STUDY OF COPPER(II) SUCCINATE COMPLEXED WITH IMIDAZOLE OR METHYL-SUBSTITUTED IMIDAZOLES

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ABSTRACT

The preparation of complexes involving copper(II) succinate and imidazole or methyl-substituted imidazoles is described. The results of thermal and spectral analysis are reported for the various complexes prepared. The TGA curves, ESR and diffuse reflectance spectra are reported. The reactional behaviour of the 1,2 dimethylimidazole towards the copper(II) succinate is seen to be different from that of other imidazoles.

INTRODUCTION

The study of copper(II) complexes in inorganic biochemistry has developed considerably over the last few years, as a good approach to obtain a better knowledge of blue copper proteins [1–3]. As many metalloenzymes and proteins have a structure which so far has not been clearly determined, it seemed interesting to prepare new organometallic-complexes. Such compounds could easily be used as models of metal containing biomolecules, like haemocyanin, plastocyanin, human albumin, ceruloplasmin, ... Moreover, a metal environment could explain the specific reactivity of active sites of metalloenzymes.

As the copper(II) ion has a real configuration $t_{2g}^6 e_g^3$, distortions can be expected in the geometry of the mixed ligand complexes, in the octahedral environment of the copper ion [4].

Several mixed ligand complexes of copper(II) have previously been studied, but it appears that complexes involving imidazoles and dicarboxylates have not yet been described. We report in this paper the preparation and thermal analysis of such complexes, where the dicarboxylate is succinate, and their electron spin resonance (ESR) and diffuse reflectance spectra.

EXPERIMENTAL

Preparation

The following methods have been used and lead to the same final products. However the first method seemed to give the better product yield.

In the first method, a mixture of succinic acid (0.02 mol) (Fluka), $Cu(CO_3)$, $Cu(OH)_2$, nH_2O (0.01 mol) (Carlo Erba) and imidazole or substituted imidazole (0.05 mol) EGA-Chemie or Janssen-Chemica) was heated in 100 cm^3 of absolute ethanol under magnetic stirring, and allowed to reflux for 1.5 h. The hot alcoholic mixture was then filtered. The powder crystals were washed with absolute ethanol and dried in air or in vacuum.

In the second method, a mixture of copper succinate nH_2O (0.02 mol) (prepared in our laboratory) and imidazole or substituted imidazole (0.1 mol) was heated to reflux in 100 cm^3 of absolute ethanol with magnetic stirring, for 1.5 h. The hot alcoholic mixture was treated according to the first method.

We prepared the following compounds: A, copper(II) succinate (imidazole)$_2 \cdot 2H_2O$; B, copper(II) succinate (1-methylimidazole)$_2$; B′, copper(II) succinate (1-methylimidazole)$_2 \cdot 2H_2O$; C, copper(II) succinate (2-methylimidazole)$_2 \cdot 2H_2O$; D, copper(II) succinate (4-methylimidazole)$_2$; E, copper(II) succinate (1-2-dimethylimidazole)$_1$. The blue compound B′ was obtained by dissolving violet powder crystals of compound B in water and slowly evaporating the solution.

Chemical analysis

The metal content was determined by EDTA titration, with murexide as an indicator.

The succinate and imidazole contents in the complexes were determined by potentiometric titration with $HClO_4$ in acetic anhydride. The curves obtained showed two inflexion points, the first corresponding to the neutralization of imidazole, the second corresponding to the neutralization of the succinate.

The water content in the samples was further confirmed by thermogravimetry. All results support the formula given above.

Thermal studies

The differential thermal analysis (DTA) was performed on a Micro ATD M4, with a heating rate of 4 K min^{-1}.

