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Thermodynamic and Spectroscopic Properties of Mixed Complexes in Aqueous Solution. Copper(II) Complexes of 2,2′-Bipyridyl and Iminodiacetic or Pyridine-2,6-dicarboxylic Acid

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Potentiometric, calorimetric, and EPR investigations on the simple and mixed complexes of copper(II) with iminodiacetate (ida) or pyridine-2,6-dicarboxylate (dipic) anions and 2,2′-bipyridyl (bpy) were carried out. On the basis of the data obtained, the two ternary complexes Cu(bpy)(dipic) and Cu(bpy)(ida) turned out to have a different coordination number and stereochemistry; in particular the former appears to be octahedrally six-coordinated while the latter is five-coordinated having a square-pyramidal geometry.

Introduction

Previously,[2,3] we reported the thermodynamic and spectroscopic properties of some ternary complexes of Cu^{II} with 2,2′-bipyridyl and some alkane or aromatic dicarboxylic acids. Considering the thermodynamic and spectroscopic (EPR and electronic) data, it was possible to observe that all the mixed complexes had the same structure because of the conformation requirements of 2,2′-bipyridyl ligand, the only exception being the complex with succinate anion, for which a square-pyramidal structure has been proposed.

In light of these results we have studied the thermodynamic and spectroscopic (EPR and electronic) parameters of mixed complexes of copper(II) with 2,2′-bipyridyl (bpy) having the same formula, Cu(bpy)(L), as the above mentioned ones, where L is now a tridentate ligand, namely, iminodiacetate (ida) or pyridine-2,6-dicarboxylate (dipic) anion.

It was therefore possible to estimate the effects of the different denticity of the ligands (bpy as bidentate and ida or dipic as tridentate) around the copper(II) ion and of the presence of different substratum of the tridentate ligands on the thermodynamic properties associated with the formation of ternary complexes, as well as the effects on their structural parameters.

The potentiometric (pH and pCu type) and calorimetric measurements were carried out in aqueous solution at 25 °C and 0.1 mol dm^{-3} $NaClO_4$. The thermodynamic and spectroscopic data were compared with those of the corresponding parent complexes measured under the same experimental conditions. We have also obtained all the thermodynamic parameters associated with the formation of the protonated and hydroxo species of the simple complexes of Cu^{II} with the tridentate dicarboxylic acids as well as the $\Delta H°$ and $\Delta S°$ values for the formation of the protonated complexes Cu(bpy)(H)(ida) and Cu(bpy)(H)(dipic) by using previously reported potentiometric data.[4]

Experimental Section

Chemicals. The 2,2′-bipyridyl (Erba RPE) was recrystallized from a water–ethanol mixture. The p*K* value found was in agreement with the value previously determined.[5] Iminodiacetic (BDH) and pyridine-2,6-dicarboxylic (Fluka) acids were recrystallized from water. The purity of these acids was checked by titrations with standard CO_2-free NaOH and in all cases a value higher than 99% was found. The disodium salts of these acids were prepared according to literature. The preparation of the solid simple and mixed complexes has been described elsewhere.[6,7] All the solutions were prepared with twice-distilled water and their ionic strength was kept at 0.1 mol dm^{-3} by addition of $NaClO_4$. The standardization of the solutions was carried out as previously described.[2]

Emf Measurements. The potentiometric measurements were carried out by means of two potentiometers (Amel 232 or Radiometer PHM 52) using a glass electrode (Ingold 201 NS) or a copper-selective electrode (Amel 201 sens-ion) and a double junction calomel electrode (Orion 90-02-200). In Table I the experimental details of potentiometric titrations are reported. Other details are as previously described.[4,5,8,9]

Calorimetric Measurements. The calorimetric measurements were carried out at 25 ± 0.001 °C employing a LKB precision calorimeter (Model 8700) and a 100-cm^3 titration vessel (Model 8726-1). The reproducibility of the system and other details have already been reported.[10] Experimental details of the calorimetric titrations are listed in Table II.

Spectroscopic Measurements. First-derivative EPR X-band spectra were recorded with a Varian E-109 instrument equipped with a standard temperature control unit. All measurements reported here were made at 133 K by using quartz sample tubes. The solutions were prepared by dissolving the solid complexes in water–methanol mixtures (1:1 ratio) and their concentrations ranged from 1 to 3 mmol dm^{-3}. Field calibration was checked by using polycrystalline di-

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Table I. Experimental Details of Potentiometric Measurements for Complex Formation

$[L]_T$[a]	$[Cu]_T$[a]	titrant (concn[a])	no. of titrations	pH range	measmt type
		L = ida			
1.45	1.0	NaOH (50–200)	4	2.3–5.4	pH
1.5	1.5		5		
4.0	2.0		3		
1.5	2.0		1		
0.74	1.0		1		
1.45	1.0		5	6.2–9.6	
4.0	2.0		3	5.1–9.7	
		L = dipic			
3.0	1.5	NaOH (100–200)	2	2.0–9.5	
2.5	2.5		2	2.0–6.5	
3.0	2.0		2	2.0–9.0	
1.2[b]	0.0	$Cu(ClO_4)_2$ (20)	3		pH and pCu
2.0[b]	0.0		3		

[a] The concentrations are expressed in mmol dm^{-3}. [b] $[H_2L]$:$[Na_2L]$ = 1:5.

phenylpicrylhydrazyl (dpph) as *g* marker.

