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N-Methylation Effects on the Coordination Chemistry of Cyclic Triamines with Divalent Transition Metals and Their Co^{II} Dioxygen Carriers

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The thermodynamics of complex formation of Co^{II} and Cd^{II} ions with the triaza macrocyclic ligand 1,4,7-triazacyclononane (tacn) and its *N*-methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) has been studied in dimethyl sulfoxide (DMSO) at 298.1 K and in an ionic medium (0.1 M Et$_4$NClO$_4$) by means of potentiometric, UV/Vis, calorimetric and FT-IR techniques. The results are discussed by taking into account electronic and steric effects as well as solvation of the species concerned. Computational methods based on density functional theory (DFT) have been used to obtain structural information about the ligands and their complexes in order to provide further, independent insights into the effect of *N*-methylation on the coordination affinity of the ligands towards the metal ions. The computational suggestions are of great help to correlate steric effects and thermodynamic results. The kinetics of dioxygen uptake for the formation of the Co(tacn)$_2$O$_2$ superoxo adduct has also been studied by means of UV/Vis measurements.

Introduction

In the last few years a wide variety of polyamines have been investigated in water[1–11] and in non-aqueous solvents[12–16] with the aim of studying how basicities and steric effects affect the selectivity pattern in metal coordination and for making direct comparison with the corresponding macrocyclic ligands.

As examples of these ligands' great interest and application, their potential use as sequestering agents for metals of environmental importance,[10] both toxic and essentials, and their employment as models for small molecules carriers,[16–21] such as in Cu^{I} or Co^{II} complexes, should be remembered.

In this context, previous studies of our group[16] on the complexation of divalent transition metal ions such as Cd^{II} and Co^{II} with differently *N*-alkylated linear di-, tri- and tetraamines in aprotic media have shown that: (i) the stabilities of the species formed decrease strongly with the increase of *N*-alkylation, with the enthalpy term being more responsible for that;[16a,16c] (ii) nitrogen functionalisation also strongly influences the stoichiometry and the nature of the metal complexes formed and, very interestingly, also the selectivity of these ligands (a higher affinity for Co^{II} than for Cd^{II} is displayed by primary and secondary polyamines, whereas the opposite is true when tertiary ones are involved);[16d] (iii) as far as cobalt(II) complexes are concerned, different *N*-alkylation of polyamines also has important effects on the behaviour of these complexes as better or worse dioxygen carriers:[16c,16e] in fact, electron transfer between the metal centre and the dioxygen depends on the electron density available at the central metal ion which, in turn, is greatly affected by the ligands;[17,20,21] (iv) steric effects due to *N*-alkylation inhibit the solvent exchange when dioxygen binding is considered, thus slowing down the oxygenation rate in the formation of the final adducts.

As an extension of this work we present here a study in the aprotic solvent dimethyl sulfoxide (DMSO) on the complex formation of Co^{II} and Cd^{II} ions with the simplest polyaza macrocyclic ligand 1,4,7-triazacyclononane (tacn) and its *N*-methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn), whose bulky methyls cause the ligand to change both its electronic and steric properties.

Despite its small cavity size, tacn is known to show an effective, strong macrocyclic effect which is manifested in its increased thermodynamic stability with respect to chelated acyclic triamines, for example in water. In addition, a

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stronger ligand field has been observed with respect to linear analogous.[22,23] These cyclic ligands also show interesting properties as potential oxidation catalysts[24,25] due to their ability in stabilizing reaction intermediates,[24] and they influence the electron-transfer rates, which are accompanied by a change in spin-state, such as in the Co^{II}/Co^{III} couple.[26]

Finally, tacn is ideally suited to coordinate[22,23,27] the metal-ion coordination sphere facially, thus functioning as a blocking group for three coordination sites.[22,28] Moreover, in the presence of suitable pendant arms the derivatised ligands are also very interesting as they can open-up a variety of fields of investigation, such as those of inorganic crystal engineering,[29] biological tracers,[30] MRI contrast agents[31] and the selective extraction and sequestering of metal ions.[1,23,32–34]

The aim of this work is mainly related to gaining information on the behaviour of simple triaza macrocycles that do not yet bear pendant arms and, in particular, on: (i) the macrocyclic effect in complex formation in solvating media other than water; (ii) the influence of *N*-methylation; (iii) the specific match of metal-ion size and the coordination requirements of the cyclic ligands; (iv) the effects of these preorganised ligands and of their *N*-methylation on the dioxygen affinity of their Co^{II} complexes.

The effect of *N*-methylation on the coordination affinity of the ligands towards Co^{II} and Cd^{II}, characterised by different types of electron configuration (d^7 and d^{10}), is also investigated here by computational methods using density functional theory (DFT). DFT provides an excellent framework to obtain structural information and a number of chemical reactivity indices about ligands and their complexes and is able to give results of quality comparable to those obtainable by correlated ab initio calculations. DFT has previously been used to study the influence of *N*-methylation on the structural[35] and electrochemical properties of transition-metal complexes with cyclic polyaza ligands[8] and to describe the properties of polyamines, such as their basicity, both in the gas phase[36] and in solvent models.[37] The kinetics of dioxygen uptake is also studied by means of UV/Vis measurements as far as the $Co(tacn)_2$ species is concerned as this is the only complex capable of binding O_2.

Results

The structures of the ligands were optimised by DFT calculations (see Supporting Information) and were compared with X-ray data available in the literature only for Me_3tacn (although in its protonated forms).[38] Some of the calculated and experimental parameters of this ligand are summarised in Table 1, and show that a good match exists between optimised and available X-ray data for Me_3tacn. This correlation is of interest as it can be taken as a proof of the reliability of these computational results and thus gives confidence in the initial calculated structure of tacn.

Table 1. Experimental[38] and calculated values for selected structural parameters of the ligand Me_3tacn.