The thermogravimetric analysis (TGA) was performed on an Adamel Chevenard thermobalance. The samples used had a weight of about 200 mg; the heating rate was 5 K min^{-1}, and the measurement was made in air.
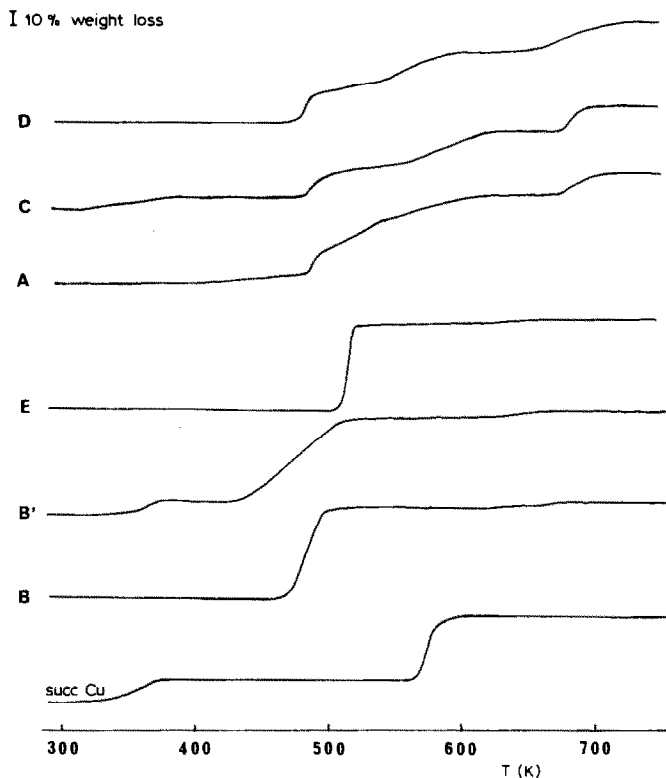
Fig. 1. TGA curves in air.

Thermoanalytical curves of the complexes are shown in Fig. 1.

Compounds A, C and D show similar thermal decomposition curves. Considering compounds A and C, up to 480 K, the weight losses correspond to water, to give copper succinate $(Imid)_2$ (for A) or copper succinate $(2Me \cdot Imid)_2$ (for C). After the plateau corresponding to the anhydrous compound, a complex decomposition occurs, leading at about 600 K to a second plateau. We assume that this intermediary corresponds to a mixture of compound X, traces of copper and carbon. The composition of compound X seems to be close to those of Cu Imid or Cu MeImid. Our hypothesis that compound X is obtained is based on two principal facts: this intermediate is found in TGA involving copper, imidazole or methylimidazole and other carboxylates (acetate, adipate, benzoate, maleate); the analytical analysis of the mixture and the percentage weight loss after this intermediary gave results agreeing with those expected. After this second plateau, the extra weight-loss from 650–670 to 690–720 K leads to CuO [5] and we note an intense exothermic peak on the DTA curve.

Compounds B, B' and E present a very different thermal decomposition curve. The decomposition is quite complete, with a steep step from 480 to

520 K for B, 500 to 520 K for E and 450 to 500 K for B′—after the loss of water from 350 to 380 K for compound B′—the curves show a small amount of extra weight loss (about 4%) between 520 and 700 K that so far we could not explain, to finally lead to $Cu^{II}O$.

A study is underway in our laboratory to explain these two types of decomposition, and to identify compound X (TGA of A, C and D) and the reason for the small extra weight loss (TGA of B, B′ and E).

The DTA curves are quite similar for all complexes with first an endothermic signal (about 380 K) corresponding to the water loss from compounds A, B′ and C. Then decomposition, confirmed by the irregular aspect of the curve occurs-about 450 to 600 K. Furthermore an exothermic broad signal at about 700 K is observed at the end of the analysis.

Spectral studies

Electron paramagnetic resonance

ESR spectra of finely crushed samples were run in a quartz tube (outside diameter, 4 mm) on a Varian V4500 A Spectrometer and recorded at 298 K and 77 K.

For samples A, B, B′, C and D the ESR signal consists of a more or less symmetrical single line characteristic of the mononuclear copper species.