Electronic absorption spectra in solution were recorded at room temperature with a Coleman-Hitachi EPS-3T spectrophotometer in 1-cm quartz cells.

Calculations. The calculations relative to the purity of the ligands and to $E°$ determination were carried out by the computer program ACBA.[11] The formation constants were calculated by using the programs SCOGSB[5,12] and MINIQUAD.[13,14]

The enthalpies of formation were evaluated by means of the computer program DOEC.[15] This program calculates the free concentrations of the components from the log β values of the different species and then computes the millimole changes of each species formed during the calorimetric titration, solving the equation: $Q_{cor} = (\delta_{n_j})(\Delta H_j)$, minimizing the function $U = \sum w(Q_{cor} - Q_{cor,calcd})^2$ by a linear least-squares method. The weight w was generally kept equal to 1 for all experimental points; sometimes the use of different w values was convenient (i.e., $w = 1/Q^2$ was used when the Q values of the various titrations were very different from each other, whereas $w = k(\delta n_j)$ was used when δn_j values varied markedly being also negligible in some of the titration points). For the potentiometric and calorimetric measurements, the calculations were first carried out on each titration separately and then on all titrations of each system simultaneously.

All the programs calculate the standard deviation of the parameters (log β or $\Delta H°$), whereas the uncertainty intervals reported in this work are the range (the maximum deviation from the mean) or are three times the standard deviation from the mean. They also evaluate Hamilton's statistical factor R[16] that is a measure of the error in the variable, the error squares sum of which is minimized. The test proposed by Vacca et al.[17] was used, when it was necessary to select from different models, in particular to check the formation of some hydroxo or protonated species. The errors reported for the formation constants are of the order of ±0.05 logaritmic units in the majority of cases. Lower values are often reported in literature, but they only account for nonsystematic errors. To make the runs as independent as possible on each other, different equipment and different standards were used throughout. The errors shown are inclusive also of the systematic errors of each run. The errors listed in Table V for the $\Delta H°$ formation values range between ±0.5 and ±2 kJ mol^{-1}. These errors, quite low, may be obtained, for systems containing simultaneously many species, making use of direct calorimetry only. In fact, by use of log β affected by an error of 0.05, working at five different temperatures within a range of 50 °C, the lowest possible error in $\Delta H°$ is ±2–3 kJ mol^{-1}.[18]

Thermodynamic data for the protonation of the ligands have already been reported[10,19] and are listed in Table III.

For the analysis of the EPR spectra a program previously described was used.[20,21] It was assumed that **g** tensor and the hyperfine coupling tensor had the same principal axis system. In the case of multispecies spectra the calculation was first performed on each species and then the summed spectrum was compared with the experimental one. The EPR parameters given in Table VI are the best fit to the final simulation.

Results and Discussion

Potentiometry. Copper(II) ion forms with ida and dipic (L) ligands two major species, CuL and CuL_2, a protonated form, CuHL, and a hydroxo form CuLOH. As for many copper(II) complexes, the dimeric species $Cu_2L_2(OH)_2$ could be detected. The formation constant values of the species present in the Cu(ida) and Cu(dipic) systems are listed in Table IV together with those already reported in literature. Few data regarding protonated and/or hydroxo species have been reported so far; the species Cu(H)(dipic), Cu(dipic)(OH), $Cu_2(dipic)_2(OH)_2$, and $Cu_2(ida)_2(OH)_2$ are determined in this work for the first time. As concerns the species CuL and CuL_2, combining the data so far reported with ours, we obtain a recommended value for the formation constants (see Table IV).

