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Complexes of Copper(II) with Chelating Agents in Ethanol, Dimethylacetamide and Dimethylsulfoxide

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Abstract

Pyrazine-2,3-dicarboxylic and pyridine-2,3-dicarboxylic acids act as chelating agents to copper(II), and give complexes whose solubility varies with respect to the solvent. The characterization of the solid compounds was carried out by IR and thermogravimetry (TG), while the thermodynamic values of the soluble complexes were determined by spectrophotometry and microcalorimetry. The effect of the solvents is discussed on thc basis of their properties (DN, DEC).

Introduction

Several authors have investigated the complexes of copper(II) with pyrazine-2,3-dicarboxylic acid (PzDC) [1–4] and pyridine-2,3-dicarboxylic acid (PyDC) in aqueous solutions [5] and in the solid state [6], thereby determining the nature or stability or structure of the species formed at different pH. However, to our knowledge the effect of the solvent has not been considered.

In this paper we have extended the study to some non-aqueous media, with the aim of investigating the effect of solvent properties on the formation equilibria of the complexes. The solvents considered are ethanol (EtOH), dimethylacetamide (DMA) and dimethylsulfoxide (DMSO) which possess different donor (DN) and dielectric properties (DEC).

Experimental

Pyrazine-2,3-dicarboxylic and pyridine-2,3-dicarboxylic acids were Fluka products purified by crystallization from H_2O:EtOH = 90:10 (v/v). The copper(II) ion was in the form of perchlorate hexahydrate. All other chemicals were analytically pure, including tetrabutylammonium perchlorate which was used to maintain the ionic strength at 0.05 M. The solvents were dried and the analysis for the water content of the products was carried out in the usual way [7].

Visible spectra were recorded on a Perkin Elmer 559 spectrophotometer. Calorimetric investigations were carried out a LKB 10700 flow microcalorimeter, equipped with a silica syringe pump (Braun Unita I) in order to avoid any possible interference by the plastic materials of a peristaltic pump, which may interact with the solvents. Infrared spectra were recorded in the range 4000–400 cm^{-1} using a Perkin Elmer 983 spectrophotometer in KBr discs.

Thermogravimetric studies were carried out with a Perkin Elmer TGS-2 analyser.

^1H and ^{13}C NMR measurements were carried out on a Bruker WP 80 in DMSO-d_6 solutions.

Results and Discussion

Complexes in Solution

All the systems were investigated by spectrophotometric and microcalorimetric measurements at constant ionic strength (0.05 M) and at fixed temperature (25 ± 0.1 °C).

The absorption spectra of the complex species possess maxima whose wavelengths and molar absorptivities are solvent-dependent. In the system copper(II)–PyDC the maximum at 800 nm due to the copper(II) ion is shifted by the addition of ligand to 750 nm in EtOH, to 700 nm in DMSO and to 670 nm in DMA when copper is in excess, and to 640 nm in DMSO and 630 nm in DMA when the ligand is in excess.

The former maximum in all the solvents was assigned to a 1:1 complex and the latter to 2:1 complex, using the 'straight line' method [8].

In the system copper(II)–PzDC, the maximum due to the metal ion was shifted to 640 nm in DMA and 680 nm in DMSO. Mathematical elaboration of the absorbance values allowed the identification of one species in both the solvents, characterized by a complexation ratio L:M = 1:1. Since only one complex is formed, it has been possible to treat the data by the 'straight line' method and by the 'Rose–Drago' method [9].