At low temperature, the intensity of the signal increased, but the shape was not modified, except for sample B. The spectra recorded at 77 K are shown in Fig. 2. Hyperfine splitting due to the interaction of unpaired electrons with the copper nucleus cannot be observed because of the magnetic interactions between neighbouring copper ions.

Experimental g values for these complexes are given in Table 1. When the spectrum exhibits a symmetrical band only, the g value ($\bar{g}$ in Table 1) corresponds to a zero in the derivative of the absorption signal. In other cases, the g values ($g_{\parallel}$ and $g_{\perp}$) represent the extrema of this derivative.

Intensity variation in the ESR line for sample A indicates clearly antiferromagnetic interactions between copper ions.

For sample B, the lower field line at $g = 2.19$ only appears at low temperature. Such behaviour may be interpreted by the presence of two different complexes. According to TGA results, complex B does not contain any water molecules. Since ESR is a very sensitive technique, the presence of a very small amount of a complex containing water molecules may be detected. However the g values are different from those of the 'B' complex containing two water molecules. These considerations suggest the presence of a complex with one water molecule that cannot be obtained in the pure form by our experimental procedure.

The spectrum recorded for sample E is completely different (Fig. 3). It comes from the superimposition of two systems of bands. Lines marked I, II, III on the figure belong to dimeric species δ, while the narrow line close
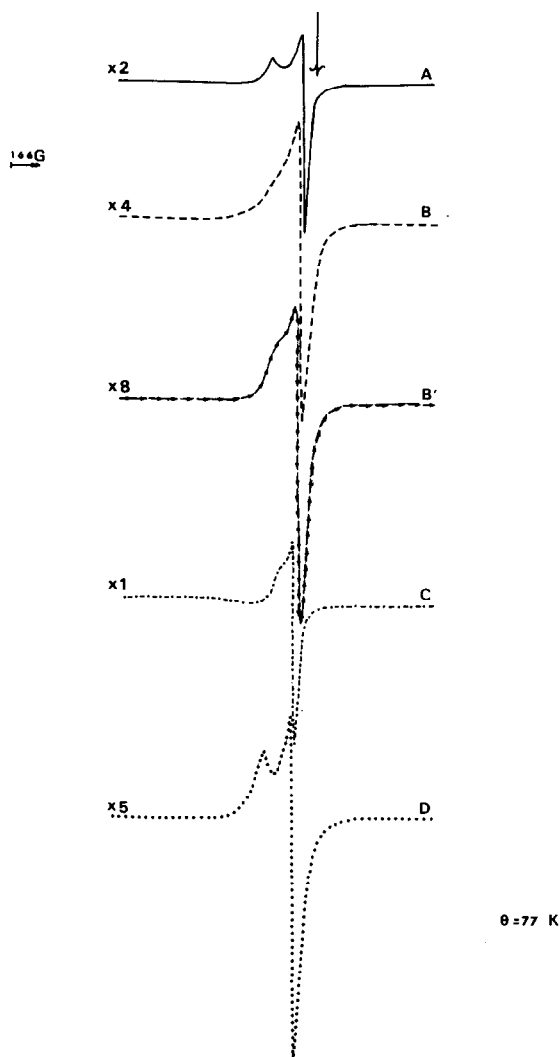
Fig. 2. ESR spectra of compounds A, B, B', C and D. ———CuSucc(Imid)$_2$2H$_2$O; - - - - - - CuSucc(Me$_1$Imid)$_2$; → → → → CuSucc(Me$_1$Imid)$_2$2H$_2$O; · — · — · — · — · CuSucc(Me$_2$Imid)$_2$2H$_2$O; · · · · · ·CuSucc(Me$_4$Imid)$_2$.

to $g = 2$ is due to monomeric copper ions μ. $g_{||}$, $g_\perp$ and D values for δ and μ forms are given in Table 2. In the case of the triplet state δ the calculated values are in good agreement with those given in the literature for carboxylic copper complexes in the case of strong magnetic interaction [7–9].