The species CuHL shows a low pK in both systems; e.g., at pH 2.3, by use of a total Cu^{II} and ida concentration of 1.0 and 1.45 mmol dm^{-3}, respectively, the copper(II) present as protonated species is about 14%. The hydroxo species begin forming in an appreciable amount above pH 7; Cu(dipic)(OH) is formed before Cu(ida)(OH). In the Cu(ida) system, at pH 9 ($[Cu]_T$ = 1.0 mmol dm^{-3}, $[ida]_T$ = 1.45 mmol dm^{-3}) 20% of the total copper(II) ion is present as Cu(ida)(OH) and $Cu_2(ida)_2(OH)_2$. It is noteworthy that whereas, when we are working with bidentate ligands such as 2,2′-bipyridyl or 1,10-phenanthroline, the dimeric species is predominant in slightly alkaline solutions (log K_d = 5),[31-33] with tridentate ligands the dimerization is less favored (log K_d = 3.5), as previously observed.[33] The constant relative to the equilibrium Cu + H + dipic $\rightleftarrows$ Cu(H)(dipic) was also calculated from calorimetric data; the value obtained is in agreement with that determined

Table II. Experimental Details of Calorimetric Measurements for Complex Formation

$[Cu]_T$[a]	$[ida]_T$[a]	$[dipic]_T$[a]	$[bpy]_T$[a]	titrant (concn[a])	no. of titrations	$[H]_T$[a]
2.0	2.2			$HClO_4$ (240)	3	−0.16
1.5	1.5				4	0.06
2.5	5.2				2	−2.1
5.6	7.2				2	−0.74
4.0	0.0			ida (37.5), NaOH (25.0)	2	2.85
2.5		6.0		$HClO_4$ (240)	3	11.1
3.1		4.8			2	2.1
4.0		0.0		Na_2dipic (25.0)	2	2.8
2.5	5.2		0.0	bpy (14.9), $HClO_4$ (24.1)	2	−2.1
2.0	2.2		0.0		2	−0.2
1.5	1.5		0.0		1	0.6
4.5	6.0		4.0	$HClO_4$ (240)	2	1.9
3.1		4.8	0.0	bpy (14.9), $HClO_4$ (24.1)	7	2.1
2.5		6.5	0.0		4	11.1
2.0		0.0	2.0	Na_2dipic (24.4)	2	3.6

[a] The concentrations are expressed in mmol dm^{-3}.

Table III. log K^H and ΔH^a Values for the Protonation of Pyridine-2,6-dicarboxylic Acid, Iminodiacetic Acid, and 2,2′-Bipyridyl at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$)

ligand	log K_1^H	log K_2^H	log K_3^H	$\Delta H_1°$	$\Delta H_2°$	$\Delta H_3°$
dipic[b]	4.63	1.99		4.1	−3.1	
ida[b]	9.29	2.60	1.7	−32.3	−3.2	−3.6
bpy[c]	4.46			−14.5		

[a] $\Delta H°$ values in kJ mol^{-1}. [b] Reference 19. [c] Reference 10.

from potentiometric measurements (see Table IV).

Calorimetry. $\Delta G°$, $\Delta H°$, and $\Delta S°$ values relative to the formation of the simple complexes are reported in Table V. The thermodynamic data available from the literature for the formation of Cu(ida) complex[28] is in agreement with our results, provided that allowance is made for the different experimental conditions under which they were obtained.

The species relative to the equilibrium $Cu + L \rightleftarrows CuL$ are enthalpically favored, but, above all, they are entropically stabilized. Comparing $\Delta H°$ and $\Delta S°$ values with the ones obtained for similar complexes,[2,3] we can assert that all potential donor atoms are engaged in the coordination sphere of the copper(II) ion. The Cu(ida) complex is more stable than the Cu(dipic) one, because of the relevant contribution of the imino nitrogen, more basic than a pyridine one; furthermore if we consider that the coordination of the ida anion involves a "stiffening" of the ligand, the similar values of $\Delta S°$ between Cu(ida) and Cu(dipic) complexes indicate that ida neutralizes better than dipic the metal ion charges.

The bis complexes are enthalpically more stabilized than the mono complexes and show a less remarkable entropic positive contribution. This marked difference between $\Delta S_2°$ and $\Delta S_1°$ values can be explained, considering that the formation of the mono species involves a decrease of the coordination number with respect to that of exaquo ion; thus the number of solvent molecules released from the first coordination sphere of the copper(II) ion is higher than the number of donor atoms. Furthermore the low $\Delta S_2°$ values are due to the formation of species with negative charges. Table V shows that the Cu(dipic)$_2$ complex is enthalpically and entropically more favored than Cu(ida)$_2$. In order to elucidate this result, it is necessary to bring up the structural differences between the two ligands. While in the formation of the mono complexes the flexible ida molecule allows the donor atoms to interact better than dipic with the copper(II) ion (in dipic, in fact, the carboxylate groups are forced to stand coplanar with the pyridinic ring), in the bis complexes this situation does not play a relevant role, since the cation is already bonded to another ligand molecule. The protonated complexes, Cu(H)(dipic) and Cu(H)(ida), show enthalpic and entropic changes that follow the same trend found for the mono complexes.

