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Affinity of Polypyridines Towards Cd^{II} and Co^{II} Ions: a Thermodynamic and DFT Study

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Cd^{II} and Co^{II} complex formation with pyridine (py), 2,2′-bipyridine (bipy), 2,2′6′,2′′-terpyridine (terpy), 2-(aminomethyl)pyridine (amp), and bis[(2-pyridyl)methyl]amine (dpma) was 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 in anaerobic conditions. Potentiometric, UV/Vis spectrophotometric, and calorimetric measurements were carried out to obtain the thermodynamic parameters of the systems investigated. Enthalpy-stabilized mononuclear ML_j complexes are formed, whereas entropy changes counteract complex formation. These results are discussed in terms of different basicities, steric requirements, and solvation, of both the ligands and the resulting complexes. Density functional theory (DFT) calculations were carried out in order to obtain structural information and binding energies in vacuo. The DFT results are correlated with the solution studies.
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Introduction

In recent years, a variety of polyamine N-donor ligands have been investigated in water[1–7] and nonaqueous solvents[8–12] with the aim of studying the influence of basicity and steric effects on selectivity patterns in metal coordination. Examples of the attractive properties and applications of these ligands are their potential use as building blocks of sequestering agents for metals of environmental importance, such as Cd or Pb,[4] fluorescent chemosensors,[3e] catalysts,[3f] or models for small molecule carriers, as in Cu^{I} or Co^{II} dioxygen complexes.[13–18]

In this context, some of our published papers concerning the complexation of transition-metal ions like Cd^{II} and Co^{II}[11] have shown that steric effects and N-methylation strongly influence not only the stoichiometry and nature of all metal ion complexes formed, but also the selectivity of these ligands toward metal ions. Systematic studies confirm that different N-alkylation of polyamines, or merely the substitution of only one amine with one alcohol group, causes important differences in the dioxygen affinity of Co^{II} complexes:[11b,11e] this affinity greatly depends on the electron density at the central metal ion, which, in turn, is affected by the electron donor and steric properties of the coordinated ligands.

As an extension of previous works, we report here the results of research on quantifying the complexing ability of pyridine functions toward Cd^{II} and Co^{II} metal ions in DMSO. The sp^2 hybridized N can exert high ligand field strength, even though its basicity may be less significant than that of sp^3 hybridized nitrogens.[19–21] Moreover, their lower σ-donor ability, greater rigidity with respect to linear polyamines, and their ability to give rise to π backbonding makes them suitable to tune the electronic and steric effects that govern ligand affinity for metal ions.[22,23] Pyridine functions are often found in multifunctional compounds with desirable or predictable properties such as luminescence, electrochemical, or catalytic activity.[22,23]

The model ligands chosen were: pyridine (py), 2,2′-bipyridine (bipy), and 2,2′6′,2′′-terpyridine (terpy). In order to highlight the subtle interplays between steric and electronic effects, intermediate 2-(aminomethyl)pyridine (amp) and bis[(2-pyridyl)methyl]-amine (dpma) ligands were also studied. The latter possess potentially interesting and versatile ways of binding, and may also give rise to polymetallic complexes with luminescent properties or favor spin-crossover phenomena.[24–27]

The stability constants for Cd^{II} were determined by direct potentiometric titration techniques, and UV/Vis spectroscopic measurements were employed for the Co^{II} systems. Enthalpy values were obtained by direct calorimetric titration.

To obtain a gas-phase picture of metal–ligand interactions, the study was completed with calculations using den-

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sity functional theory (DFT). DFT provides an excellent framework, yielding structural information and a number of chemical reactivity indices about ligands and their complexes, and gives 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 structural properties of transition-metal complexes with cyclic polyaza ligands[11g,28] and to describe the properties of polyamines, such as their basicity in both gas-phase[29] and solvent models.[30]

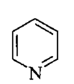
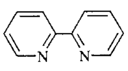
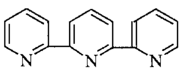
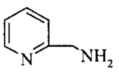
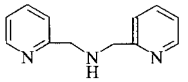
Results

Solution Thermodymamics

Computer treatment of the potentiometric, spectrophotometric, and calorimetric experimental data shows that the best fit is obtained when only mononuclear ML_j species are considered. The overall stability constants and thermodynamic functions obtained, together with the corresponding limits of error, are listed in Table 1. For the Co^{II}–bipy system, stability constants in DMSO have been previously given[31] and are in good agreement with the data reported here.

