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Copper(II) Complexes with 2,2'-Dipyridyl, 1,10-Phenanthroline or 2,2',2"-Terpyridyl and Bidentate or Tridentate Dicarboxylic Acids

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Mixed complexes of copper(II) with 2,2'-dipyridyl, 1,10-phenanthroline or 2,2',2"-terpyridyl and some dicarboxylic acids, having heteroatoms in their chains, have been prepared and characterized. Infrared and electronic spectra are also presented and discussed.

Introduction

In recent years the number of studies concerning the preparation of mixed complexes of transition metals has increased [1–5]; in particular the copper(II) complexes have been extensively studied for the peculiarity of this ion in displaying a variety of coordination shapes. In a recent article J. Gazo *et al.* have examined the various factors that determine the several stable configurations assumed by the copper(II) complexes; to describe this feature they have introduced the term "plasticity" [6].

In order to understand how factors such as the aromaticity of the ligand substrate, the number of the chelate-ring members, the possibility of π-bond formation and the flexibility of the ligand can play a considerable role in the different kinds of coordination of the copper(II) ion we have prepared the mixed complexes of the copper(II) with the neutral bases 2,2'-dipyridyl (dipy), 1,10-phenanthroline (phen) or 2,2',2"-terpyridyl (terpy) and some dicarboxylic acids having heteroatoms in their chains. The abbreviations of the acids taken into account are reported below:

iminodiacetic acid	IDA
oxydiacetic acid	ODA
thiodiacetic acid	THDA
diphenylether-2,2'-dicarboxylic acid	DPED
diphenylamino-2,2'-dicarboxylic acid	DPAD
cyclopropan-1,1-dicarboxylic acid	CPRD
succinic acid	SUCC

The study of infrared and electronic spectra was carried out to distinguish the different types of coordination polyhedra. The DPAD and DPED have been included in order to examine the properties of copper(II) complexes arising from the same chromophoric group O_2N or O_3 and the same number of chelate-ring members, but different structures and substrates with respect to the IDA and ODA.

Experimental

The preparation procedure for the mixed complexes, the reagents and the apparatus for physical measurements were the same as previously described [1, 2]. The DPAD was prepared according to the procedure described by P. N. Mohan Das *et al.* [7], but the melting point (305 °C) does not agree with that reported (149 °C). We have assigned the formula to the acid on the basis of the elemental analysis and the structure on the basis of the NMR spectrum. Other preparations report the following melting points: 278–9 °C [8], 301–2 °C [9], 296–7 °C [10]. The DPED was prepared according to the procedure described by R. Anschutz and W. Claasen [11]. The preparation of CPRD has been previously described [1]; the other acids were used as received from Fluka.

Results and Discussion

The analytical data of the prepared complexes are presented in Table I. All complexes are blue or blue–green and can be represented by the general formula $Cu(B)(A)\cdot nH_2O$, where B is the neutral base, A the anion of the dicarboxylic acid and n = 0–2. The dehydration of the hydrated species begins at relatively low temperatures (80–110 °C) and is complete without decomposition down 160 °C. The mixed complexes with DPAD and DPED are insoluble in water and common organic solvents; the other complexes are soluble in DMSO, pyridine, water and alcohols. The conductivity values obtained from DMSO, pyridine, water and methanol solutions are generally lower than 20 $ohm^{-1}\ cm^2\ M^{-1}$ and indicate a non-electrolytic behaviour.

Infrared Spectra

The IR spectra of each series of complexes show enhancements in the position and relative intensity of the imine bands comparable with those reported for other complexes with the same ligands; on the other hand, they are those expected for nitrogen to cation coordination. Some IR data are reported in Table II.

The IR spectra of the copper(II) dicarboxylates exhibit two strong bands around 1580 and 1410 cm^{-1} assigned respectively to the ν_{as} and ν_s modes of

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TABLE I. Analytical Data for Copper(II) Mixed Complexes.