	Distances [Å]			Angles [°]	
	Exp.	Calcd.		Exp.	Calcd.
N–C	1.356–1.458	1.457	C–N–C	112.4–115.1	113.4
$N–C_{(methyl)}$	1.450	1.451	$C–N–C_{(methyl)}$	110.5–115.2	116.4
C–C	1.403–1.488	1.542			

The optimised structures of the ML^{2+} complexes in the gas phase, together with calculated M–N distances, are reported in Figure 1: as far as the $M(tacn)^{2+}$ structures are concerned (Figure 1a and b), the M–N distances are shorter than the X-ray ones (Cd–N = 2.351–2.382 Å;[39] Co–N = 2.127–2.157 Å[40]), and this is true especially in the case of the Co^{II} complexes. This may be due to the simplified models chosen, to the limited basis sets and also because repulsive interactions present in the experimental structures are absent in the model complexes. As a matter of fact, when optimised structures of $M(tacn)_2^{2+}$ are considered (Figure 1c and d) the M–N distances are longer and very close to the experimental data.

The calculated binding energies ($E_{bind} = E_{ML^{2+}} - E_{M^{2+}} - E_L$) for the complex formation in vacuo are reported in Table 2, and the energies of the ligands in their "free" form and at the coordinates in the optimised complexes are given in Table 3.

The overall stability constants obtained after the analysis of the potentiometric (for Cd^{2+}) and UV/Vis data (for Co^{2+}) are listed in Table 4 for metal(II)–tacn and –Me_3tacn systems. In the same table the whole of the thermodynamic functions, with the corresponding error limits, are also reported together with the available data in water.[41] Previously published data[16a,16b] hare given for the same metal(II)–*N,N''*-dimethyldiethylenetriamine (dmdien) and –*N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien) systems, which were chosen as examples of comparable secondary and tertiary linear triamines.

The spectral changes observed during reactions between Co^{II} and the ligands in the presence of Cd^{II} as a competitive ion,[42] under anaerobic conditions, in terms of molar absorptions of the *j* species vs. wavelengths, are similar to the previous ones[16a] and are therefore not reported. The absorption maximum for $Co(ClO_4)_2$ in DMSO occurs at 535 nm (ε = 11.9 $\text{M}^{-1}\,\text{cm}^{-1}$) and is shifted to lower wavelengths after ligand addition, in line with an increase in the ligand field strength when CoL_j species are formed.

Δh_v, the total molar enthalpy change, is plotted as a function of R_c (= C_L/C_M, total ligand/total metal concentration) for the Cd^{II}– and Co^{II}–ligand systems in Figure 2.

The shape of the curves confirms the formation of consecutive, stable ML_j complexes when L = tacn (*j* = 1,2), whereas the absence of heat evolved after R_c = 1 clearly indicates that no other species are formed beyond ML when L = Me_3tacn. The fit between experimental and calculated (full lines) data is good.