For the Co^{II}–amp and –dpma systems, some experimental details must be given to explain why thermodynamic data for Co^{II}–amp are not reported. The color of the solutions turns from pink to deep blue as titration proceeds with both amp and dpma, as clearly shown in Figure 1, in which absorbances at increasing times are reported for the Co^{II}–dpma systems at $R_c = C_L/C_M$ (the total ligand-to-metal ratio) of 1. This spectral change had already been observed in basic aqueous solutions in the presence of O_2 and explained by catalytic oxidative dehydrogenation of the ligand, with the transformation of the amine to imine.[32,33] Evidently, this reaction also occurs in our case, although the concentrations of water and O_2 were very low in our experimental conditions. The Co–imine product was expected to be present in very low amounts; nevertheless, its very high molar extinction coefficients in the visible range prevented the use of d-d Co^{II} bands to follow aminopyridine complexation. The rate of the undesired reaction was influenced by C_L/C_M: the lower this ratio, the slower the reaction. The inset in Figure 1 shows absorbance at 588 nm (A_{588}) as a function of time for various R_c. At a C_L/C_M

Table 1. Overall stability constants and thermodynamic functions for the reaction $M^{2+} + jL \rightleftharpoons ML_j^{2+}$ in DMSO at 298 K and I = 0.1 mol dm^{-3} (L = ligand) and in water.[34–38] Errors quoted correspond to three standard deviations.

Ligand	Species	DMSO				Water			
		$\log\beta_j$	$-\Delta G°_{\beta j}$ [kJmol^{-1}]	$-\Delta H°_{\beta j}$ [kJmol^{-1}]	$-T\Delta S°_{\beta j}$ [kJmol^{-1}]	$\log\beta_j$	$-\Delta G°_{\beta j}$ [kJmol^{-1}]	$-\Delta H°_{\beta j}$ [kJmol^{-1}]	$-T\Delta S°_{\beta j}$ [kJmol^{-1}]
 py	CoL	0.7(0.3)	4(1)	24(5)	20	1.16[a]	6.62	–	–
	CoL_2	–	–	–	–	2.93	10.10	–	–
	CdL	–	–	–	–	1.20[b]	6.85	–	–
	CdL_2	–	–	–	–	2.13	12.16	–	–
	CdL_3	–	–	–	–	2.14	12.22	–	–
 bipy	CoL	3.86(0.1)	22.0(0.6)	29(1)	7	6.06[c]	34.01	34.33[c]	0.32
	CoL_2	7.35(0.1)	41.9(1.1)	52(1)	10.1	11.42	64.10	63.64	–0.46
	CoL_3	8.66(0.2)	49.4(1.1)	67(1)	17.6	16.02	89.92	89.18	–0.74
	CdL	1.56(0.01)	8.9(0.1)	15.3(0.5)	6.4	4.25[c]	23.86	21.35[c]	–2.51
	CdL_2	2.65(0.03)	15.1(0.2)	23(1)	8.2	7.85	44.06	39.34	–4.72
						10.55	59.22	58.62	–0.60
 terpy	CoL	5.56(0.15)	31.0(0.9)	33(1)	2	8.4[d]	47.95	–	–
	CoL_2	10.52(0.15)	60(1)	63(1)	3	18.3	104.46	–	–
	CdL	2.27(0.02)	12.9(0.1)	10.6(0.3)	–2.3	5.1[d]	29.11	–	–
	CdL_2	4.57(0.05)	26.1(0.3)	27.8(0.3)	1.7	–	–	–	–
 amp	CoL	–	–	–	–	5.47[e]	31.23	29.1[e]	–2.13
	CoL_2	–	–	–	–	10.11	57.70	60.6	2.88
	CoL_3	–	–	–	–	13.56	77.40	91.9	14.49
	CdL	4.12(0.01)	23.5(0.2)	32.6(0.5)	9.1	4.38[f]	25.01	–	–
	CdL_2	7.79(0.01)	44.4(0.4)	65.0(0.5)	20.6	8.30	47.40		
	CdL_3	10.47(0.01)	59.7(0.6)	103.6(0.6)	43.8	11.33	64.70		
 dpma	CoL	6.2(0.3)	35.4(0.1)	49(1)	14	8.05[g]	45.18	36.2[g]	–8.98
	CoL_2	11.2(0.6)	63.9(0.2)	86(2)	23	13.85	77.74	68.2	–9.54
	CdL	4.49(0.01)	25.6(0.2)	27.3(3)	1.7	6.40[g]	36.52	24.7	–11.22
	CdL_2	8.69(0.02)	49.6(0.9)	73 (0.7)	23.4	11.76	67.11	57.7	–8.31

[a] Ref.[34] [b] Ref.[35] [c] Ref.[36a,36b] [d] Ref.[37] [e] Ref.[38] [f] Ref.[36d] [g] Ref.[36c]

value ≤0.7, this process does not occur within a reasonable interval of time, sufficient to collect reliable spectrophotometric titration point data. This was not the case when amp was used, as this secondary reaction was much faster and also not prevented at very low C_L/C_M ratios.