The thermodynamic parameters relative to the formation of ternary complexes (Table V) show negative enthalpic and positive entropic changes. Comparing these values with those obtained for the copper(II) mixed complexes with bpy and dicarboxylates,[2,3] it is possible to assert that all potential donor atoms are involved in bonding to metal ion. The Cu(bpy)(ida) complex is more stable than Cu(bpy)(dipic) and this is to be

Table IV. Formation Constants[a] for Cu-L Systems (L = Pyridine-2,6-dicarboxylate, Iminodiacetate, and 2,2′-Bipyridyl)

T, °C	I, mol dm^{-3}	log K_1	log K_2	log β_2	log K_{CuHL}	log K_{CuLOH}	log $^*K_{CuLOH}$	log K_d	ref
				Pyridine-2,6-dicarboxylic Acid					
20	0.1 $NaNO_3$	9.14	7.38	16.52					22
30	0.1 KCl	10.0	6.3	16.3					23
20	0.5	9.14	7.37	16.51					24
	0.2	8.9	8.2	17.1					25
25	0.1 $NaClO_4$	9.15 ± 0.15	7.22 ± 0.05	16.37 ± 0.2	2.0 ± 0.1		−7.5 ± 0.2	3.6 ± 0.3	this work
		9.2 ± 0.1	7.3 ± 0.1	16.5 ± 0.2					recommended values
					1.8 ± 0.1				this work, from calorimetry
				Iminodiacetic Acid					
30	0.1 KCl	10.55	5.65	16.20					26
30	0.1 KCl	10.4							23
25	0.1		5.65						27
20	0.1 KNO_3	10.63	6.05	16.68					28
25	0.05 KNO_3					6.26			29
25	0.1 KNO_3				1.5				30
25	0.1 $NaClO_4$	10.42 ± 0.02	5.60 ± 0.02	16.02 ± 0.02	1.93 ± 0.05		−9.37 ± 0.05	3.5 ± 0.3	this work
		10.5 ± 0.1	5.7 ± 0.1	16.2 ± 0.2					recommended values
				2,2′-Bipyridyl					
25	0.1 $NaClO_4$	8.11		13.66					10

[a] $K_{CuHL} = CuL + H \leftrightarrows CuHL$; $K_{CuLOH} = CuL + OH \rightleftarrows CuLOH$; $^*K_{CuLOH} = CuL + H_2O \leftrightarrows CuLOH + H$; $K_d = 2CuLOH \rightleftarrows Cu_2L_2(OH)_2$.

Table V. Thermodynamic Values for Cu^{II} Simple and Mixed Complexes at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$)

reaction	log β	$-\Delta G°$, kJ mol^{-1}	$-\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}
$Cu + ida \leftrightarrows Cu(ida)$	10.42	59.4 ± 0.1	16.6 ± 0.4	144 ± 1
$Cu + dipic \leftrightarrows Cu(dipic)$	9.15	52.2 ± 0.9	11.5 ± 0.4	137 ± 2
$Cu + 2ida \leftrightarrows Cu(ida)_2$	16.02	91.4 ± 0.1	43.1 ± 0.6	162 ± 1
$Cu + 2dipic \leftrightarrows Cu(dipic)_2$	16.37	93.4 ± 0.9	40.8 ± 0.6	176 ± 1
$Cu + ida + H \leftrightarrows Cu(H)(ida)$	12.35	70.4 ± 0.3	19 ± 2	172 ± 3
$Cu + dipic + H \leftrightarrows Cu(H)(dipic)$	11.2	64 ± 2	14 ± 1	168 ± 3
$Cu + bpy + ida \leftrightarrows Cu(bpy)(ida)$	16.63	94.8 ± 0.1	61.5 ± 0.8	112 ± 1
$Cu + bpy + dipic \leftrightarrows Cu(bpy)(dipic)$	16.11	91.9 ± 0.3	74.1 ± 1.2	60 ± 2
$Cu + bpy \leftrightarrows Cu(bpy)$[a]	8.11	16.2	44.6	5.4
$Cu + 2bpy \leftrightarrows Cu(bpy)_2$	13.66	77.9	70.0	26.4
$H + OH \leftrightarrows H_2O$[b]	13.75	78.2 ± 0.1	56.4 ± 1	−73.1 ± 0.4

[a] Reference 10. [b] Reference 34.