A cage like structure may be suggested. In such a structure, Cu–Cu interactions between the two unpaired electrons occur though the formation of a Cu–Cu bond has not been emphasized.

It has not been possible to prepare the δ and μ forms separately.

TABLE 1

ESR measurements and interpreted parameters for solid state complexes A, B, B', C and D = Cu(II)Succ.L_2nH_2O

L	Imid		Me-1-Imid		Me-1-Imid		Me-2-Imid		Me-4-Imid	
n	2		0		2		2		0	
θ (K)	298	77	298	77	298	77	298	77	298	77
$g_\parallel$	2.29	2.29	2.108	2.19 [a]	2.25	2.25	2.22	2.22	2.29	2.29
$g_\perp$	2.064	2.059	2.061	2.063	2.068	2.066	2.102	2.097	2.056	2.059
g_{iso}	2.138	2.136	2.076	2.105	2.129	2.127	2.141	2.137	2.134	2.136
$\bar{g}$			2.086	2.098						
Purity of the sample	Mononuclear		Mononuclear		Mononuclear		Mononuclear		Mononuclear	

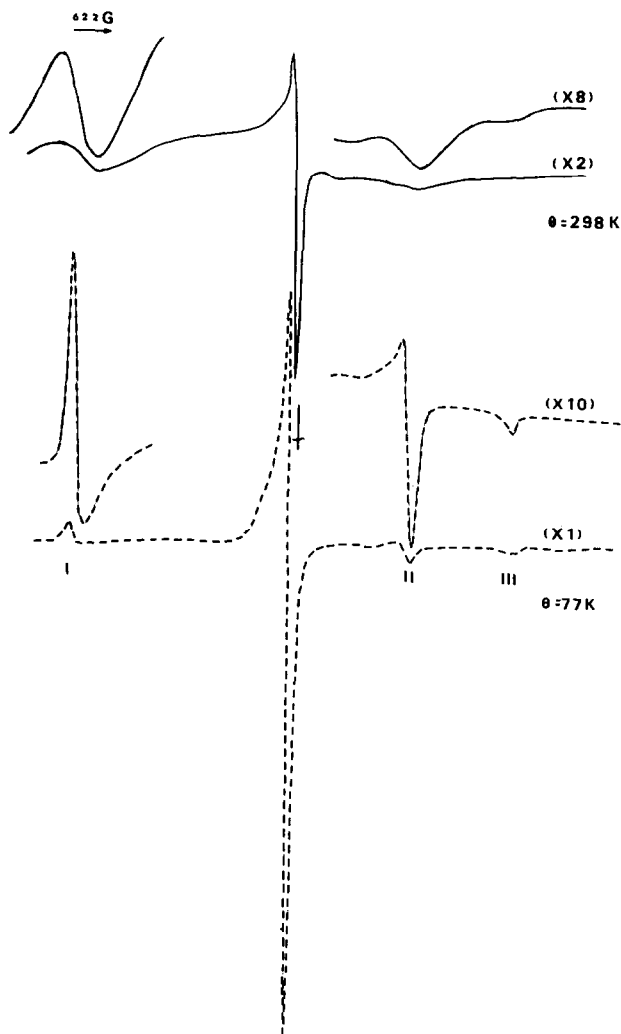[a] This line only appears as a shoulder in the low field part at 77 K.

Fig. 3. ESR spectra of compound E.

Infrared spectra

The IR spectra of all compounds, powdered with KBr or as film samples (1-methylimidazole, 4-methylimidazole and 1-2-dimethylimidazole) were recorded in the range 4200–200 cm^{-1} on a Perkin Elmer 684 spectrometer.

The spectra of the complexes were compared with those of the free ligands and with that of cupric succinate. Several bands in the complexes seemed to be shifted or split due to the complexing effect and distortions from an idealized octahedral environment of the cupric ion, but vibrational assignments are complicated.