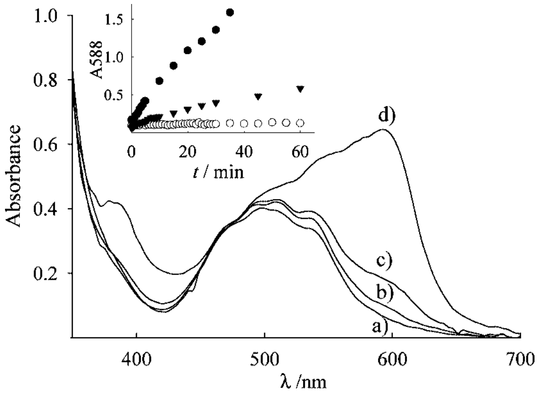


Figure 1. Spectral changes of a Co/dpma solution (C_L/C_M = 1) at increasing times: a) 5 s; b) 30 s; c) 5 min; d) 75 min. Time evolution (small graph) of absorbance at λ = 588 nm in case of different Co/dpma ratios: (○) C_L/C_M = 0.7; (▼) C_L/C_M = 1; (●) C_L/C_M = 1.5.

Figure 2 and Figure 3 show Δh_v, the total molar enthalpy change, as a function of R_c for Cd^{2+}- and Co^{2+}-ligand systems. The fit between experimental and calculated curves (full lines in the figures) is good, and their shapes are fully consistent with the information obtained from analysis of potentiometric and spectrophotometric data.

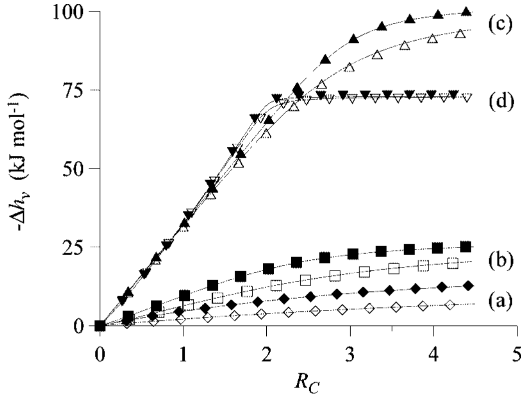


Figure 2. Total molar enthalpy changes Δh_v as a function of $R_c = C_L/C_M$ for Cd^{II} complex formation in DMSO. (a) bipy, (◊) 5.05, (♦) 15.01 mmol dm^{-3} in Cd^{2+}; (b) terpy, (□) 5.04, (■) 15.10 mmol dm^{-3} in Cd^{2+}; (c) amp, (△) 4.98, (▲) 14.97 mmol dm^{-3} in Cd^{2+}; (d) dpma, (▽) 5.07, (▼) 14.93 mmol dm^{-3} in Cd^{2+}. Solid lines calculated from values of β_j and $\Delta H°_{\beta_j}$, Table 1.

Some considerations may be made: (*i*) differentiation of curves of the complexation of Cd with bipy and terpy at various C_M indicates the formation of complexes of low stability; (*ii*) for Co with bipy, differentiation after R_c = 1 is explained by the formation of a very stable mononuclear ML complex, followed by other ML$_j$ species of lower stability; (*iii*) the linear trend of the curve for the Co–terpy and –dpma systems up to R_c = 2 and the absence of heat evolving beyond this value are consistent with the formation of ML and ML$_2$ complexes of comparable stability; (*iv*) as regards Co–dpma, the presence of an equivalent point at exactly R_c = 2 is in good agreement with the hypothesis that the secondary reaction is negligible from a calorimetric point of view.

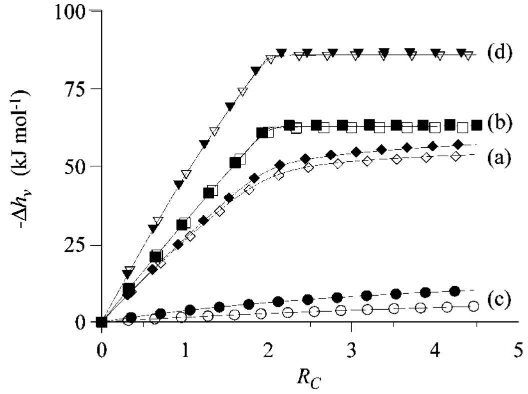


Figure 3. Total molar enthalpy changes Δh_v as a function of $R_c = C_L/C_M$ for Co^{II} complex formation in DMSO. For (a), (b), and (d), see legend of Figure 2 for same (a), (b), and (d) systems. In this case, (c) refers to py, (○) 15.05, (●) 45.01 mmol dm^{-3} in Co^{2+}.

