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SOME COMPLEXES OF COPPER(II) WITH N,N'-DISUBSTITUTED DITHIOOXAMIDES DERIVED FROM α - AMINOACIDS AND α - AMINOACID ESTERS

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ABSTRACT

The binuclear copper(II) complexes $Cu_2(L\text{-}4H)(H_2O)_2$ (L = N,N'-bis (carboxymethyl) dithiooxamide - GlyDTO and N,N'-bis(1-carboxyethyl) dithiooxamide - AlaDTO) and $Cu_2(L'\text{-}2H)Cl_2$ (L' = methyl or ethyl ester of L) were synthesized. The structure of the complexes were studied employing IR, electronic and ESR spectroscopy and conductivity measurements. The IR data indicate that the ligands act as bistridentates, with N, S, O - coordination to the copper(II) ion.

RESUMO

Os complexos binucleares de cobre (II) $Cu_2(L\text{-}4H)(H_2O)_2$ (L= N,N'-bis(carboximetil) ditiooxamida -GlyDTO e N,N'-bis (1-carboxietil) ditiooxamida - AlaDTO e $Cu_2(L'\text{-}2H)Cl_2$ (L' = éster de metila ou etila de L) foram sintetizados. A estrutura dos complexos foi estudada usando técnicas de espectroscopia eletrônica, no infravermelho e de ressonância do spin do eletron. Os resultados obtidos no infravermelho indicam que os ligantes são bis-tridentados, com coordenação do N,S e O com o íon de Cu(II).

KEYWORDS: ethanedithioamides, copper(II) complexes, ESR spectroscopy, square planar complexes.

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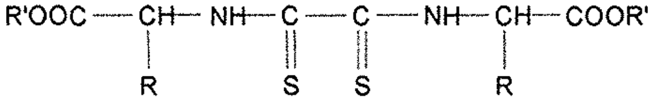
INTRODUCTION

In the last years, O. Kahn and coworkers have described several copper(II) binuclear complexes with N,N' - dithiooxamides derived from aminoacids, peptides and esters of aminoacids or peptides[1,2]. Recently, the synthesis, crystal structure and magnetic properties of binuclear copper(II) complexes bridged by dithiooxamidate group were reported[3-5]. The magnetic behaviour of these compounds revealed that the metal centers were strongly coupled in an antiferromagnetic way[2].

N,N' - disubstituted dithiooxamides have interesting properties as complexing agents, since it is possible to obtain ionic, neutral or polymeric metal complexes depending on the pH of the solution, solvent or metal salt[6,7]. Internal rotation around the C-C bond in the molecules of dithiooxamides allows the preparation of complexes of trans or cis configuration[8].

In this paper we describe the synthesis of the Cu(II) complexes with N,N'-disubstituted dithiooxamides:



$$R'OOC-\underset{\underset{R}{|}}{CH}-NH-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{R}{|}}{CH}-COOR'$$

R = R' = H, N,N' - bis (carboxymethyl)ethanedithioamide (L_1 - GlyDTO)
R = CH_3; R' = H, N,N' - bis (1-carboxyethyl)ethanedithioamide (L_2 - AlaDTO)
R = H; R' = CH_3, N,N' - bis (methoxycarbonylmethyl)ethanedithioamide (L_3 - GlyOMeDTO)
R = R' = CH_3, N,N' - bis (1-methoxycarbonylethyl)ethanedithioamide (L_4 - AlaOMeDTO)
R = H; R' = CH_2-CH_3, N,N' - bis (ethoxycarbonylmethyl)ethanedithioamide (L_5 - GlyOEtDTO)
R = CH_3; R' = CH_2-CH_3, N,N' - bis (1-ethoxycarbonylethyl)ethanedithioamide (L_6 - AlaOEtDTO).

The L_4 ligand has been structurally characterized. The results are indicative of a trans configuration of the molecule[9]. Upon loosing two protons, this molecule is expected to play the role of a novel bis(tridentate)bichelating ligand. The structure of the complexes were deduced from IR, electronic and ESR spectra and conductivity measurements.

EXPERIMENTAL PART

Materials. All solvents and chemicals were AR grade and used without further purification. The ligands L_1 - L_6 were prepared according to literature methods[2,10].