For stability constant determinations, the absorbance readings were taken at the above selected

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TABLE I. Absorbance Values at Certain Wavelengths (A_λ) of the Copper(II)–Pyridine-2,3-dicarboxylic Acid System in Ethanol, Dimethylacetamide, Dimethylsulfoxide at Constant Metal Concentration $C_M = 2 \times 10^{-3}$ M and Various Initial Molar Concentration Ratios. Blank: solvent; b = 5 cm; T = 25 °C

C_L/C_M	EtOH	DMA		C_L/C_M	DMSO	
	A_λ = 750 nm	A_λ = 670 nm	A_λ = 630 nm		A_λ = 700 nm	A_λ = 640 nm
0.1	0.200	0.140	0.050	1.0	0.110	0.225
0.2	0.300	0.190	0.085	2.0	0.192	0.355
0.3	0.370	0.240	0.127	3.0	0.250	0.415
0.4	0.410	0.275	0.160	4.0	0.298	0.455
0.5	0.432	0.305	0.172	5.0	0.340	0.490
0.6	0.445	0.330	0.215	6.0	0.370	0.515
0.7	0.455	0.350	0.230	8.0	0.425	0.540
0.8	0.460	0.370	0.250	10.0	0.457	0.500
0.9	0.465	0.385	0.275	12.0	0.475	0.550
1.0	0.470	0.395	0.292	14.0	0.483	0.560
1.2	0.475	0.400	0.330	16.0	0.490	0.565
1.4		0.400	0.375	18.0	0.495	0.570
1.6		0.400	0.415	20.0	0.500	0.573
1.8		0.400	0.420	25.0	0.550	0.580
2.0		0.400	0.420	30.0	0.590	0.582

wavelengths in a solution containing 2 mM of copper and 0.2–80 mM of the ligands (Tables I and II).

The data obtained, which are summarized in Table III, allow us to formulate some hypotheses about the influence of the solvent on the complexation equilibria for both the systems. The stability of the complex species in solution decreases with the increase of the donor number of the solvent. In fact larger DN values opposes the complex formation, because of a greater solvent–ligand competition in the metal coordination.

Also the dielectric properties of the solvents contribute to determine the stability order of the complexes, as a higher DEC value corresponds to an increase of both metal ion and ligand solvation, which renders their interactions more difficult.

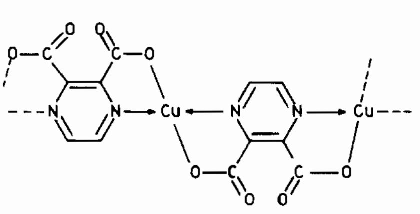
It is possible to correlate the complex formation enthalpy values to the donor power order of the solvents tested, confirming the competition between ligand and solvent.

From the point of view of the difference between the two kinds of ligands, the stability constants and the enthalpy values of the 1:1 complex species obtained with the PzDC are higher than those obtained with the PyDC. This fact can be explained by the polymeric structure of the complex formed by PzDC, which is confirmed by proton NMR measurements on the ligand and the complex (Fig. 1). In fact the PzDC holds its symmetry after copper coordination, in agreement with a contemporary joint between the two chelation sides of the molecule (Scheme 1).

As regards the Cu–PyDC system, the ^{13}C NMR measurements show that the pyridinic nitrogen atom and the carboxylic group near to the heteroatom are involved in the copper coordination. In this way a five membered ring is formed; in fact only the signs related to C_6 and C_7 are influenced (Fig. 2) by the copper coordination.

TABLE II. Absorbance Values at Certain Wavelengths (A_λ) of the Copper(II)–Pyrazine-2,3-dicarboxylic Acid System in Dimethylacetamide, Dimethylsulfoxide at Constant Metal Concentration $C_M = 2 \times 10^{-3}$ M and Various Initial Molar Concentration Ratios. Blank: solvent; b = 5 cm; T = 25 °C

DMA		DMSO	
C_L/C_M	A_λ = 640 nm	C_L/C_M	A_λ = 680 nm
0.3	0.170	1.0	0.290
0.5	0.220	2.0	0.340
0.7	0.270	3.0	0.366
0.9	0.317	4.0	0.385
1.1	0.347	5.0	0.400
1.3	0.365	6.0	0.407
1.5	0.377	7.0	0.415
1.7	0.382	8.0	0.420
1.9	0.385	10.0	0.425
2.1	0.387	15.0	0.440
2.5	0.390	20.0	0.455
3.0	0.393	30.0	0.475



Scheme 1.