Table VI. EPR Spectral Data of Cu^{II} Simple and Mixed Complexes with 2,2′-Bipyridyl and Iminodiacetic or Pyridine-2,6-dicarboxylic Acids

complex	g_z	g_y	g_x	A_z[a]	A_y[a]	A_x[a]	$A_\parallel{}^N$[a]	$A_\perp{}^N$[a]	ref
Cu(bpy)	2.308 ± 0.004	2.068 ± 0.004	2.068 ± 0.004	166 ± 2	7 ± 2	7 ± 2	~14[b]	~10[b]	*d*
Cu(dipic)	2.374 ± 0.002	2.098 ± 0.002	2.098 ± 0.002	134 ± 1	20 ± 2	20 ± 2			this work
Cu(ida)	2.293 ± 0.002	2.068 ± 0.005	2.057 ± 0.005	172 ± 1	7 ± 2	12 ± 2	17 ± 2	(12 ± 2)[c]	this work
Cu(bpy)(dipic)	2.282 ± 0.001	2.075 ± 0.005	2.055 ± 0.005	165 ± 1	3 ± 2	5 ± 2	14 ± 2	(8 ± 2)[c]	this work
(bpy)(dipic) + py	2.266 ± 0.001	2.059 ± 0.005	2.053 ± 0.005	178 ± 1	4 ± 2	9 ± 2	17 ± 2	12 ± 2	this work
Cu(bpy)(ida)	2.256 ± 0.001	2.068 ± 0.005	2.040 ± 0.005	179 ± 1	10 ± 2	7 ± 2	(9 ± 2)[c]	(6 ± 2)[c]	this work
Cu(bpy)(ida) in 30% py	2.280 ± 0.001	2.068 ± 0.005	2.045 ± 0.005	165 ± 1	8 ± 2	5 ± 2	16 ± 2	(9 ± 2)[c]	this work

[a] All hyperfine coupling constants are in 10^4 cm^{-1}. [b] Not resolved. [c] The values in parentheses are the input required for the best simulation; they are not resolved in the experimental spectrum. [d] F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).

ascribed to a higher entropic contribution. A different degree of desolvation can account for the significant diversity of the entropic values, thus suggesting that these complexes have a different coordination number. It is possible that the mixed complex Cu(bpy)(dipic) reaches the six-coordination through a water molecule. The less exothermic value of the enthalpic change for the Cu(bpy)(ida) complex also strengthens the previous assertion, because the release of a larger number of solvent molecules from the coordination sphere of the copper(II) ion results in a higher endothermic contribution.

Electronic and EPR Spectroscopy. EPR spectra of Cu(ida) and Cu(dipic) solutions have values of $g_z > g_{x,y} > 2.040$, thus suggesting for both complexes a $d_{x^2-y^2}$ or d_{xy} ground state, characteristic of square-planar, square-base-pyramidal, or octahedral stereochemistries.[35,36] The experimental EPR spectra of the two complexes are reported in Figure 1; their spin-Hamiltonian parameters are presented in Table VI. It must be pointed out that these spectra are not due to a single species; Cu(dipic) in methanolic solution behaves as a dimeric species with dipolar coupled copper(II)–copper(II) pairs,[37] whereas in water–methanol mixtures the monomeric complex predominates, even if the presence of a certain amount of the dimeric species cannot be excluded.[38] In the case of Cu(ida), the methanolic and the aqueous–methanolic solutions give spectra that are superimposable, showing the presence of at least two species; under different conditions, i.e., ligand/metal ratio >1 and pH 4 (corresponding to the maximum percentage of Cu(ida) formation), only one species is found and corresponds to that having the highest g_z value. The second species is probably a complex with different coordination level or a protonated system. As shown from the spin-Hamiltonian parameters (Table VI), in the case of Cu(ida) complex, the simulation procedure needed the introduction of a slight rhombic component in plane, in order to fit closely the experimental spectrum, while in the case of Cu(dipic) an axial spin Hamiltonian was practically sufficient. The differences between the $g_\parallel$ and $A_\parallel$ of Cu(dipic) and g_z and A_z of Cu(ida) are undoubtedly surprising. Both ligands behave as tridentate; thus such a difference in their magnetic parameters can be ascribed to unlike arrangements around the copper(II) ion. In particular, the value of $g_\parallel$, about 2.4 for Cu(dipic) complex, points out that we are dealing with a strong ionic environment in plane, while the relatively low value of $A_\parallel$ suggests a considerable axial interaction.[39-41] In the case of Cu(ida) complex the lower g_z and the relatively higher A_z values, together with the appearance of both hyperfine structure due to the ligand (the imino nitrogen) and rhombic component in plane, suggest a stronger covalent character and a distortion from the square symmetry of equatorial plane. These considerations led us to think that nitrogen coordination of these dicarboxylates occurs in a different way, namely, the dipic one in an apical position, thus leaving an almost symmetric bonding situation in the equatorial plane, and the ida one in an equatorial site, thus imposing a distortion from the square geometry of the plane. This interpretation is supported by the studies on the crystal and molecular structure of Cu(dipic)·$2H_2O$[42] and Cu(ida)·$2H_2O$,[43] although it should be borne in mind that solution and solid structures must be carefully correlated.