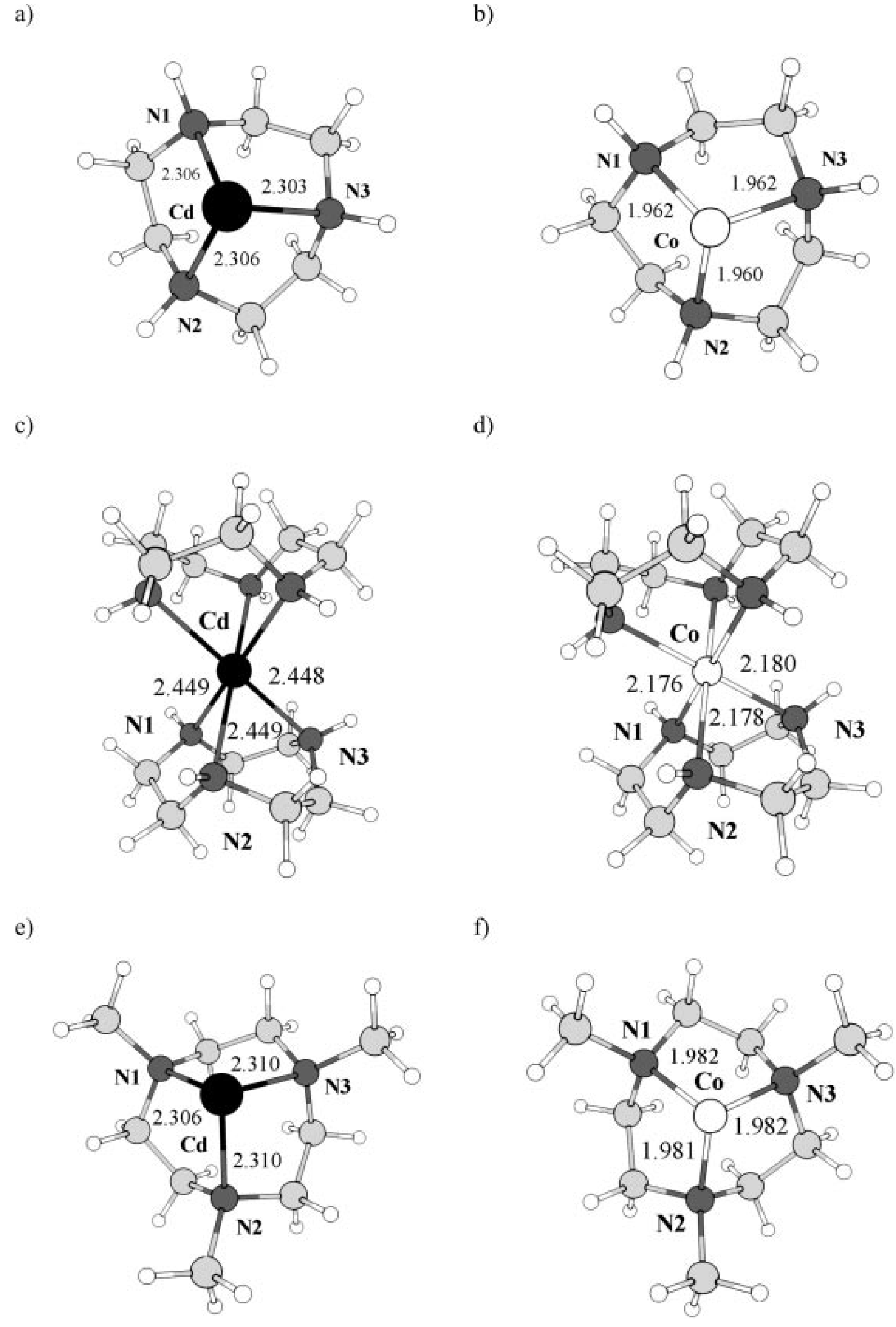


Figure 1. Optimised structures of a) $Cd(tacn)^{2+}$, b) $Co(tacn)^{2+}$, c) $Cd(tacn)_2{}^{2+}$, d) $Co(tacn)_2{}^{2+}$, e) $Cd(Me_3tacn)^{2+}$ and f) $Co(Me_3tacn)^{2+}$. Selected bond lengths are given in angstroms.

Table 2. Calculated binding energies ($E_{\text{bind}} = E_{\text{ML}^{2+}} - \text{E}_{\text{M}^{2+}} - E_{\text{L}}$) for ML^{2+} ($M = Cd^{2+}, Co^{2+}$) complex formation in vacuo.

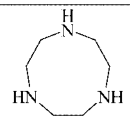
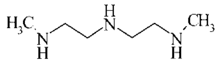
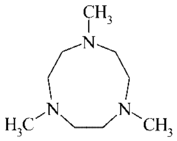
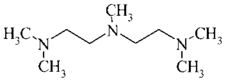
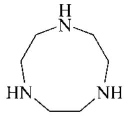
	Binding energy [kJ mol^{-1}]
$Cd(tacn)^{2+}$	–973.2
$Cd(Me_3tacn)^{2+}$	–989.7
$Co(tacn)^{2+}$	–1145.2
$Co(Me_3tacn)^{2+}$	–1196.5

The oxygenated spectra of a $Co(tacn)_2$ solution at different times are displayed in part a of Figure 3, while part b shows the experimental data and fitting curves for the oxygenation of $Co(tacn)_2{}^{2+}$ as a plot of absorbance at 336 nm vs. time. In particular, maxima at 528, 400 and 336 nm appear initially due to the fast formation of an oxygenated species and grow in intensity until about 20 min.

Table 3. Calculated energies [Hartree] of the optimised ML structures, free (E_{free}) and frozen (E_{bound}) at the coordinates found in the Cd and Co complexes, and strain energies ΔE_{strain} [kJ mol^{-1}].

$Cd(Me_3tacn)^{2+}$	E_{bound}	–519.801513	$Co(Me_3tacn)^{2+}$	E_{bound}	–519.797987
	E_{free}	–519.814060		E_{free}	–519.814066
	ΔE_{strain}	–32.9		ΔE_{strain}	–42.2
$Cd(tacn)^{2+}$	E_{bound}	–401.8754428	$Co(tacn)^{2+}$	E_{bound}	–401.8718334
	E_{free}	–401.8839462		E_{free}	–401.8839619
	ΔE_{strain}	–22.3		ΔE_{strain}	–31.8

Table 4. Overall stability constants and thermodynamic functions for the reactions $M^{n+} + jL \rightleftharpoons ML_j^{n+}$ ($M = Cd^{2+}, Co^{2+}$) in DMSO (0.1 M NEt_4ClO_4, 298.15 K) and in water; the errors quoted correspond to three standard deviations.

	Complex	$\log\beta_j$	$-\Delta G^\circ_{\beta j}$/kJmol^{-1}	$-\Delta H^\circ_{\beta j}$/kJmol^{-1}	$-T\Delta S^\circ_{\beta j}$/kJmol^{-1}
DMSO					
 tacn	CdL	9.56(0.02)	54.6(0.1)	60.6(3)	6.0
	CdL_2	18.59(0.03)	106.1(0.2)	130.4(3)	24.3
	CoL	10.5(0.3)	60(2)	87(3)	27
	CoL_2	19.7(0.3)	112(2)	171(3)	59
 Dmdien	CdL[a]	7.51	42.8	60.2	17.4
	CdL_2[a]	13.42	76.6	109.7	33.1
	CoL[b]	8.3	47.4	66.0	18.6
	CoL_2[b]	14.15	80.8	127	46.2
 Me_3tacn	CdL	7.51(0.01)	42.86(0.05)	54.8(0.6)	11.9
	CoL	7.7(0.1)	43.9(0.6)	74.6(1.6)	30.7
 Pmdien	CdL[a]	3.8	21.7	43.5	21.8
	CoL[b]	4.19	23.9	29.8	5.9
Water					
 tacn	CdL[c]	9.5	54.2	31.8[b]	–22.4
	CdL_2[c]	17.9	102.1		
	CoL[d]	11.2	63.9		
	CoL_2[d]	19.0	108.4		

[a] Ref.[16b] [b] Ref.[16a] [c] Ref.[41a] [d] Ref.[41b]

This species then evolves and decreases in concentration very slowly, as can be seen from curve 3 in Figure 3a.

The best fit of the analysed experimental data reported in Figure 3b is consistent with the reaction mechanism (charges omitted) proposed in Equation (1).

Degradation reactions appear to be negligible in the time range investigated, as can also be seen from the above-described analysis of the curves (Figure 3a).