TABLE III. Concentration Quotients at Equilibrium, log K_i, Molar Absorptivities, ϵ_i (mol^{-1} 1 cm^{-1}) and Formation Enthalpies ΔH_i (Kcal mol^{-1}) for the Copper(II)–Pyridine-2,3-dicarboxylic Acid and Copper(II)–Pyrazine-2,3-dicarboxylic Acid Systems in Solution at 25 °C. Complexation ratios for the solid complexes obtained in ethanol

Systems	EtOH DN = 24.0, DEC = 24.3[a]		DMA DN = 27.8, DEC = 37.9[a]		DMSO DN = 29.8, DEC = 45.0[a]	
	Solution	Solid state	Solution		Solution	
Copper(II)–pyridine-2,3-dicarboxylic acid	log K_1 = 3.19 ϵ_1 = 50 (λ = 750 nm) ΔH_1 = −6.6	Cu(PyDC)$_2$ ↓	log K_1 = 2.97 ϵ_1 = 54 (λ = 670 nm) ΔH_1 = −5.0	log K_2 = 2.56 ϵ_2 = 100 (λ = 630 nm) ΔH_2 = −7.6	log K_1 = 2.61 ϵ_1 = 72 (λ = 700 nm) ΔH_1 = −3.0	log K_2 = 0.89 ϵ_2 = 43 (λ = 640 nm) ΔH_2 = −5.0
Copper(II)–pyrazine-2,3-dicarboxylic acid		Cu(PzDC) ↓	log K_1 = 3.75 ϵ_1 = 42 (λ = 640 nm) ΔH_1 = −7.5		log K_1 = 2.84 ϵ_1 = 44 (λ = 680 nm) ΔH_1 = −4.4	

[a]For solvent parameters see refs. [10, 11].

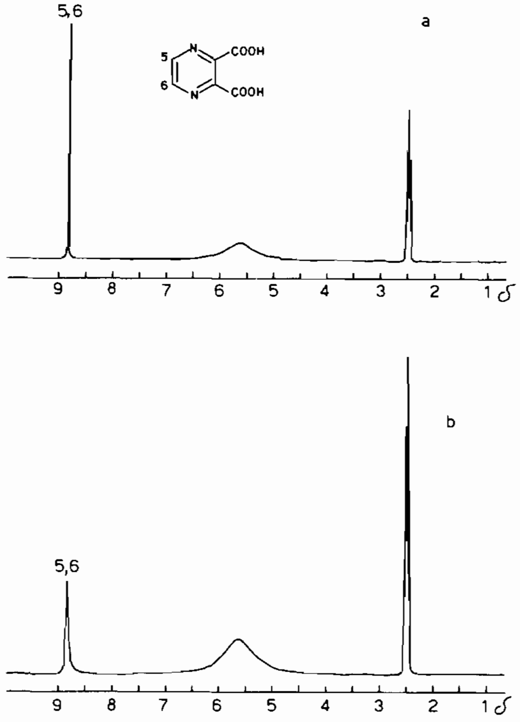


Fig. 1. ^{1}H NMR spectrum in DMSO-d$_6$ of: (a) pyrazine-2,3-dicarboxylic acid, (b) copper(II)–pyrazine-2,3-dicarboxylic acid system.

Complexes in the Solid State

The complex species formation in the solid state occurs only in ethanol, which presents both the lowest dielectric constant and polarity among the considered solvents (Table III).

When the ligand is PyDC and the initial concentration ratio $C_L/C_M \geq 1.3$, a blue compound precipitates.

