nm.[26,41] The 2:1 CoL/O_2 adduct formation agrees with the general tendency of Co^{II} complexes with simple polyazaalkanes to form dinuclear dioxygen species in dipolar solvents rather than end-on species, which normally requires superstructured ligands able to form a protective cavity around the metal ion.[26,31,41] Detailed thermodynamic and kinetic studies on this system are in progress.[42]

Conclusions

The *N*-functionalization of the ligands has a strong influence on the stoichiometry and the nature of the complexes formed, as well as, much more interestingly, on the selectivities of the ligands towards metal ions, as suggested by the behaviour of primary and secondary amines with respect to the tertiary ones. The former pair show the general stability trend increasing in the order $Ag^I < Cd^{II} < Co^{II}$, the latter reverse this trend and the complex stability increases in the order $Co^{II} < Cd^{II} < Ag^I$. The Cd^{II} ion generally coordinates all the donor sites of the nitrogen ligands, whereas Co^{II} does not when tertiary amino groups are involved.

The decreasingly hard nature of the nitrogen donors is mainly responsible for the fact that *N*-alkylation of trien prevents the Co/hmtrien system from being able to take up dioxygen. The E_{pc} value of -1.50 V allows this behaviour to be predicted, on the basis of all of the reported data, and provides additional insights into the correlation between electrochemical properties, number of methyl substituents and consequent dioxygen affinity of the anaerobic Co^{II} complexes.

Finally, it is suggested that a 2:1 $[Co(trien)_2]^{2+}/O_2$ complex is formed under aerobic conditions.

Experimental Section

General Remarks: $Co(ClO_4)_2 \cdot 6DMSO$ and $Cd(ClO_4)_2 \cdot 6DMSO$ were prepared and purified as described.[8b] Anhydrous silver perchlorate was obtained from $AgClO_4 \cdot H_2O$ (Fluka; puriss) as described previously.[22a] Dimethyl sulfoxide (Fluka; > 99%) was purified by distillation according to the described procedures,[22a] degassed by a pumping-freezing procedure, and stored in the presence of 4-Å molecular sieves. The ligands trien and hmtrien (Aldrich; > 97%) were purified by fractional distillation.[43] Stock perchlorate solutions of Cd^{II} and Co^{II} ions were prepared by dissolution of weighed amounts of the adducts in anhydrous degassed DMSO, and their concentrations were determined by titration with EDTA.[44] The solutions of $AgClO_4$ were prepared and standardized as before.[22a] The background salt Et_4NClO_4 was recrystallized twice from methanol and dried at 110 °C. Solutions of the ligands were prepared by dissolution of weighed amounts in DMSO and standardized by thermometric titration with standard $HClO_4$ solutions. All standard solutions were prepared and stored in an MB Braun 150 glovebox 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 with the aid of a Metrohm 684 KF Coulometer.

Potentiometric Measurements: All measurements were carried out under dry, oxygen-free nitrogen in an MB Braun-150 glovebox, in a thermostatted cell maintained at 298.0 ± 0.1 K. The experimental data required for the determination of the stability constants of the Ag^I/hmtrien and the Cd^{II}/trien and Cd^{II} /hmtreien systems were the equilibrium concentrations of the silver and cadmium ions, respectively, obtained from the electromotive force (emf) data of a galvanic cell similar to that reported previously.[22a] The emf values were measured with the aid of an Amel 338 pHmeter equipped with a Metrohm 6.0328.000 silver electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference in the first case and with a Weiss WCD1001 Cd ion selective electrode as working electrode and a Methrom 6.0718.000 silver electrode as reference one in the second case. Aliquots of ligand solutions of known concentrations were first added to the cell containing only solutions of metal (metal = Ag^{I} or Cd^{II}) perchlorate ($2.00 < c°_{Metal} < 30.00$ mmol·dm^{-3}) of exact known concentration and the free metal ion concentration was measured after each titrant addition. Some titrations were carried out in duplicate to verify the reproducibility of the system. Equilibrium was typically reached in 2−5 min. The Nernstian response of the Ag and Cd electrodes were obtained in the range 10^{-7} < metal ion < 10^{-2} mmol·dm^{-3}. The computer program Hyperquad[45] was used for calculation of the stability constants.