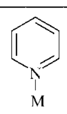
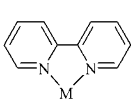
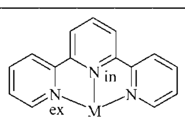
Calorimetric data show that a very small thermal effect occurs between Cd and py, even at high metal concentrations (C_M = 50 mmol dm^{-3}). For this reason, no $\Delta H°_{\beta_j}$ are reported, and only a rough value of $\log\beta_1$ ($\log\beta_1$ = 0.5 ± 0.2) could be calculated from potentiometric measurements. A similar trend was found for Co^{II}, but the higher thermal effects due to metal–ligand interaction allow the calculation of reliable values for $\log\beta_1$ and $\Delta H°_{\beta_1}$ by treatment of calorimetric data.

For the sake of comparison, Table 1 lists the available stability constants and thermodynamic functions for complex formation in water.[34–38] The set of data presented are the most complete in the literature, independently of the fact that some of them[36] refer to 20 °C. The choice seems to be reasonable, as the stability constants available at 25 °C, for which enthalpy data are not given,[39,40] are very close to those reported at 20 °C.

Computational Results

The M–N distances of complexes [CdL]$^{2+}$ and [CoL]$^{2+}$, whose geometries were optimized in vacuo, are listed in Table 2. A comprehensive list of bond lengths and angles is given as supporting information also for the free ligands (Supporting Information, Tables S1–S6): the results are in good agreement with experimental X-ray data.[41] To check the reliability of model chemistry in predicting the structural features of the compounds, the geometry of the structurally known[42] [Co(terpy)$_2$]$^{2+}$ was optimized (Supporting Information, Table S7) and also in this case the match between calculated and experimental data is good.

Table 2. M–N distances in Å.

				
	$d_{M–N}$	$d_{M–N}$	$d_{M–Nin}$	$d_{N–Nex}$
Co^{2+}	1.782	1.853	1.871	1.936
Cd^{2+}	2.169	2.205	2.205	2.267

In all cases, the M–N bond lengths appear to be shorter than in crystal structures;[41,43] this is of course due to the approximate models used and to the absence of other electrodonating ligands. The qualitative result of longer Cd–N distances of 0.33–0.39 Å with respect to Co–N is consistent with experimental structures, although in the last case the gap is in the range 0.18–0.31 Å. Table 3 lists total binding energies, E_{bind}, calculated for the formation of ML adducts. Energies for σ donation from the nitrogen lone pair to the metal, $E_{LP(N) \rightarrow M}$, calculated by using natural bond orbital (NBO) analysis,[44] are also listed in Table 3. In order to provide some indication of the role of π acceptor pyridine units in ligand–metal bonds, the NBO charges of the N atoms and metals in the compounds are calculated and listed in Table 4.

Table 3. Binding energies (E_{bind}) and strengths of N lone pair → metal interactions from NBO analysis ($E_{LP(N)\rightarrow M}$) in $kJ\,mol^{-1}$ for formation of ML^{2+} complexes. $\Delta E = E^{Co^{2+}} - E^{Cd^{2+}}$.

		E_{bind}	
	py	bipy	terpy
Co^{2+}	–615.0	–1007.9	–1341.8
Cd^{2+}	–548.8	–841.4	–1090.7
ΔE_{bind}	–66.3	–166.5	–251.1
		$E_{LP(N)\rightarrow M}$	
Co^{2+}	205.1	317.5	455.7
Cd^{2+}	193.1	292.8	412.0
$\Delta E_{LP(N)\rightarrow M}$	12.0	24.7	43.7

Table 4. NBO charges on metals and N atoms in compounds.

L	Cd^{2+}	Co^{2+}	CdL^{2+}	CoL^{2+}	CdL^{2+}	CoL^{2+}
			N_{in}		N_{ex}	
py	1.611	1.663	–0.650	–0.736	–	–
bipy	1.610	1.579	–0.659	–0.701	–	–
terpy	1.597	1.550	–0.642	–0.648	–0.638	–0.688

Discussion

General Remarks on Solvent Role

All complexes form in highly exothermic reactions, whereas entropy terms oppose reactions (Table 1), with the exception of the Cd^{II}–terpy system, for which a small positive entropy value was found. Negative enthalpy and entropy values are typical of reactions involving complexation of metal ions by neutral ligands in aprotic solvents.[8–12]

Pyridine complexes are characterized by higher stabilities in water than in DMSO: the trend is opposite to that found for simple primary and secondary aliphatic amines, in which the greater solvation of ligands in water through strong hydrogen bonds[45,46] overcomes the greater solvation[11a,47] of metal ions in DMSO. In the present case, the role of ligand solvation is evidently of minor importance, and the stability constants follow the trend expected on the basis of metal ion solvation. As regards amp and dpma, higher stability is still observed in water although it is much less marked. This higher stability in the case of dpma systems, for which all the thermodynamic functions are available in the two solvents, is essentially entropic in origin, as enthalpy terms are more favorable in DMSO. This indicates that the desolvation effects of the amino group, more important in water than in DMSO, play a major role in determining the stability trend in the two solvents.