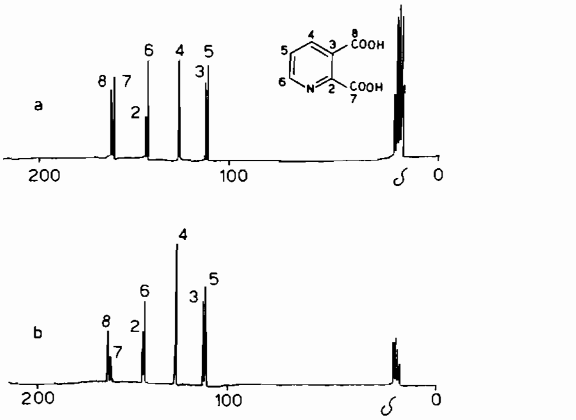


Fig. 2. ^{13}C NMR spectrum in DMSO-d$_6$ of: (a) pyrdine-2,3-dicarboxylic acid, (b) copper(II)–pyrdine-2,3-dicarboxylic acid system.

The decomposition of the anhydrous compound in air starts at 140 °C (Fig. 3) and occurs in two steps until the CuO is obtained (calculated 18.3%, found 19.0%). The IR spectrum of the copper(II)–PyDC system possesses a band around 1700 cm^{-1} and a split band at 1650 cm^{-1}, showing the simultaneous presence of an ionized carboxylic group and a non-ionized one.

The results of elemental analysis and thermogravimetric and IR data are in agreement with a complexation ratio L:M = 2:1, and it is reasonable to hypothesize the same structure suggested for the analogous compound obtained from water [5, 6] which involves nitrogen atom and only a carboxylic group probably, with octahedral geometry.

When the ligand is PzDC a green complex precipitates at all concentration ratios. In this case the

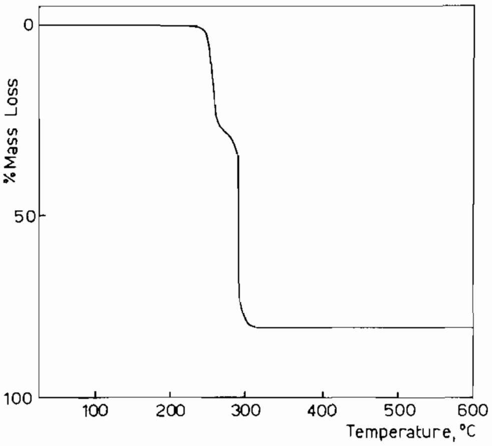


Fig. 3. Thermogravimetric curve of the copper(II)-bis(pyridine-2,3-dicarboxylato)complex in air (10 °C min^{-1}).

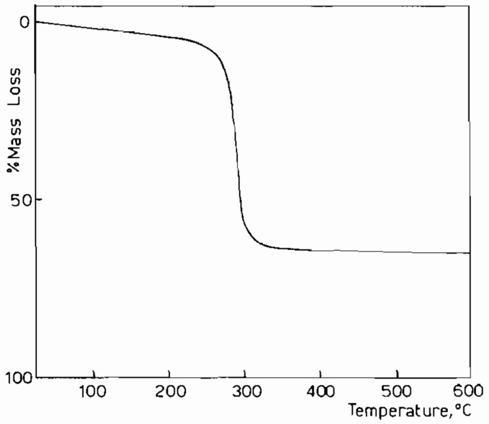


Fig. 4. Thermogravimetric curve of the copper(II)–pyrazine-2,3-dicarboxylato complex in air (10 °C min^{-1}).

complexation ratio L:M = 1:1 results from the data obtained with the same analytical method as above.

The compound appears to decompose in a single step process and it reaches a constant weight ascribed to the oxide CuO at 350 °C (calculated 34.4%; found 33.8%), indicating that two carboxylic groups of the PzDC are involved in coordination of the metal ion (Fig. 4). The IR bands around 1650 and 1350 cm^{-1} could be identified as the asymmetric and symmetric stretching frequencies of the carboxylate anion respectively, and the broad band around 3000 cm^{-1} is assigned to the ν(O–H) stretching frequencies of the carboxylic groups. These IR results are in good agreement with the thermogravimetric data. Also in this case it is possible to hypothesize the same structure suggested for the analogous compound obtained from aqueous solutions [3, 4], in which a polymeric structure involves both nitrogen atoms and carboxylic group with a probable square planar geometry.

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