Spectrophotometric Measurements: UV/Vis spectra were recorded with a Varian Cary 50 Spectrophotometer directly inside the glovebox, by use of optic fibre probes and a quartz cuvette with a pathlength of 1 cm (117.100 Bracco cell). The data were recorded over the wavelength range 300−650 nm. Different types of titrations were carried out in order to obtain the best competition between Cd^{II} and Co^{II} for the same ligand and/or to provide evidence of possible formation of mixed or polynuclear species. The absorption maximum for $Co(ClO_4)_2$ in DMSO occurs at 535 nm, with an extinction molar coefficient $\varepsilon = 11.9$ mol^{-1}·dm^{3}·cm^{-1}. The absorption maximum of CoL_j complexes are shifted to lower wavelengths, in line with an increase in the ligand field strength. The fact that equilibrium was attained was supported by the observation that addition of titrant solution produce an immediate spectral change with no further change noted after several hours. The absorbance data at about 20 different wavelengths in the 450−550-nm range were analysed and the formation constants of the Co_iL_j complexes (i = 1, j = 1 for L = hmtrien; i = 1, j = 1, 2 and i = 2, j = 3 for L = trien) were determined, together with the molar extinction coefficients of the complexes at each relevant wavelength, by use of the Hyperquad program.[45] The UV/Vis measurements for dioxygen uptake were carried out by use of an analogous apparatus with the aid of optic fibre probes (Hellma) of 1-cm length dipped directly into the reaction vessel.

Calorimetric Measurements: A Tronac model 87−558 precision calorimeter was employed to measure the heats of reaction. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be $\Delta H° = -47.59$ kJ·mol^{-1}, in good agreement with the accepted value of -47.53 ± 0.13 kJ·mol^{-1}.[7] The calorimetric titrations were performed at 298.00 ± 0.02 K by addition of known volumes of ligand solutions ($50 < c°_{L} < 400$ mmol·dm^{-3}) to 20 mL of metal ion (Ag^{I}, Cd^{II}, Co^{II}) solutions ($2.00 < c°_{Metal} < 30.0$ mmol·dm^{-3}). For each titration run, n experimental values of the total heat produced in the reaction vessel were calculated as a function of the added titrant. These values were corrected only for the heat of dilution of the titrant, which was determined separately. The heat of dilution of the titrate was found to be negligible in the metal ion concentration range used. The quantity Δh_v, total heat per mol of metal ion, was defined and calculated by dividing the net reaction heat by the number of mol of metal ion in the calorimetric vessel. The least-squares computer program Letagrop Kalle[46] was used for the calculation of the enthalpy changes.

FT-IR Spectroscopy: The FT-IR spectra were obtained with a Bio-Rad FTS 40 spectrometer (maximum resolution 4 cm^{-1}; 16 scans). A cell with barium fluoride windows (thickness of 25 µm) was used. The cells were filled and closed in the glovebox and quickly transferred to the spectrometer. The $c°_{Co}$ and $c°_{trien}$ values in the DMSO solutions were about 50 mmol·dm^{-3}.

Cyclic Voltammetry: The cyclic voltammograms of CoL_1 complexes were carried out with an EG&G Princetown Applied Research Model 263A potentiostat controlled by a Win/PC-based program. A saturated Ag/AgCl electrode was employed as reference and a Pt electrode was used as working electrode, with a Pt wire being present as auxiliary electrode. The measurements were carried out with a scan rate of 100 mV/s.

O_2 Absorption: Measurement of O_2 absorption was performed with the aid of a gas burette connected to a vessel containing 0.6 mmol of total cobalt(II) in 20 mL of DMSO (I = 0.1 M) in the presence of 0.6 mmol of trien. The system was thermostatted at 298.0 K with a water circulating bath. The solution was vigorously stirred to minimize diffusion effects.

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