Pyridine Ligands

Pyridine shows a much lower affinity for Cd^{2+} and Co^{2+} ions with respect to monoamines ($\log K_1^{n\text{-butylamine}} = 2.6$ and 1.91 for Cd and Co, respectively):[11a,11b] this point is certainly due to the lower basicity of pyridine nitrogen when compared with amines in DMSO.[45,46] Steric effects may also be considered, as *ortho* hydrogens on pyridine rings produce steric hindrance once coordinated to a metal ion.[2]

The higher stabilities and more negative enthalpy and entropy data for the Co^{II}–bipy system, as compared with py, fit the formation of chelated complexes, although some steric strain, due to hydrogens in 3,3′-positions, occurs in the *cis*-conformer allowing coordination to metal ion.[2]

Certainly, the entry of the third bipy molecule causes unfavorable electronic and steric effects due to the other two ligands, and this explains the lower stability and enthalpy gain for the third complexation step. This fits crystallographic data, which show that, in the solid state, a distorted octahedron is formed by three bipy molecules around Co^{II}.[48]

When $[Co(terpy)]^{2+}$ (and $[Co(terpy)_2]^{2+}$) is formed, the ligand behaves as a terdentate: the low gain in the enthalpy term with respect to $[Co(bipy)]^{2+}$ complex formation ($\Delta\Delta H°_{\beta_1}{}^{Co(terpy)\rightarrow Co(bipy)} = -4\,kJ\,mol^{-1}$) is mainly due to extensive desolvation effects that come into play when this rigid terdentate ligand coordinates. This is confirmed by the low unfavorable entropy term associated with the same complexation step for the two ligands ($\Delta T\Delta S°_{\beta_1}{}^{Co(terpy)\rightarrow Co(bipy)} = +5\,kJ\,mol^{-1}$). Extra energy should also be considered for terpy rearrangement in the preorganized planar conformer with convergent nitrogen atoms. Lastly, strain is also produced by the resulting two fused five-membered chelate rings.

Analysis of thermodynamic data on Cd^{2+} reactions suggests some preliminary considerations: (*i*) the positive increase in the stability constants of Co^{II} complexes on going from py to bipy and terpy (in both solvents) is not observable in the Cd^{II} systems; (*ii*) the lower affinity for Cd^{II} than for Co^{II} is a peculiarity of all the pyridine ligands examined here. This effect is connected to the intrinsic nature of the ligands and the size of the metal ions, and not to the different solvation of central ions, as this was presumed to be larger for Co^{II} than for Cd^{II},[11c] which would give an opposite trend in stability.

The calculated M–N distances (Table 2) show that, in the gas phase, this higher affinity for Co^{II} is also present: bond lengths are always longer for Cd^{II}– than for Co^{II}–pyridine systems, these differences being more marked for the less stable M^{II}–py complexes (0.387 Å longer in Cd^{II}–py than in Co^{II}–py). It is noteworthy that the difference in $M–N_{in}$ bond lengths calculated with DFT in Cd^{II}– and Co^{II}–terpy complexes (0.334 Å) is slightly higher than that of the $M–N_{ex}$ bond (0.331 Å): this is in agreement with previous studies which found that small cations are able to better interact with the central nitrogen, due to the steric constraint of this rigid ligand.[49]

As regards the binding energies (Table 3), the high values found (549–1542 $kJ\,mol^{-1}$) cannot be compared with experimental ones, as solvation effects were not taken into account in calculations. However, they are important because they show relative trends equal to those experimentally determined: even in this case, the affinity of pyridine ligands is higher for Co^{II} than for Cd^{II}. Certainly, one of the main factors influencing this trend is the higher charge density on Co^{II}, which causes this smaller ion to be a harder acid than Cd^{II}.

The π backbonding does not appear to be important as far as these bipositive metal ions are concerned. In fact, the trend in total binding energies (E_{bind} in Table 3) is parallel to that found in $E_{LP(N)\rightarrow M}$, that is σ donation plays a dominant role in ligand–metal bond stabilization. The calculated NBO charges on metal ions and nitrogens in the compounds (Table 4) give the same indications. The addition of π-acceptor units (from py to terpy) leads to a decrease in metal charges (and a simultaneous increase in N charges), showing that electron transfer mainly goes from the ligand to the metal by σ donation. An opposite trend in the positive metal charge was observed when the number of pyridine units was increased in complexes where π backbonding played an important role.[50]

The stability of Co^{II} complexes increases much more than that of Cd^{II} ones on going from bidentate bipy to terdentate terpy ($\Delta\Delta G^{\circ}_{Cd(terpy-bipy)} = 0.7$; $\Delta\Delta G^{\circ}_{Co(terpy-bipy)} = 1.7$). This indicates that, whereas the affinity of the ligands towards Co^{II} becomes larger and larger on increasing the number of pyridine donors, the stability of Cd^{II} complexes is not so affected by the increase of binding sites in the ligand. This is also confirmed by the total binding energy values (Table 3), which show that ΔE_{bind} (= $E_{bind}{}^{Co^{2+}} - E_{bind}{}^{Cd^{2+}}$) increases on going from py to terpy, particularly for terpy, clearly indicating more marked selectivity for Co^{2+}.