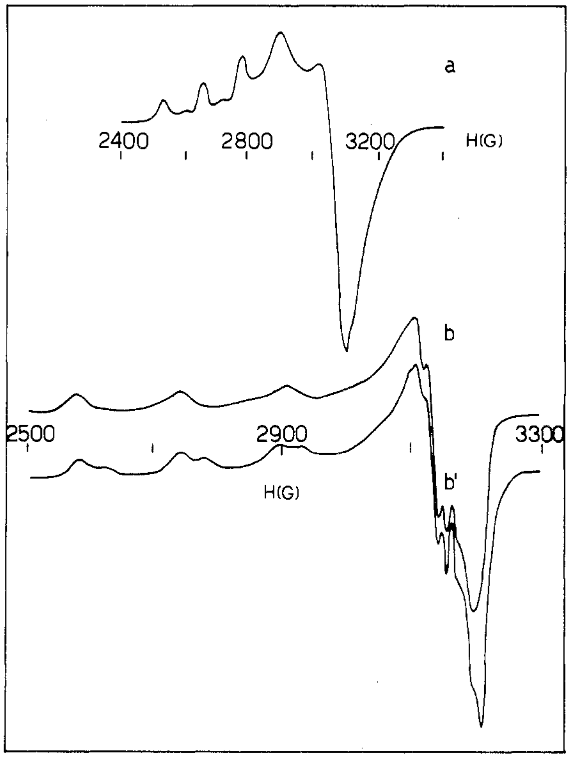

Figure 1. Frozen-solution EPR spectra (X band) of Cu(dipic) in H_2O–CH_3OH at 133 K (a), Cu(ida) in H_2O–CH_3OH at 133 K (b′), and Cu(ida) in H_2O–CH_3OH at 133 K with ida/Cu > 1 and pH 4 (b).

The mixed complexes, Cu(bpy)(ida) and Cu(bpy)(dipic), also have a $d_{x^2-y^2}$ or d_{xy} ground state as both the lowest *g* factors lie higher than 2.040; their g_z and A_z values are, respectively, lower and higher than g_z and A_z of simple parent complexes, as predictable by considering the substitution of two water molecules by means of the two bipyridyl nitrogens in the coordination sphere of the copper(II) ion.[44,45] The EPR spectra of these compounds are presented in Figures 2 and 3, while their spin-Hamiltonian parameters are shown in Table VI.

Cu(bpy)(dipic) shows a superhyperfine structure due to the ligand nitrogens in the perpendicular part of the spectrum; the simulation procedure needed the introduction of a rhombic component in plane. Cu(bpy)(ida) gives rise to a well-resolved rhombic component; furthermore the addition of a slight amount of pyridine to the solution of the complex does not affect the band positions (only an increase in the signal intensity was observed). On the contrary, the addition of pyridine alters essentially the nature of the paramagnetic site in Cu(bpy)(dipic) solution, because it appears a noteworthy superhyperfine structure even in the parallel part of its spectrum; moreover the g_z and A_z values become lower and higher, respectively, than those observed in the spectrum of Cu(bpy)-

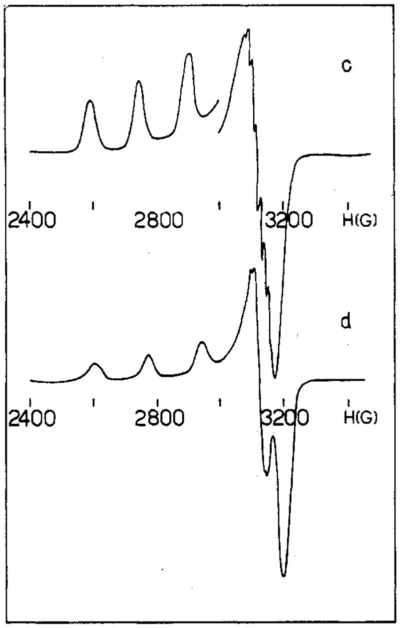

Figure 2. Frozen-solution EPR spectra (X band) of Cu(bpy)(dipic) (c) and Cu(bpy)(ida) (d) in H_2O–CH_3OH at 133 K.