Preparation of the complexes. The complexes $Cu_2(L - 4H)(H_2O)_2$ type were prepared by adding 0,236 g (1 mmole) of L_1 (or 0.264 g, 1 mmole of L_2) to a solution of 0.5 g (2 mmole) of $CuSO_4 \cdot 5H_2O$ in 10 ml of water. The mixture was stirred during half an hour. The resulting solid was filtered after two days, washed with hot water and dried under vacuum. These complexes are insolubles in the usual solvents. The complexes $Cu_2(L' - 2H)Cl_2$ type were prepared by adding 0.264 g (1 mmole) of L_3 (or 0.292 g, 1 mmole of L_4 and L_5 or 0.320 g, 1mmole of L_6) to a solution of 0.270 g (2 mmoles) of

$CuCl_2$ in 10 ml ethanol. The mixture was stirred during 15 minutes. The resulting solid was filtered, washed with ethanol and dried under vacuum. The complexes are very soluble in DMF.

Physical measurements. Elementary analyses were been performed with a Carlo Erba L1108 automatic analyzer (C, H). Copper contents of the complexes were determined by a conventional method[11]. IR spectra were recorded on a FT-IR BIORAD FTS spectrophotometer in the 4000 - 500 cm^{-1} and on a SPECORD M80 Carl Zeiss Jena spectrophotometer in the 500 - 250 cm^{-1}, in KBr pellets. The electronic spectra of complexes with ligands L_1 and L_2 were obtained by the diffuse reflectance method, using MgO as a dilution matrix with SPECORD M40 Carl Zeiss Jena. The electronic spectra of complexes with ligands L_3 - L_6 were studied with a SHIMADZU UV 160A spectrophotometer, using DMF solutions. The ESR spectra of copper(II) complexes were recorded on polycrystalline powders at room temperature with a ART-5 spectrometer operating in the X-band at 100 kHz modulation. In order to determine the g values, we used Mn^{2+} ion in a CaO matrix as standard.. Conductivities were measured at room temperature in DMF with a HACH TDS - meter.

RESULTS AND DISCUSSION

The coordination behaviour of GlyDTO and AlaDTO was studied by isolating and characterizing the binuclear neutral cobalt(II) complexes[12]. The analytical results and conductivity values for the complexes are given in Table 1. The molar conductance of 10^{-3}M DMF solutions of the complexes were found to be in the range 5.8-10.8 ohm^{-1}·cm^{2}·mol^{-1}. The complexes may be regarded as essentially nonelectrolytes.

Selected IR spectral data are summarized in Table 2. Figures 1 and 2 shows the spectra of L_1 ligand and $Cu_2(L_1\text{-}4H)(H_2O)_2$ complex. Differences between the infrared spectra of the ligands and those of all their copper complexes are confined to regions of 3200, 1700, 1500 and 890 cm^{-1}. The loss of the two protons of the carboxy group of the GlyDTO and AlaDTO is confirmed by the dissapearance of the $\nu_{CO}(CO_2)$ vibration[1], at 1712 cm^{-1} and 1715 cm^{-1} respectively, as can be seen in Figures 1 and 2. The frequency at ~3200 cm^{-1} assigned to ν(NH) vibration disappears in all spectra of the complexes. This shows that a deprotonation of the N-H group has occured upon coordination.

The ν(CN) vibration for ligands is assigned to the intense band at 1516, 1495, 1517, 1532, 1519 and 1526 cm^{-1} respectively. The same vibration is found in the spectra of all complexes at a higher frequency (1582, 1574, 1579, 1556, 1580 and 1553 cm^{-1} respectively). This increase in frequency can be explained as resulting from a greater double bond character of the carbon - nitrogen bond upon complex formation[13].

The band involved between 845 - 899 cm^{-1} for ligands, assigned to the ν(CS) vibration is shifted to 834 - 874 cm^{-1} for complexes. The frequency decrease can be explained by the lesser double bond character of carbon - sulphur bond upon complexation[14]. In the infrared spectra, below 500 cm^{-1}, almost all the bands of the ligands are observed in the spectra of the complexes and the few distinct new bands can be assigned to complex modes. The assignments of the new far infrared bands to ν(CuO) (340 - 352 cm^{-1}), ν(CuS) (325 - 335 cm^{-1}) and ν(CuN) (260 - 290 cm^{-1}) are in agreement with literature data[13,15,16].

Table 1. Elementary analysis and molar conductivities of the complexes.