The kinetics of the process obey a second-order rate law and the values of the obtained kinetic constants, calculated by the computer treatment of the absorbance values at 336 nm, are given in Table 5 together with the equilibrium constant for the overall reaction relative to the formation of species A. This is calculated by combining the rate constants of the direct and reverse reactions at 298.1 K, which is the standard state for O_2 in 1 M solution.

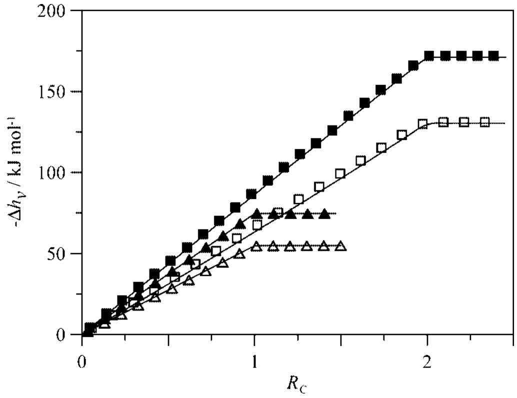


Figure 2. The total molar enthalpy changes, Δh_v, as a function of R_c (= C_L/C_M) for Cd^{II}/L (open symbols) and Co^{II}/L (filled symbols) systems in DMSO: (□,■) L = tacn; (Δ,▲) L = Me$_3$tacn. The solid lines were calculated from the log β_j and $\Delta H_{\beta j}°$ values in Table 1.

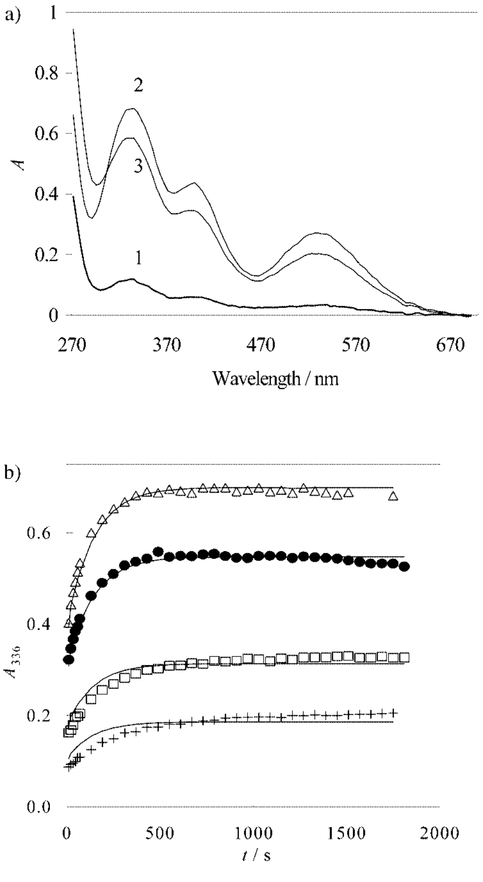


Figure 3. a) Electronic spectra of [Co(tacn)$_2^{2+}$] (0.5 mM) in the presence of P_{O_2} = 38 Torr after 1) 10 s, 2) 15 min, 3) 4 h; b) experimental data and fitting curves for the oxygenation of Co(tacn)$_2^{2+}$ in the presence of P_{O_2} = 760 Torr: (+) [Co^{2+}] = 0.21, [tacn] = 0.46 mM; (□) [Co^{2+}] = 0.34, [tacn] = 0.72 mM; (●) [Co^{2+}] = 0.58, [tacn] = 1.2 mM; (Δ) [Co^{2+}] = 0.68, [tacn] = 1.4 mM. Calculated molar absorbance at 336 nm: $\varepsilon_{ML_2O_2} = 2.5(3) \times 10^3$ M^{-1}cm^{-1}.

$$\mathrm{Co(tacn)_{2(solv)} + O_{2(solv)}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{A}}{\mathrm{[Co(tacn)_2O_2]_{(solv)}}} \qquad (1)$$

Table 5. Kinetic parameters for the oxygenation reactions reported in Equation (1) and thermodynamic stability constants for the reaction: $\mathrm{CoL_{2(solv)} + O_{2(solv)} \rightleftharpoons (CoL_2)O_{2(solv)}}$ (L = tacn) in DMSO at 298.1 K and I = 0.1 M. The errors in parentheses are one standard deviation.

Complex	k_1 [M^{-1} s^{-1}]	k_{-1} [s^{-1}]	log K_{O_2}
[Co(tacn)$_2$O$_2$]$^{2+}$	32(5)	0.22(3)	2.15

Discussion

DFT Calculations

The distances reported in Figure 1 show that the introduction of a methyl group on the tacn secondary nitrogens results in an elongation of the calculated M–N bond lengths (Figure 1e and f), which is more evident in the Co^{II}–L complexes (approx. 0.02 Å) than in the Cd^{II}–L complexes (approx. 0.005 Å). A similar elongation has been observed in the solid state for dinuclear Co^{II} complexes of formula [Co$_2$(Me$_3$tacn)$_2$X$_3$][43] for which X-ray data are available. This finding is in agreement with previous observations which show that the metal–N bond lengths increase with N-methylation as a consequence of steric effects in the gas phase,[44] and also of solvation effects in solution, thus leading to a stabilisation of the lower oxidation state in the ML_j^{n+1}/ML_j^n redox couples.[10]

As far as the binding energies in Table 2 are concerned, it should be underlined that they are important only as far as their relative trends are conscerned: the high values found ($E_{bind} \approx -970$ to -1200 kJ mol^{-1}) cannot be compared to experimental values as environmental effects are not taken into account in the calculations, which means that additional energy terms, such as breaking of M–dmso bonds, are not considered.