The results of this terpy complexation with Cd^{II} are difficult to explain solely by desolvation and steric effects, already discussed for Co^{II}. An attempt to explain these data is that the ligand behaves as a terdentate one, and this is achieved by structural rearrangement in the metal ion coordination sphere, giving rise to a pentacoordinate species. A certain misfit between the size of the large cadmium ion and the steric requirements of the ligand lies at the origin of this behavior. Also in the solid state, some preference for pentacoordination has already been highlighted in Cd–terpy compounds with crowded anions.[43a] Reaction enthalpies, lower for $[Cd(terpy)]^{2+}$ than for $[Cd(bipy)]^{2+}$, and especially the favorable entropy term for the formation of the terpyridyl complex, compared with the unfavorable entropy of formation of the bipyridyl complex, fit this hypothesis.

Aminopyridine Ligands

The thermodynamic data, when compared with those obtained for mono- and bidentate aliphatic amines[11a,11b] and with py, suggest the involvement of all the N atoms in metal complex formation with amp and dpma. In order to support this hypothesis, some ^1H NMR spectra of solutions of Cd^{II} and dpma at various R_c values were recorded. In particular, the spectrum of $[Cd(dpma)_2]^{2+}$ in $[D_6]$DMSO solution (Figure S1, Supporting Information) shows that the multiplet centered at δ = 8.49 ppm in the free ligand, assigned to *ortho* pyridine protons, is shifted by 0.38 ppm (δ = 8.11 ppm) after complexation. This effect, together with the symmetric pattern of the given spectrum, reflects the binding of all pyridine nitrogens to Cd^{II} atoms in complex formation. The weak, broad signal due to the proton of the secondary -NH- amino group is also shifted by about 2 ppm on complex formation (from about 3.2 to 5.1 ppm). Another proof of the coordination of the amino group of dpma comes from FTIR spectra, recorded for a DMSO solution with a dpma-to-cadmium ratio of 2, where no bands for free secondary amino groups (at 3305 cm^{-1}) can be detected, whereas only the band due to bonded amine (at 3192 cm^{-1}) was observed.

Amp complexes with Cd are characterized by much higher stabilities with respect to bipy ($\Delta\log\beta_1 = 2.56$ and $\Delta\log\beta_2 = 5.14$), especially as regards the second complexation step. This is mainly due to the higher affinity for metal ions of amines compared with pyridines in DMSO.[45,46] More favorable steric and solvational effects certainly also play an important role, as indicated by the large gain in stability produced when the more crowded $[Cd(amp)_2]^{2+}$ is formed. At the origin of this large stability gain, there is a considerable and favorable increase in enthalpy that largely overcomes the parallel unfavorable decrease in entropy. This may reflect greater solvation of amp complexes in which the hydrogens of amines bonded to the metal ion can organize the solvent molecules near the metal complex by forming hydrogen bonds. This explanation is also in agreement with the formation of $[Cd(amp)_3]^{2+}$, a stable M/L = 1:3 species, which is not formed by the more rigid and less solvent-ordering bipy with the cadmium ion. When the third complexation step is examined, desolvation effects are already over, as indicated by the higher negative stepwise enthalpy and entropy values. The same trend in desolvation effects, to an even more marked extent, is observed when examining the second complexation step with dpma.

When a pyridine ring is added to amp, a trend similar to that found on going from bipy to terpy is obtained for Cd^{II} amp and dpma complexation. The gain in stability is very small, due to a less unfavorable entropy term, whereas the $\Delta H°_{\beta_1}$ value is even less favorable than for amp: the enthalpy gain due to the additional $Cd–N_{py}$ bond is overcome by the enthalpy spent during desolvation. As dpma donor atoms are undoubtedly all bonded to Cd^{II}, this result clearly confirms the low affinity of the pyridine moiety for Cd^{II}, which is even more enhanced when more py units are part of a more complex structural frame, as in dpma (and terpy).

From another point of view, as regards differences in complex stability between one metal ion with terpy and dpma, it should be noted that the gain in stability is much more significant for Cd^{II} ($\Delta\log\beta_1^{\text{dpma–terpy}} = 2.22$) than for Co^{II} ($\Delta\log\beta_1^{\text{dpma–terpy}} = 0.64$), that is, the relative selectivity towards Co^{II} is decreased. This evidences the great influence of structural constraints in governing metal–ligand affinity: substitution of the central pyridine unit with a flexible amino group relaxes ligand structural requirements and decreases the particular misfit cited for Cd–terpy systems. Obviously, as two pyridines are still inserted in the ligand frame, residual strains still occur, and also contribute to the low gain in stability with respect to the Cd–amp system (see above).