Complex	C %		H %		N %		Cu %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(dipy) IDA	47.93	48.37	3.74	3.65	11.98	11.74	18.11	17.73
Cu(phen)IDA·$2H_2O$	44.81	44.06	4.00	4.15	9.80	9.63	14.82	14.65
Cu(terpy)IDA·$2H_2O$	49.18	50.25	4.35	4.47	12.08	11.97	13.70	13.92
Cu(dipy)THDA	45.71	46.07	3.29	3.32	7.62	7.81	17.27	17.34
Cu(phen)THDA·$2H_2O$	43.09	44.11	3.62	3.78	6.28	5.99	14.25	13.96
Cu(terpy)THDA	51.28	50.76	3.40	3.51	9.44	9.13	14.28	14.07
Cu(dipy)ODA·H_2O	45.47	46.22	3.82	3.80	7.58	7.62	17.18	17.24
Cu(phen)ODA	48.79	48.12	3.07	3.11	7.11	7.28	16.13	16.52
Cu(terpy)ODA·H_2O	53.20	52.94	4.00	4.15	9.80	9.69	14.81	14.70
Cu(dipy)DPAD	60.69	61.24	3.61	3.68	8.85	8.90	13.38	13.54
Cu(phen)DPAD	60.40	59.75	3.31	3.24	8.13	7.98	12.29	12.43
Cu(dipy)DPED	60.56	60.12	3.39	3.41	5.89	6.03	13.35	13.08
Cu(phen)DPED	60.29	60.57	3.11	3.07	5.41	5.20	12.27	12.64
Cu(terpy)CPRD·$2H_2O$	52.11	52.87	4.16	4.21	9.12	9.02	13.78	13.81
Cu(terpy)SUCC·H_2O	52.96	53.31	3.98	4.05	9.75	9.64	14.75	14.63

TABLE II. Infrared Spectra.

Complex	$\nu_{as}(COO)^a$			$\nu_s(COO)^a$	
Cu(dipy)IDA	1635 s.br.		(1575 s.br.)	1370 s.	(1420 s.)
Cu(phen)IDA·$2H_2O$	1630 s.br.			1380 m.	
Cu(terpy)IDA·$2H_2O$	1600 s.br.			1390 s.	
Cu(dipy)THDA	1630 s.br.		(1560 s.br.)	1370 s.	(1420 s.)
Cu(phen)THDA·$2H_2O$	1630 s.br.			1370 m.	
Cu(terpy)THDA	1620 s.br.			1370 s.	
Cu(dipy)ODA·H_2O	1625 s.br.;	1605 s.	(1570 s.br.)	1390 m.	b
Cu(phen)ODA	1620 s.;	1600 s.		1390 m.	
Cu(terpy)ODA·H_2O	1610 s.;	1590 s.br.		1400 m.	
Cu(dipy)DPAD	1620 s.;	1570 s.br.	(1615 s.; 1580 s.br.)	1375 s.	(1400 s.)
Cu(phen)DPAD	1615 s.;	1570 s.br.		1370 s.	
Cu(dipy)DPED	1615 s.;	1590 s.br.	(1610 s.; 1580 s.br.)	1380 s.	(1410 s.)
Cu(phen)DPED	1615 s.;	1590 s.br.		1380 s.	
Cu(terpy)CPRD·$2H_2O$	1610 s.br.		(1600 m.; 1550 s.)	1390 s.	(1420 s.)
Cu(terpy)SUCC·H_2O	1630 s.br.		(1590 s.)	b	(1430 s.)

[a] Values in parenthesis refer to copper(II) dicarboxylates. [b] Unassigned.

the carboxylate group. These frequency values agree with those reported for other copper(II) carboxylates, for which X-ray crystal structures have shown a bidentate carboxylate group [12–14].

The IR spectra of the mixed complexes of copper(II) ion with dipy or phen and SUCC, CPRD, IDA, ODA and THDA show the ν_{as} and ν_s modes at 1640–1620 and 1400–1370 cm^{-1}, respectively. These values are similar to those previously observed for some analogous mixed systems [1, 2] and suggest carboxylate groups unsymmetrically bound to the copper(II) ion through an oxygen atom only; however, the splitting of the ν_{as} occurring for some mixed systems indicates that interactions between the second oxygen atom of the carboxylate group and the axial positions of the copper(II) take place causing the formation of polymeric species. Crystalline effects and permanence of hydrogen bondings [15] as well as coordination of the nitrogen or oxygen atom to copper(II) ion [16–19], may be the

TABLE III. Electronic Spectra (frequency values in kK; in parenthesis the ε values).