Some interesting points can be outlined: i) Co^{2+} binds much more strongly than Cd^{2+} to the two polyamines, ii) the binding energies are higher for Me$_3$tacn than tacn for both metal ions, and iii) the difference between Me$_3$tacn and tacn is much higher when Co^{II} is concerned [$\Delta E_{bindCo^{II}} = E_{bind(Co-Me_3tacn)} - E_{bind(Co-tacn)} = -51.3$ kJ mol^{-1}; $\Delta E_{bindCd^{II}} = -16.5$ kJ mol^{-1}].

Point i) may be reasonably explained by taking into account that Co^{II}, given its higher charge density, is a stronger Brønsted acid than Cd^{II}.

The higher affinity of the methylated amine for the two ions [point ii)] reflects the gas-phase basicity order of amines, which has been shown to be higher for tertiary amino groups than for secondary ones both experimentally[45] and theoretically.[35,36a,37] The effect of methyl groups on gas-phase basicity has been explained not only by the inductive effect of the CH$_3$ groups but also considering that, in the interaction of the amines with the H$^+$ ion, methyl groups are responsible for a better redistribution of the positive charge,[46] thus stabilizing the resulting cation. Even though in this case dipositive metal ions and not protons are involved, the same factors should be considered to be governing the energy trends found here.

As far as point iii) is concerned, the enhancement of stabilisation is probably due to a synergistic action that is effective when the stronger Brønsted acid Co^{II} reacts with the stronger base Me_3tacn.

Steric effects due to *N*-methylation are investigated here with a particular attention to the fact that they are also reflected in the reorganisation of the ligands when they bind the metal ion, which influences their stability. Therefore, the energies of the ligands have been calculated in their "free" form and at the coordinates in the optimised complexes (Table 3): their difference $\Delta E_{\text{strain}} = E_{\text{free}} - E_{\text{bound}}$ can be considered a measure of this reorganisation. Although these differences are relatively low ($\Delta E_{\text{strain}} \approx$ 20–40 kJ mol^{-1}), they are nevertheless very important as these values are intrinsic in the ligands and therefore act in the gas phase as well as in solution.

The data for ML complexes in Table 3 mean that both ligands have to spend more energy to reorganize around Co^{II} than Cd^{II} ($\Delta\Delta E_{\text{strain(L)}} = \Delta E_{\text{strain(Cd–L)}} - \Delta E_{\text{strain(Co–L)}}$ = 9.3 and 9.5 kJ mol^{-1} for L = Me_3tacn and tacn, respectively); this is reasonable due to the larger ionic radius of Cd^{II}, which allows longer bond lengths and therefore lower strain, both of which imply lower steric repulsions and minor energy costs for the reorientation of the dipoles represented by N–H/CH_3 bonds.

To sum up, the DFT results for the gas phase forecast a higher affinity of both polyamines for Co^{II} than for Cd^{II}, the higher difference found for Me_3tacn than for tacn being rationalised in terms of their gas-phase basicities. In addition, the importance of steric strain in the reorganisation of the ligands around the metals is pointed out.

Thermodynamics

General Remarks

The complex formation is accompanied by negative enthalpy values, typical of reactions between metal ions and neutral ligands in aprotic solvents.[12] The negative entropy terms found here 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 loss of translational entropy by the reagents upon complexation.

Thermodynamic data are available in water[41] for tacn systems, and these are also reported in Table 1. Although the enthalpy data are referred to a slightly different experimental ionic medium (0.2 M), this value nevertheless reflects different, significant effects of the two solvent media on complex formation: in water the stability with tacn is mainly due to a less favourable enthalpy term ($\Delta H°_1$ = –31.8 kJ mol^{-1}), whereas the entropy term is positive. This trend has already been observed for other primary and secondary polyamines and generally results in a lower complex stabilisation in water than in DMSO.[16]

In polar solvents, where ion-pairing of counterions with metal cations and their complexes is negligible, the equilibrium constant for the complexation reaction varies with the solvation energies of the reactants (cations and ligands) and products (complexes). In many cases, the free-energy changes for ligand and complex solvation cancel each other out and the free-energy term for cation solvation is largely dominant.[12] The free-energy changes for metal-ion transfer from water to DMSO available for Cd^{II} ($\Delta G°_{\text{tr(water}\rightarrow\text{dmso)}}$ = –60.4 kJ mol^{-1}),[47] and reasonably hypothesized to be negative for Co^{II},[16a] show that these metal ions are more strongly solvated in DMSO than in water. This is in agreement with the different electron-donating abilities of the two solvent molecules, as measured by the empirical Gutmann's donor number (DN = 29.8 for DMSO and 18 for H_2O).[48]

In the hypothesis that the solvation energies of Cd^{II} and Co^{II} are the dominating solvation terms in our complexation reactions, we should expect a greater complex stability in water than in DMSO. As this does not occur, this suggests that amine solvation, rather than metal-ion solvation, plays a major role in determining the stability of tacn complexes in the two solvents. Indeed, it is known that primary and secondary amines are more solvated in water than in DMSO[15,49] and, consequently, are stronger bases in DMSO than in water. Tacn is more solvated in water, therefore complexation is a more expensive desolvation process, in terms of enthalpic contribution, but produces a greater gain in translational entropy. Accordingly, the enthalpic contribution available for the Cd^{II}–tacn system in water is largely less favourable than in DMSO, while the entropic one shows an opposite trend.

Complex Formation with Cyclic Triamines in DMSO

Cyclisation of linear polyamines affects the stabilities and selectivities of their metal complexes: in particular, an extra stability is observed when complex formation with cyclic rather than linear polyamines is concerned. Although enthalpic and entropic arguments have been presented to account for this effect, it does not appear that one factor is unequivocally more important than the other.[3]

The results reported here show that an increase of the complex stability with both Cd^{II} and Co^{II} ions is effective when tacn (but also its methylated analogues) is considered with respect to the linear dmdien. This is true even if the comparison is extended to the more σ-donating primary linear triamine diethylenetriamine (dien).[16a]

This effect can be better understood by a separate analysis of the $\Delta H°$ and $\Delta S°$ contributions, which, in turn, are associated with metal, ligand and/or complex structural features.