When comparing analogous bidentate and tridentate aliphatic ligands, such as primary ethylenediamine (en), diethylenetriamine (dien), and secondary *N*,*N′*-dimethylethylenediammine (dmen) and *N*,*N′′*-dimethyldiethylenetriamine (dmdien), much higher stability and exothermicity are found,[11c,11d,11e] due to the higher basicity of the aliphatic ligands. The opposite occurs with the corresponding tertiary *N*,*N*,*N′*,*N′*-tetramethylethylenediammine (tmen) and *N*,*N*,*N*,*′N′*,*N′′*-pentamethyldiethylenetriamine (pmdien) although the basicity order in DMSO is still $R_3N > py$.[45,46] In this case, steric hindrance due to the methyl groups of the ligands in the complexes evidently explains this reverse behavior.

Dioxygen Affinity

Reversible dioxygen-binding properties were found for $[Co(bipy)(terpy)]^{2+}$ mixed complexes in nonaqueous low-coordinating media, such as acetonitrile or nitrobenzene, and μ-peroxo adducts were isolated.[51] In order to verify if oxygen binding also occurs in DMSO, O_2 was bubbled in solutions containing the mixed complex $[Co(terpy)(bipy)]^{2+}$ {the stability constant for the reaction $Co^{2+} + terpy + bipy \rightleftharpoons [Co(terpy)(bipy)]^{2+}$ was also evaluated by spectrophotometric titration and its value was $\log K = 8.9(0.1)$}. No changes in UV/Vis spectra were observed in the range 300–650 nm, thus showing that no O_2 absorption occurred. Fitting the dissociative mechanism at the basis of dioxygen coordination,[52] higher activation energy is probably required for the bond breaking necessary for O_2 coordination, when the $[Co(terpy)(bipy)]^{2+}$ species is solvated by the more-coordinating solvent DMSO.

Conclusions

Much lower affinities are shown by pyridine ligands for Cd^{II} than for Co^{II}: this is due to the poorer acid properties of the former ion, confirmed by the calculated binding energies of the complex and by longer M–N lengths in Cd^{2+} complexes. No important π backbonding seems to be involved as far as these bipositive metal ion–ligand systems are concerned, as evidenced by DFT calculations on model systems. This selectivity increases with the number of pyridine units in the ligands: when the larger Cd^{II} with rigid planar terpy is considered, a misfit between ion size and ligand structural requirement is invoked to explain the results. This point is also confirmed by the huge gain in the stability of the Cd^{II} complex when one py unit is substituted with an amino group in dpma. This extra stability, especially with respect to cobalt systems, is not explained only in terms of the higher σ-donor properties of the amino group, but also by taking into account the particular relaxation introduced into the Cd–ligand system when the central py is substituted with an aliphatic moiety. A comparison with data available in water shows that the desolvation effects of the amino group, more important in water than in DMSO, play a crucial role in determining the stability trend in the two solvents, especially for aminopyridine ligands.

Experimental Section

General Remarks: Solvated salts, $Co(ClO_4)_2·6DMSO$ and $Cd(ClO_4)_2·6DMSO$, ligands, and solvents were prepared and purified as described previously.[11a,11b,11c] All experiments in anaerobic conditions were carried out at room temperature in a MB Braun 150 glovebox under a controlled atmosphere containing less than 1 ppm of water and less than 1 ppm of oxygen.

Potentiometric Measurements: In a typical titration, known volumes of ligand solutions ($50 < C°_L < 400$ mmol dm^{-3}) were added to Cd^{II} solutions (20 mL) ($2 < C°_{Cd} < 20$ mmol dm^{-3}) at 298.1 ± 0.1 K. The equilibrium concentrations of cadmium(II), necessary to calculate stability constants, were obtained from the emf data of a galvanic cell similar to that reported previously.[11a] Emf data were ascertained with an Amel 338 pHmeter equipped with a Weiss WCD1001 Cd ion-selective electrode as working electrode and a Methrom 6.0718.000 silver electrode as reference. The Nernstian response of Cd electrodes was checked in the range $10^{-7} <$ metal $< 10^{-2}$ mmol dm^{-3}. Equilibrium was typically reached in 2–5 min. The Hyperquad[53] minimization program was used to calculate stability constants.