Complex	Methanol^{a}		Pyridine^{b}	Solid State	
Cu(dipy)IDA	15.27(46);	12.35sh	14.50(57)	15.15;	12.50
Cu(phen)IDA·2H_2O	15.15(52);	12.05sh	14.28(60)	15.05;	12.50sh
Cu(terpy)IDA·2H_2O	14.20(108)^{c}			14.08^{c}	
Cu(dipy)THDA	15.27(68);	12.90sh	14.71(74)	15.15^{e}	
Cu(phen)THDA·2H_2O	15.15(91);	12.82	14.50	16.13;	13.89
Cu(terpy)THDA	14.50(112)			13.89;	~10
Cu(dipy)ODA·H_2O	14.92(77)		14.50(64)	15.38	
Cu(phen)ODA	14.81(93)		14.50(72)	15.27	
Cu(terpy)ODA·H_2O	14.28(105)^{c}			14.08^{c}	
Cu(dipy)DPAD	d			15.15	
Cu(phen)DPAD	d			14.71	
Cu(dipy)DPED	d		14.50(68)	15.62	
Cu(phen)DPED	d			15.15	
Cu(terpy)CPRD·2H_2O	13.70(125);	11.36sh	14.71(74)	13.51;	11.11sh
Cu(terpy)SUCC·H_2O	14.92(59)			14.28	

^{a}In water or on addition of small portions of DMSO the ϵ_{max} is almost the same as found for the methanolic solutions. ^{b} Or on addition of 30% of pyridine to the methanolic solution. ^{c}Very broad. ^{d}Insoluble. ^{e}Flattened.

causes of the shifts to lower frequencies of the N–H and C–O–C stretching modes observed in the spectra of the IDA and ODA mixed complexes.

The IR spectra of the mixed complexes with terpy, except the complex with THDA, show a strong and broad band covering the region 1620 cm^{-1}; since these systems were obtained as hydrates the broadness of this band can be attributed to intense mixing of (COO) stretching, H_2O bending and pyridine ring stretching modes.

Two strong bands, both assigned to the ν_{as} mode of the carboxylate group, appear around 1620 and 1580 cm^{-1} in the spectra of DPAD and DPED mixed complexes and suggest bridging bidentate carboxylate group.

Electronic Spectra

Electronic spectral data are reported in Table III and Fig. 1.

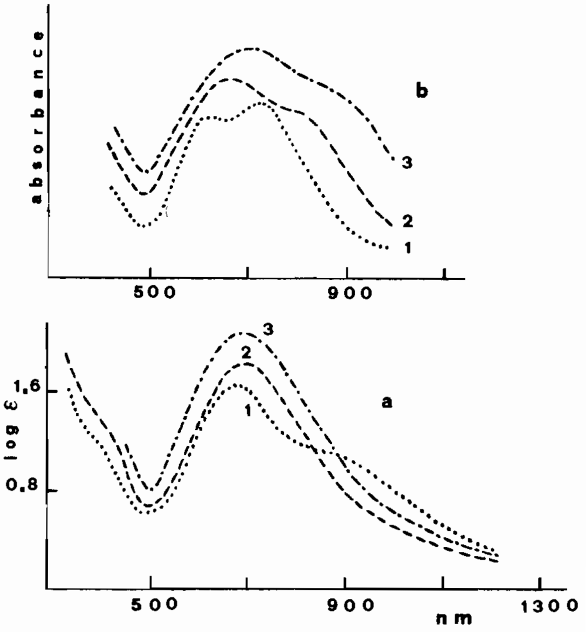

Figure 1. Absorption (a) and reflectance (b) spectra of copper(II) complexes: (a_1) Cu(dipy)IDA in MeOH; (a_2) Cu(terpy)CPRD·2H_2O in pyridine; (a_3) Cu(terpy)THDA in MeOH; (b_1) Cu(phen)THDA·2H_2O; (b_2) Cu(dipy)IDA; (b_3) Cu(terpy)CPRD·2H_2O.