Complex	Colour	%C		%H		%Cu		Λ_M
		exp.	calc.	exp.	calc.	exp.	calc.	$(ohm^{-1}\cdot cm^{2}\cdot mol^{-1})$
$Cu_2(L_1 - 4H)(H_2O)_2$	dark-green	17.89	18.18	2.40	2.02	31.98	32.32	*
$Cu_2(L_2 - 4H)(H_2O)_2$	dark-green	22.17	22.64	2.98	2.83	30.04	30.18	*
$Cu_2(L_3 - 2H)Cl_2$	brown	20.63	20.82	2.43	2.16	27.56	27.76	10.85
$Cu_2(L_4 - 2H)Cl_2$	brown	24.32	24.53	2.97	2.82	26.05	26.17	10.49
$Cu_2(L_5 - 2H)Cl_2$	brown	24.27	24.53	2.93	2.82	25.98	26.17	5.8
$Cu_2(L_6 - 2H)Cl_2$	brown	27.56	27.85	3.65	3.48	24.36	24.75	5.9

* These complexes are insolubles in DMF.

Table 2. Infrared bands (cm^{-1}) of ligands and complexes.

Compound	ν(NH) (CSNH)	ν(CO) (CO_2)	ν(CN) (CSN)	ν(CS)
L_1	3237	1712	1516	895
$Cu_2(L_1 - 4H)(H_2O)_2$	-	-	1582	869
L_2	3224	1715	1495	886
$Cu_2(L_2 - 4H)(H_2O)_2$	-	-	1574	834
L_3	3225	1734	1517	889
$Cu_2(L_3 - 2H)Cl_2$	-	1656	1579	864
L_4	3177	1737	1532	845
$Cu_2(L_4 - 2H)Cl_2$	-	1664	1556	836
L_5	3229	1731	1519	899
$Cu_2(L_5 - 2H)Cl_2$	-	1647	1580	874
L_6	3193	1735	1526	863
$Cu_2(L_6 - 2H)Cl_2$	-	1667	1553	859

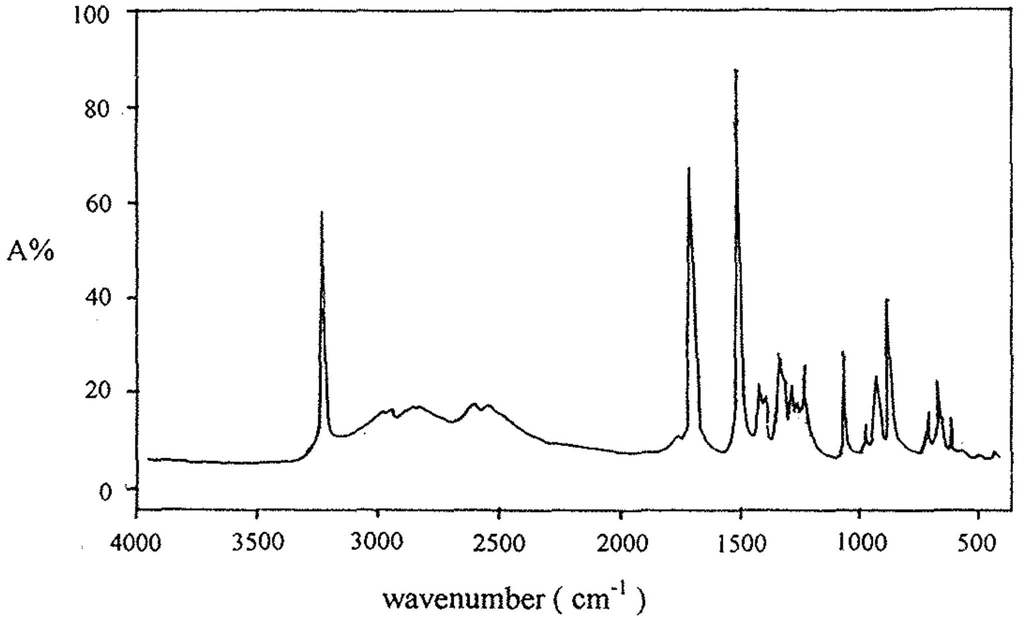


Fig. 1. IR spectrum of $C_2S_2(NHCH_2COOH)_2$ (L_1)