It should be remembered that when macrocyclic rings such as 9-aneX_3 (X = N,O,S) are concerned, the metal ions do not enter the cavity of these small macrocycles, so that these do not represent examples of classical size-match selectivity. Rather, the metal ions are responding to the geometrical requirements for coordination out of the plane of the three donor atoms,[50] that is, the mode of coordination imposed by these ligands is stereorestrictive as they sterically constrained to facial coordination, whereas linear triamines may coordinate either facially or meridionally.

1:1 Complexes

Some important considerations can be made: (i) for the Cd^{II} system with tacn, especially in the first complexation step, the extra stability with respect to the linear dmdien arises mainly from the entropy term as $\Delta H°_{\beta1}$ is almost the same [the entropy term is far less unfavourable also when $Cd(Me_3tacn)^{2+}$ formation is considered vs. $Cd(pmdien)^{2+}$]; (ii) the opposite occurs when Co^{II} complexation by the cyclic vs. the linear triamines is analysed. It must be underlined that both Cd^{II} and Co^{II} are octahedrally coordinated by six DMSO molecules in solution and that this coordination mode is retained in their 1:1 complexes, as indicated by UV/Vis measurements. In addition, from FT-IR spectra recorded for solutions where R_c − the tacn-to-metal ratio − is varied up to 2, it can be seen that only the bands due to the bonded amine (at 3233 cm^{-1}) are present and no bands for free secondary (at 3345 cm^{-1}) amino groups could be detected, thus showing that the *N*-donor groups are all bonded to the central metal ion both in ML and ML_2 species.

The restricted conformational freedom of the cyclic tacn (but also Me_3tacn) before coordination, and hence the lower entropy loss on coordination, with respect to the linear one is one of the factors affecting this trend but certainly not the only one, as this should also influence the Co^{II} system. The constraining nature of the rigid ligand, which forces a distorted octahedral structure in its facial coordination, is probably also responsible for this behaviour: in fact, with the larger Cd^{II} ion (octahedral Shannon radius = 0.95 Å)[51] the steric strains of the three coordinated nitrogen atoms should be better minimised with respect to the small Co^{II} ion (octahedral Shannon radius, high spin = 0.74 Å) and this may explain the great difference in entropy terms. These conclusions are also supported by the computational results in the gas phase, which show lower $\Delta\Delta E_{strain}$ values for Cd complexes than Co ones (Table 3). As a matter of fact, a special disorder has also been shown to be present in a $Cd(tacn)_2^{2+}$ solid structure,[39] and has been explained by observing that the ligands have two alternative positions which are twisted by about 56° with respect to each other.

The enthalpy values are, on the contrary, much more favourable when the Co^{II}–tacn system is considered with respect to Cd^{II} and this should reflect stronger coordination bonds when the more (Brønsted) acidic Co^{II} centre interacts with the ligands. This agrees with observed data which propose that, for metal ions which have considerable tendency for covalent bond formation, the enthalpic contribution to chelate formation can be important if their electronegativities are appreciable.[3]

Some additional points are outlined when the metal(II)–Me_3tacn systems are considered: (i) a huge drop occurs in the complex stability with respect to the tacn system, and (ii) a huge gain in stability is observed as far as the complexation of the same ions with the tertiary, linear pmdien ligand are considered.

Point (i) may be explained as being due to several main reasons, especially: the different basicity of the amino group, which decreases in the order $NH_2 > NHR > NR_2$, in DMSO,[52] opposite from what occurs in gas phase; the elongation of the M–N bonds, due to the steric hindrance of the ligands[10] and the decreased solvation of the complexes as a consequence both of their increased radii and of the minor extent of hydrogen bonding brought about by the *N*-alkylated amines.[10]

The great importance of steric effects in the stability of the metal complexes formed is again clearly evident from the computational results in Table 3: the relative strain energies, in other words the repulsive forces in the M^{II} complexes, are higher for Me_3tacn complexes than for tacn itself ($\Delta\Delta E_{strain(tacn\rightarrow Me3tacn)}$ = 10.6 and 10.4 kJ mol^{-1} for Cd and Co respectively). This destabilisation must be overcome in complex formation and thus is one of the causes of the decrease in complex stability.

As far as point (ii) is concerned, it should be remembered that data relative to pmdien agree with a bidentate behaviour of the ligand due to steric repulsions between the methyl groups.[16a,16b] In the case of Me_3tacn, the thermodynamic data suggest that the three nitrogens are all involved in coordination: the preorganisation of the cyclic ligand "drives" the N atoms towards the metal centre and evidently prevails over the steric repulsions between the methyl groups.

It is interesting to note that in the formation of the 1:1 complexes, $\Delta\Delta H°_1$, which is the difference between $\Delta H°_{\beta1}{}^{Cd^{II}}$ and $\Delta H°_1{}^{Co^{II}}$ is less markedly positive for Cd^{II} in the case of Me_3tacn (Table 4, $\Delta\Delta H°_1$ = 19.8 kJ mol^{-1}) than in the case of tacn ($\Delta\Delta H°_{\beta1}$ = 26.4 kJ mol^{-1}). This should once more be due to the better ability of the large Cd^{II} to minimise steric hindrances. In addition, the increasingly soft nature of the tertiary amino groups should cause a less marked preference for Co^{II} than for Cd^{II} with respect to the secondary ones.

1:2 Complexes

N-Methylation is also responsible for the inability of Me_3tacn to form an $M(Me_3tacn)_2^{2+}$ species: in fact, strong intramolecular repulsive forces would be exerted by the two rings due to non-bonding Me–Me interactions. Only one example of an ML_2 structure exists in the literature for this methylated ligand, namely the $Ag(Me_3tacn)_2^+$ complex.[53] In this case the Ag–N bond lengths are much greater (approx. 2.6 Å) and therefore the methyl groups are distant enough to allow a stabilisation of the ML_2 compound.