The absorption spectra of the copper(II) complexes with THDA, IDA, ODA or SUCC and terpy in water or methanol are all consistent with a single broad band at 14.71–14.50 kK; the ϵ_{max} shifts to the longer wavelengths in the solid spectra while a shoulder appears around 10 kK. These spectra resemble those reported for copper(II) complexes with 6-coordinate environments and suggest octahedral geometries.

Both reflectance and absorption spectra in methanol of the complex Cu(terpy)CPRD·2H_2O exhibit a broad band at 13.70–13.50 kK with a pronounced shoulder at 11.36–11.11 kK; the ϵ_{max} shifts to 14.70 kK in pyridine solution while the shoulder disappears. This behaviour is probably due to a conversion from 5-coordinate into octahedral tetragonally distorted structures.

The reflectance and absorption spectra in methanol or water of the copper(II) complexes with

IDA and dipy or phen are consistent with a relatively low intensity band at 15.30–15.00 kK and a pronounced shoulder at 12.5–12.05 kK. The reflectance spectra of the corresponding complexes with THDA exhibit a flattened band at 15.15 kK (dipy) or two peaks at 16.13 and 13.89 kK (phen), but the absorption spectra in methanol are similar to those of the corresponding complexes with IDA. The spectra resemble those reported for some copper(II) complexes with 5-coordinate chromophores [20–22]. Both aqueous and methanolic spectra appear to be indifferent to the addition of some high donor strength ligands containing oxygen or nitrogen as donor atoms. Only the dissolution of the complexes in DMSO and pyridine or the addition of appreciable amounts of pyridine to the methanolic or aqueous solutions cause significant changes in the band shape and intensity; the band becomes in all cases more symmetric because of the disappearance of the peak or shoulder around 12.5 kK while the ϵ_{max} shifts to lower frequencies. These spectral enhancements make the spectra resemble those of the octahedral complexes of the copper(II) ion with terpy and THDA or IDA. It is extemely probable that these changes arise, like the complex $Cu(terpy)CPRD \cdot 2H_2O$, from the conversion of 5-coordinate into 6-coordinate arrangements.

The reflectance and absorption spectra in methanol of the mixed complexes of copper(II) with ODA, DPED, DPAD and dipy or phen show an almost symmetric band at 15.62–14.70 kK. These spectra are similar to those reported for copper(II) complexes in tetragonally distorted octahedral structures. No significant change is observed for the band shape and intensity of the ODA complexes on passing from solid state to solution spectra in methanol or water, but the ϵ_{max} shifts to 14.50 kK in pyridine solution. The absorption spectra of the mixed complexes of ODA, THDA and IDA with dipy or phen in pyridine are similar to the spectra in methanol of the corresponding complexes with terpy; these complexes, however, exhibit a more broadened band while the ϵ_{max} appears generally shifted to the longer wavelengths. These differences are certainly attributable to the geometrical characteristics of the terpy ligand which prevent the N–Cu–N angle from achieving 180° (23), thus causing a large distorsion from the O_h symmetry.

A shoulder appears in most spectra at 28–27 kK on the tail of an higher intraligand transition band; this shoulder is similar to that observed for some analogous copper(II) complexes [2, 24] and arises from a charge transfer or an intraligand transition [25–27].

Conclusions

A variety of 5- and 6-coordinate chromophores may form around the copper(II) ion with these ligands (N_2O_3, N_3O_2, N_3O_3, N_2SO_2, N_3SO_2); however, the frequent occurrence of polymeric structures in the solid state or the interactions in solution between the axial positions of the copper ion and solvent molecules lead us to believe that octahedral geometries are the most abundant. Only the complexes $Cu(terpy)CPRD \cdot 2H_2O$, Cu(dipy)IDA, Cu(dipy)THDA, $Cu(phen)IDA \cdot 2H_2O$ and $Cu(phen)THDA \cdot 2H_2O$ show to have 5-coordinate environments in the solid state; however, their dissolution in pyridine or DMSO or the addition of appreciable amounts of pyridine to the aqueous or methanolic solutions cause in any case an expansion of the coordination sphere from 5-coordinate into 6-coordinate arrangements.

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