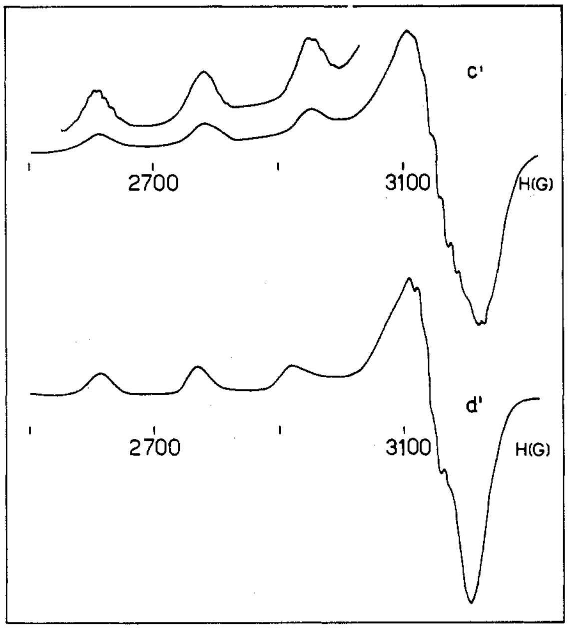

Figure 3. Frozen-solution EPR spectra (X band) of Cu(bpy)(dipic) (c′) after the addition of a slight amount of free pyridine to the aqueous–methanolic solution of the complex and Cu(bpy)(ida) (d′) in an H_2O–CH_3OH mixture with 30% pyridine at 133 K.

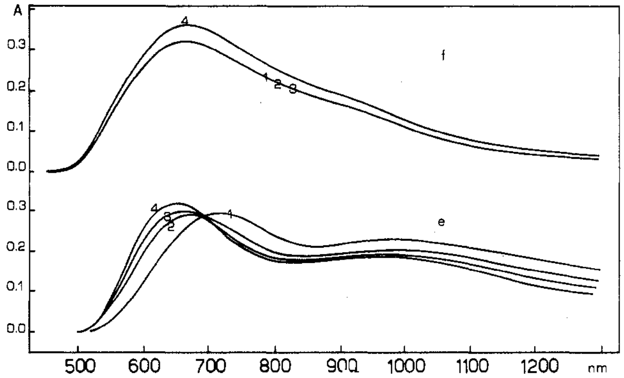

Figure 4. Electronic spectra of Cu(bpy)(dipic) (e) and Cu(bpy)(ida) (f) aqueous solutions (7 mmol dm^{-3}) with increasing concentration of free pyridine at room temperature and pH ranging from 8.5 to 9.5. Spectral values, $cm^{-1} \times 10^3$ (ϵ): e_1 without py, 13.89 (41); f_1 without py, 15.06 (46); e_2 in 28 mmol dm^{-3} py, 14.70 (41); f_2 in 56 mmol dm^{-3} py, 15.01 (47); e_3 in 56 mmol dm^{-3} py, 15.07 (43); f_3 in 126 mmol dm^{-3} py, 14.97 (48); e_4 in 252 mmol dm^{-3} py, 15.30 (47); f_4 in 30% py, 14.50 (57).

(dipic) without the addition of pyridine. All of this evidence can be ascribed to a stronger field in the equatorial plane arising from the coordination of a pyridine molecule. In fact the rhombic component becomes smaller and the superhyperfine structure can be ascribed to four quasi-equivalent nitrogens. In the case of the Cu(bpy)(dipic) complex, the coordination in plane is completed by a water molecule (the dipic ligand is accommodated in a plane containing an equatorial position and the two apical ones, the bpy occupying the remaining two coordination sites). Only the addition of about 30% pyridine causes a significant change in the spectrum of Cu(bpy)(ida): the rhombic component is reduced, the g_z value shifts toward lower field, and A_z becomes smaller. This trend is just opposite to that observed in the Cu(bpy)(dipic) system, thus suggesting that pyridine coordinates in an apical position. The behavior resulting from the addition of pyridine to the solutions of the mixed complexes can be proved by the visible spectra. The electronic spectra of the two complexes are reported in Figure 4. The Cu(bpy)(dipic) ν_m is influenced greatly by the addition of a small amount of pyridine; in particular it shifts toward lower frequencies. The Cu(bpy)(ida) ν_m is practically indifferent; only the addition of 30% pyridine produces a significant shift. In the case of Cu(bpy)(ida) the relatively strong rhombic component in plane supports the fact that the donor atoms of the ligands in the equatorial plane are very different. The nonresponse to the addition of slight amounts of pyridine, the absence of a clear superhyperfine structure, and the coordination of a pyridine molecule (when the mixed complex is placed in 30% pyridinic solution) suggest that a distorted square-pyramidal geometry is formed when ida and bpy ligands are arranged around the copper(II).

Conclusion

On the grounds of thermodynamic and spectroscopic data it is possible to point out the different coordination degree as well as the different structure between the two mixed complexes, Cu(bpy)(dipic) and Cu(bpy)(ida). In the ternary complexes of Cu^{II} with bpy and dicarboxylates[2,3] the calorimetric, the EPR and the electronic data were so similar as to indicate an essentially identical structure for all the mixed compounds. This similarity was not so evident in the case of the simple parent complexes and it was therefore ascribed to the presence of bpy which must force the dicarboxylate ligands to adopt the same configuration in all cases. On the contrary as regards the ternary systems here considered, it appears evident that bpy does not play an important role in determining the structure of the ternary complex, because the differences between the two simple complexes persist also after the coordination of the heterocyclic diimine.