The thermodynamic data for $M(tacn)_2^{2+}$ systems show that the formation of the second complex is accompanied by a great stability (log K_2 = 9.03 and 9.2 for Cd and Co, respectively), which once more overcomes that relative to $M(dmdien)_2^{2+}$ complex formation. The presence of a stronger ligand-field for cyclic vs. linear triamines is evident from a comparison between the experimental UV/Vis spectra for the $Co(dmdien)_2$ and $Co(tacn)_2$ complexes: the value of λ_{max} in the former is shifted from 535 [λ_{max} for $Co(ClO_4)_2$ in DMSO solution] to 490 nm, whereas in the latter it is centred at 471 nm.

If we examine the values of the stepwise enthalpy and entropy data for M–tacn systems more deeply we can observe that the trend with both metals is in agreement with desolvation effects being more extensive in the first complexation step, and more markedly for Cd^{II} than for Co^{II}. This desolvation effect should also play a role in explaining the low unfavourable entropy value found in the first step for Cd.

Kinetics in Aerobic Conditions

The k_1 value found here for reaction (1) is slightly lower, although of the same order of magnitude, as that found for the formation of the saturated superoxo species $[Co(dien)_2O_2]^{2+}$ ($k_1 = 69\ \text{M}^{-1}\,\text{s}^{-1}$), higher than that found for the formation of $[Co(dmdien)_2O_2]^{2+}$ ($k_1 = 0.035\ \text{M}^{-1}\,\text{s}^{-1}$)[16h] and much lower than those found for $[CoL_2O_2]^{2+}$ [L = ethylenediamine (en), *N*,*N*′-dimethylethylenediamine (dmen)].[16e] The trend in k_1 values is therefore in agreement with a dissociative mechanism,[54] where a higher activation energy is required for the Co–N bond cleavage due to O_2 coordination in $Co(tacn)_2^{2+}$ than for the $Co–O_{(dmso)}$ bond cleavage in unsaturated CoL_2 complexes, the Co–N interaction being stronger than the $Co–O_{(dmso)}$ one.

The presence of steric interactions due to the methyl groups in dmdien makes the O_2 coordination slower[55] and this is in agreement with the k_1 value found for the $Co(dmdien)_2$ system with respect to $Co(tacn)_2$.

The stability constant for O_2 uptake is similar to that found when the secondary dmdien ligand is used [$\log K_{O_2}^{Co(dmdien)_2} = 2.8$] and lower than that found for dien [$\log K_{O_2}^{Co(dien)_2} = 4.6$]. The value of $\log K_{O_2}$ has been related[17] to the sum of $\log K_a$ of the ligands in water, which is a measure of the simple σ-donor ability of a ligand and therefore of the consequent electron density on the metal centre. When tacn is considered, a strongly acidic behaviour is observed for the first dissociation step due to the close proximity of the NH_2^+ groups, which results from the cyclic nature of the amine. Therefore, $\Sigma\log K_a$ of tacn is not available for a direct comparison with dmdien ($\Sigma\log K_a = 22.59$) or with dien ($\Sigma\log K_a = 23.22$). In a previous work the huge difference in stability of the dioxygen complexes of dmdien and dien systems was explained mainly by taking into account the statistical presence of a primary amino group (in dien) *trans* to the coordinated O_2,[16h] and this argument can also be used to explain the lower $\log K_{O_2}$ value found for the $[Co(tacn)_2O_2]^{2+}$ system with respect to $[Co(dien)_2O_2]^{2+}$. As far as the tacn and dmdien systems are compared, both possess only secondary amino groups, thus similar $\log K_{O_2}$ values are expected, as is the case. In light of the fact that the repulsion between the methyl groups in the dmdien system should lower the thermodynamic stability of the O_2 adduct with respect to tacn, the opposite result found here can be explained by supposing that the opening of a Co–N bond in $[Co(tacn)_2O_2]^{2+}$ causes the over-stability gained thanks to effects of "preorganisation" to partially drop.

Conclusions

Some interesting features emerge from the combination of thermodynamic and DFT investigations. The extra stability of tacn complexes with respect to tridentate dmdien is mainly due to entropic effects for Cd, whereas the enthalpy term plays a fundamental role when Co is concerned.

This is an example of the great influence of the metal's ionic radius in satisfying the out-of-plane, facial coordination requirements of the cyclic triamine: in fact, the larger Cd^{II} can better minimize steric strain, as clearly emerges from the values of the calculated strain energies in the gas phase for the same systems. On the other hand, the smaller Co^{II} is more acid and achieves stronger coordination bonds than Cd^{II}, as confirmed by calculated binding energies of their complexes and by quite lower metal–N bond lengths in the Co–ligand systems. The enthalpy and entropy terms are therefore the result of a subtle interplay of steric and electronic effects. The *N*-methylation of tacn does not prevent Me_3tacn from behaving as a terdentate ligand, as occurs when linear pmdien is considered, due to a "preorganisation" of the ligand, which prevails over Me–Me steric repulsions. On the other hand, *N*-methylation, which is responsible for a less basic character of Me_3tacn than tacn in DMSO, causes a less marked preference for Co^{II} than for the softer, larger Cd^{II} with respect to tacn.

Finally, *N*-methylation strongly influences the stoichiometry of the species formed, as the $M(Me_3tacn)_2^{2+}$ (M = Co, Cd) species do not exist. As a consequence, only in the $Co(tacn)_2^{2+\cdot}$ complex does the central metal ion achieve sufficient electron density to be able to take up dioxygen.