Spectrophotometric Measurements: UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer, using optic fiber probes connected directly with the cell inside the glovebox. The concentrations of cobalt(II) and ligands were in the range $2 < C^{\circ}_{\mathrm{Co}} < 20\ \mathrm{mmol\,dm^{-3}}$ and $50 < C^{\circ}_{\mathrm{L}} < 400\ \mathrm{mmol\,dm^{-3}}$, respectively. Data were recorded over the wavelength range 300–650 nm. The absorption maximum for $Co(ClO_4)_2$ in DMSO occurs at 535 nm, with an extinction molar coefficient of $\varepsilon = 11.9\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$.[11a] Maximum absorption of CoL_j complexes is shifted to lower wavelengths (Supporting Information, Figure S2 as an example), in line with an increase in ligand field strength. In the case of dpma with Co^{II}, UV/Vis data were collected in the presence of Cd^{II} as a competitive ion, in order to obtain more reliable values for the stability constants.

The absorbance data at about 20 different wavelengths in the range 450–550 nm were analyzed and the formation constants of CoL_j complexes were determined, together with the molar extinction coefficients of the complexes at each relevant wavelength, using the Hyperquad program.[53] UV/Vis measurements for dioxygen uptake were carried out on similar apparatus by means of 1-cm optic fiber probes (Hellma) dipped directly into the reaction vessel.

Calorimetric Measurements: A Tronac model 87-558 precision calorimeter was employed to measure reaction heats. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (Tham) with a standard solution of HCl in water. The experimental value of the neutralization heat of Tham was $\Delta H^{\circ} = -47.59\ \mathrm{kJ\,mol^{-1}}$, in good agreement with the accepted value of $-47.53 \pm 0.13\ \mathrm{kJ\,mol^{-1}}$.[1]

Calorimetric titrations were performed at 298.00 ± 0.02 K by adding known volumes of ligand solutions ($50 < C^{\circ}_{\mathrm{L}} < 400\ \mathrm{mmol\,dm^{-3}}$) to 20 mL of metal (metal = Cd^{II}, Co^{II}) solutions ($2.00 < C^{\circ}_{\mathrm{metal}} < 50.0\ \mathrm{mmol\,dm^{-3}}$).

For each titration run, the 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 dilution heat of the titrant, which was determined separately. The dilution heat of the titrate was found to be negligible in the metal concentration range used.

Quantity Δh_v, total heat per mole of metal ion, was defined and calculated by dividing the net reaction heat by the number of moles of metal ion in the calorimetric vessel. The Letagrop Kalle[54] least-squares computer program was used to calculate enthalpy changes.

NMR Measurements: ^1H NMR spectra were recorded at 298 K with a Bruker AC-200 spectrometer. Measurements were performed on [D$_6$]DMSO solutions containing metal ions (ca. $30\ \mathrm{mmol\,dm^{-3}}$) and the dpma ligand in the molar ratio $R_c = 1$ or 2. Analogous measurements were carried out on solutions containing only the ligand concerned.

FTIR Spectroscopy: FTIR spectra were obtained on a Bio-Rad FTS 40 spectrometer (maximum resolution $4\ \mathrm{cm^{-1}}$; 16 scans). A cell with barium fluoride windows (thickness 25 µm) was used. Cells were filled, closed in a glovebox, and quickly transferred to the spectrometer. C°_{Cd} and C°_{L} in the DMSO solutions were about $50\ \mathrm{mmol\,dm^{-3}}$.

Computational Procedure: DFT calculations on ML^{2+} complexes (M = Co, Cd; L = py, bipy, terpy) were performed using Gaussian03[55] with the B3LYP three-parameter hybrid density functional.[56] For the Co^{2+} complexes the unrestricted formalism was employed with three unpaired electrons ($S = 4$). The split valence basis set 6-31G(d) was employed for the atoms of the ligands, and a 3-21G basis was applied for the metal ions. The use of the small 3-21G basis set was due to the observation that sometimes the application of ECPs with Co^{2+} gave convergence problems with open-shell SCF in DFT calculations. Nevertheless, the choice of this basis set for the metal ions does not affect the qualitative trend of the results.

All geometries were optimized by symmetry constraints. After optimization, equilibrium points were characterized by calculating vibrational frequencies, in order to confirm that they were local minima.

Binding energies were corrected for zero-point energy and basis set superposition error (BSSE) by the counterpoise correction ($E_{\mathrm{bind}} = E_{\mathrm{ML^{2+}}} - E_{\mathrm{M^{2+}}} - E_{\mathrm{L}} + E_{\mathrm{BSSE}}$).[57] NBO analysis was performed by the NBO3.1 program included in Gaussian.

Supporting Information (see footnote on the first page of this article): Figure S1 shows ^1H NMR spectra for the Cd–dmpa system in [D$_6$]DMSO. Figure S2 shows spectral changes, in terms of molar absorption of *j* species versus wavelengths, for the Co–bipy species. Tables S1–S7 list DFT-optimized distances and angles of py, bipy, and terpy, their ML (M = Cd^{II}, Co^{II}) and $Co(terpy)_2$ complexes, and the numbering scheme.

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