This behavior is noteworthy from a thermodynamic viewpoint, if one also considers that for the ternary complexes of Cu^{II} with bpy and dicarboxylates log $K^{Cu}{}_{Cu(bpy)}$ is always higher than log $K^{Cu}{}_{CuL}$ (L = dicarboxylate), while for both Cu(bpy)(dipic) and Cu(bpy)(ida) the value of log $K^{Cu}{}_{Cu(bpy)}$ is lower than log $K^{Cu}{}_{CuL'}$ (when L′ is ida or dipic). As previously hypothesized,[46] one can assert that the geometric and electronic characteristics of the "strongest" ligand bound to the metal ion govern the chelation of the second ligand.

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Registry No. Cu, 7440-50-8; 2,2′-bipyridyl, 366-18-7; iminodiacetic acid, 142-73-4; pyridine-2,6-dicarboxylic acid, 499-83-2.

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(38) Cu(dipic) simulation was carried out supposing that the experimental spectrum was attributable to the contribution of three probable species. The spectrum of the first species Cu(dipic) predominates; the second one is due to a species with a different coordination level or to a protonated complex, the magnetic parameters of which are $g_{\parallel} = 2.332 \pm 0.005$, $g_{\perp} = 2.066 \pm 0.005$, $A_{\parallel} = (115 \pm 5) \times 10^{-4}$ cm^{-1}, and $A_{\perp} = (18 \pm 5) \times 10^{-4}$ cm^{-1}; the third spectrum is due to a certain amount of a dimeric species that raise the baseline of the overall spectrum parallel part, owing to its broad absorption. The parameters relative to the second species present in the spectrum of Cu(ida) complex (see in Figure 1 the spectrum designated b′) are $g_{\parallel} = 2.278 \pm 0.005$, $g_{\perp} = 2.050 \pm 0.005$, $A_{\parallel} = (164 \pm 5) \times 10^{-4}$ cm^{-1}, and $A_{\perp} = (15 \pm 5) \times 10^{-4}$ cm^{-1}.

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X-ray Photoelectron Spectra of Binuclear Palladium–Palladium-Bonded Complexes and Their Insertion Products

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X-ray photoelectron spectroscopic (XPS) data have been obtained for the binuclear Pd(I) complexes $Pd_2(dpm)_2Cl_2$ and $Pd_2(dam)_2Cl_2$ (dpm = bis(diphenylphosphino)methane and dam = bis(diphenylarsino)methane) and products resulting from the insertion of carbon monoxide, methyl isocyanide, sulfur dioxide, and atomic sulfur into the metal–metal bond. The insertion of these small molecules into the Pd–Pd bond results in either no change or modest increases in the Pd $3d_{5/2}$ binding energies (ΔE_B of 0.0 to +0.6 eV) while the Cl $2p_{3/2}$, P $2p_{3/2}$, or As 3d binding energies of the attendant ligands remain constant. The largest Pd $3d_{5/2}$ binding energy shifts arise from insertion of SO_2. When observable, the binding energies of atoms in the inserted ligands decrease, sometimes substantially (0.9–2.5 eV), compared with those of their precursors. The small binding energy shifts of the Pd 3d levels are reasonable because only half of the charge donated to the inserted ligand comes from each half of the dipalladium complex. Similarly the binding energy shifts of the atoms of the inserted ligands (compared to those of their free, neutral precursors) become smaller, where detectable, as the number of atoms which compose the ligand increases. Nitrogen 1s binding energies for bridging methyl isocyanide in $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$ and $[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2](PF_6)_2$ are ~1 eV lower than those for terminal methyl isocyanide. For comparison, XPS data are also presented for $[Pd_2(CNCH_3)_6](PF_6)_2$, $[Pd(CNCH_3)_4](PF_6)_2$, $Pd(CNCH_3)_2I_2$, and $[Pt_2(CNCH_3)_6](BF_4)_2$, which contain only terminal, linearly bound $CNCH_3$ ligands.

Introduction

The unprecedented insertion of small molecules into the metal–metal bond of the dipalladium complexes $Pd_2(dpm)_2Cl_2$ (dpm = bis(diphenylphosphino)methane) and $Pd_2(dam)_2Cl_2$ (dam = bis(diphenylarsino)methane) via eq 1 has attracted widespread attention. As a consequence of the insertion reaction, the metal–metal bond is broken and the palladium ions move about 0.5 Å further apart. Carbon monoxide[2-5] and

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