Experimental Section

Materials: $[Co(DMSO)_6(ClO_4)_2]$ and $[Cd(DMSO)_6(ClO_4)_2]$ were prepared as described previously.[16a] Tetraethylammonium perchlorate (TEAP; >97%, Aldrich) was recrystallised from methanol and then dried under vacuum at 110 °C. The ligands tacn and Me_3tacn (Aldrich) were used without further purification. Dimethyl sulfoxide (99%, Aldrich) was purified by distillation according to the described procedures[16a] and stored under nitrogen over 4-Å molecular sieves. Perchlorate stock solutions of Cd^{II} and Co^{II} ions were prepared by dissolving weighed amounts of the adducts in anhydrous degassed DMSO; their concentrations were checked by titration against EDTA.[56]

Solutions of the ligands were prepared by dissolving weighed amounts in DMSO and standardised 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 a Metrohm 684 KF Coulometer.

Potentiometric Measurements: All measurements employed for the determination of the stability constants of the Cd^{II} complexes with tacn and Me_3tacn were carried out in 0.1 M NEt_4ClO_4 by using a thermostatted cell maintained at 298.1 ± 0.1 K, and kept under inert atmosphere in an MB Braun 150 glovebox. The concentrations of Cd^{II} were obtained from the emf data of a galvanic cell measured with an Amel 338 pHmeter equipped with a Weiss WCD1001 Cd ion selective electrode as working electrode and a Metrohm 6.0718.000 silver electrode as reference electrode. Aliquots of ligand solutions of known concentrations were added to solutions of cadmium(II) perchlorate only ($[Cd^{2+}]$ = 2.00–10.00 mM) of known concentration and the free-metal concentration was measured. Equilibrium was reached typically in 2–5 min. The Nernstian response of the Cd electrode was obtained in the range 10^{-7}–10^{-2} M.

The computer program Hyperquad[57] was used for the calculation of the stability constants.

Calorimetric Measurements: 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 neutralisation of tham was found to be $\Delta H°$ = –47.58 kJ mol^{-1}, in good agreement with the accepted value of –47.53 ± 0.13 kJ mol^{-1}.[1b]

The calorimetric titrations were performed at 298.15 ± 0.02 K by adding known volumes of ligand solutions ([L] = 20–50 mM) to 20 mL of metal (Cd^{II}, Co^{II}) solutions ([M] = 2.00–5.00 mM). The measured heats were corrected for the dilution heat of the ligands.

The least-squares computer program Letagrop Kalle[58] was used for the calculation of the enthalpy changes.

FT-IR Spectroscopy: The FT-IR spectra were obtained using a Bio-Rad FTS 40 spectrometer (maximum resolution 4 cm^{-1}; 16 scans). Cells with barium fluoride windows (thickness of 25 µm) were used. The cells were filled and closed in a glovebox and quickly transferred to the spectrometer. Spectra were also collected for solutions containing the ligand alone.

UV/Vis Spectrophotometric Measurements: UV/Vis spectra were recorded with a Varian Cary 50 Spectrophotometer directly inside the glovebox when the anaerobic CoL_j (j = 1, 2, L = tacn; j = 1, L = Me_3tacn) complex formation was studied. Optic fibre probes and a quartz cuvette with a path length of 1 cm (117.100 Bracco cell) were used. The data were recorded over the wavelength range 300–650 nm.

The formation constants of the CoL_j complexes were obtained by performing different titrations with varying Co^{II} and Cd^{II} concentrations in order to obtain the best competition between the two metal ions for the same ligand and/or provide evidence of possible formation of mixed or polynuclear species, and treating the data with the Hyperquad program.[57]

The kinetics of oxygenation reactions of $Co(tacn)_2$ species were studied using an analogous apparatus by means of optic fibre probes (Hellma) of 1 cm length dipped directly into the reaction vessel. The appearance of the MLCT band(s) associated with the formation of the dioxygen adduct/s[16,17a,20,21] was followed.

The whole of the apparatus and the automatic procedure used to collect the kinetic runs, in the range 270–670 nm, were as described previously.[16e] The concentration of dissolved O_2 in solution was calculated assuming the validity of Henry's law[59] and a value of 2.1×10^{-3} M for the equilibrium concentration of O_2 in DMSO + TEAP solution at 298 K with a partial pressure of 760 Torr of O_2 in the gas phase.[60] The data were analysed with the DYNAFIT program.[61]

Computational Details: The acyclic systems were not considered for calculations as they are flexible and give many possible coordination isomers, especially as far as the dmdien ligand is concerned. On the other hand, DFT calculations were performed on the cyclic triamines, which are more suitable to gain information about N-methylation effects, and on their ML_j^{2+} complexes (M = Co, Cd). For this purpose, the program PC GAMESS version 6.5[62] was used with the B3LYP three-parameter hybrid density functional,[63] which has been shown to be reliable for the description of metal complexes. The split-valence basis set 6-31G+(d) was employed for the atoms of the ligands, while a 3-21G basis set was employed for the metal ions. For the Co^{2+} complexes the unrestricted formalism was employed with three unpaired electrons (S = 4).

All the geometries were optimised without symmetry constraints, except the $M(tacn)_2^{2+}$ complexes, which were optimised within the C_i point group, until the maximum component of the gradient of the energy was below 0.0001 Hartree/Bohr and the rms gradient below 1/3 of the latter. After the optimisations, stationary points were characterised by the calculation of the vibrational frequencies in order to confirm they were local minima.

The binding energies ($E = E_{ML^{2+}} - E_{M^{2+}} - E_L$) were corrected for the basis set superposition error (BSSE) by the counterpoise correction.[64]

Supporting Information (see footnote on the first page of this article): Figure S1 shows the DFT-optimised structures of tacn and Me_3tacn with the numbering scheme and Table S1 contains the distances between all the ligands' numbered atoms.

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