The $\Delta\nu$ values of almost 200 cm^{-1} ($\nu_{asym}C{=}O - \nu_{sym}C{=}O$) clearly show a bidentate coordination through the carboxylate group [12,13].

TABLE 2

ESR measurements and interpreted parameters for solid state complex E. (Copper succinate 1,2 dimethylimidazole)

	298 K	77 K
$g_\parallel$	2.416	2.415
$g_\perp$	2.054	2.068
g	2.075	2.065
I	518 G	517 G
II	4784 G	4750 G
III	6018 G	6017 G
D/β	38.87 m^{-1} [a]	36.84 m^{-1} [a]
Purity of the sample	Binuclear + mononuclear form	

[a] Calculated by (8a).

Diffuse reflectance spectra

Diffuse reflectance spectra were recorded at room temperature for all compounds on a Beckman UV 6240 spectrophotometer, over the range 4000–40000 cm^{-1}. Kodak white reflectance standard was used as a reference for this and for the dilution of copper samples.

In the near-IR sharp peaks of weak intensity correspond to harmonics and combination bands of fundamental vibrations. These bands are very
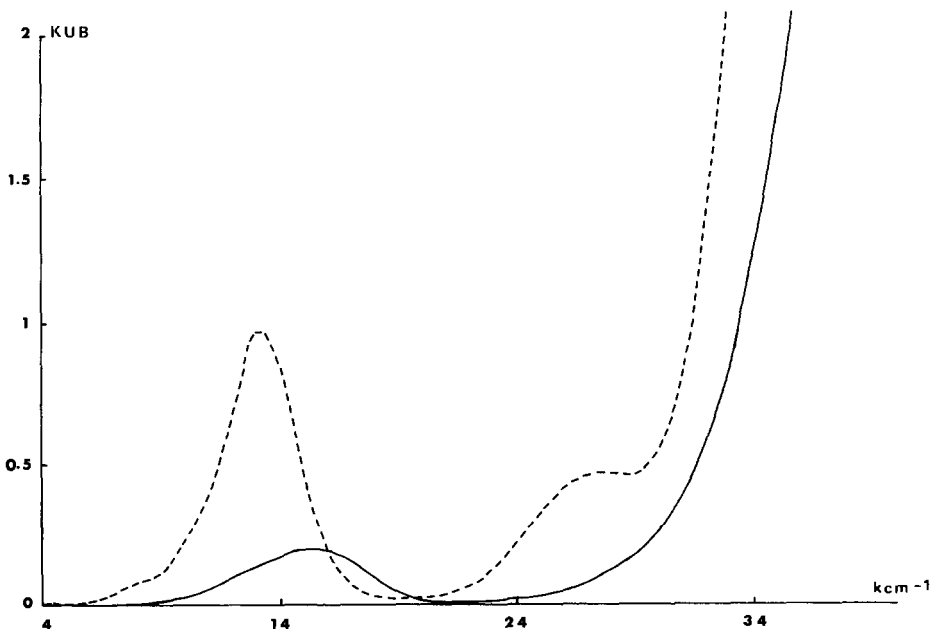

Fig. 4. Diffuse reflectance spectra. (a) Compounds A, B, B′, C and D, ———; (b) compound E, - - - - - -.

difficult to assign. The other wider bands are due to the electronic spectrum of copper(II) in the complexes.

Two types of spectra have been recorded and are shown in Fig. 4.

Samples corresponding to Fig. 4(a) exhibit an asymetrical band with an ill defined shoulder located between 12 400 and 14 500 cm^{-1}. Such a spectrum is characteristic of an octahedral complex of mononuclear copper species [14,15].

For sample E the spectrum (Fig. 4(b)) is completely different. It looks like the copper succinate sample with a small shift in the band position. Two bands are identified at 26 310 and 26 780 cm^{-1}. According to the literature this is in agreement with a binuclear complex of copper [16,17].

For all compounds there is a charge transfer band in the region above 30 000 cm^{-1}, which can be explained by an electronic transfer from the ligand toward the cupric ion.

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