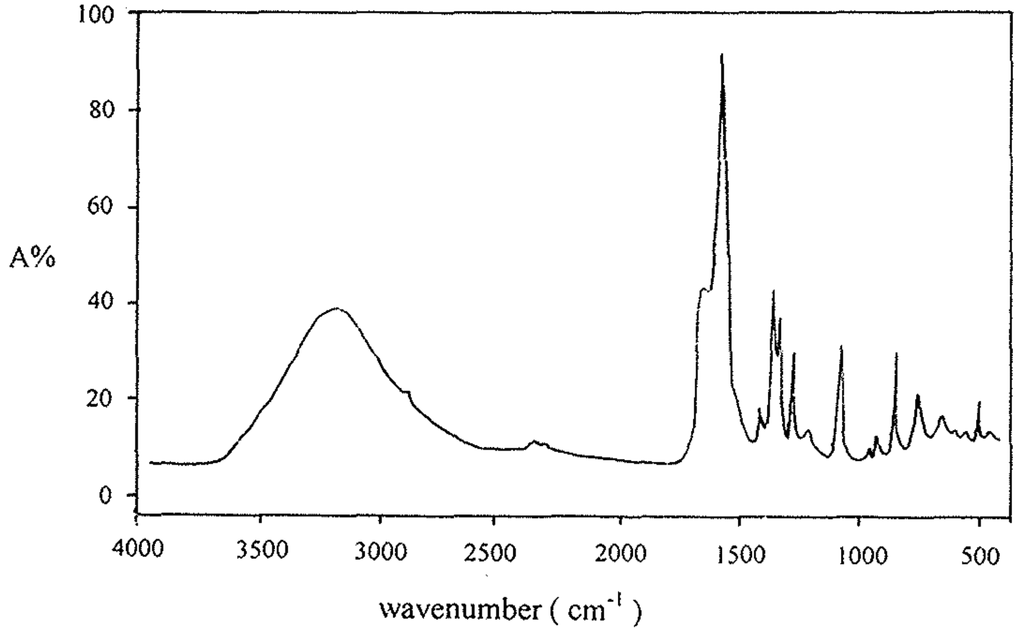


Fig. 2. IR spectrum of $Cu_2(L_1\text{-}4H)(H_2O)_2$ complex

Table 3. Electronic spectra of the complexes (λ_{max} in nm).

Complex		Assignments	
	$\pi \rightarrow \pi^*$	$\sigma(S) \rightarrow Cu(II)$ CT	d - d
$Cu_2(L_1 - 4H)(H_2O)_2$	333	440	606
$Cu_2(L_2 - 4H)(H_2O)_2$	327	468	634
$Cu_2(L_3 - 2H)Cl_2$	348	488	615
$Cu_2(L_4 - 2H)Cl_2$	320	485	630
$Cu_2(L_5 - 2H)Cl_2$	342	478	620
$Cu_2(L_6 - 2H)Cl_2$	332	472	638

Table 4. ESR data for the copper(II) complexes.

Complex	g_1	$g_{\parallel}$	g_2	$g_{\perp}$	g_3	g_{iso}
$Cu_2(L_1 - 4H)(H_2O)_2$						2.18
$Cu_2(L_2 - 4H)(H_2O)_2$						2.18
$Cu_2(L_3 - 2H)Cl_2$		2.27		2.14		
$Cu_2(L_4 - 2H)Cl_2$						2.16
$Cu_2(L_5 - 2H)Cl_2$						2.11
$Cu_2(L_6 - 2H)Cl_2$	2.40		2.15		1.87	

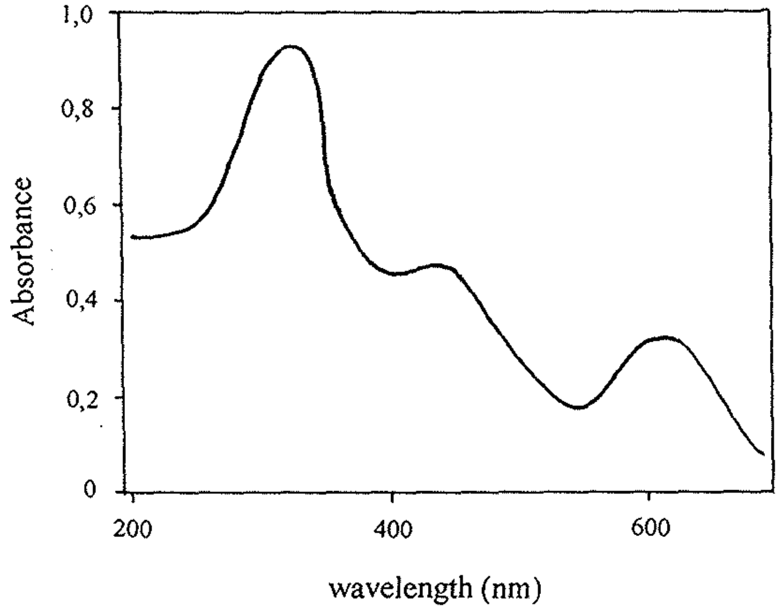


Fig. 3. UV-VIS spectrum of $Cu_2(L_1\text{-}4H)(H_2O)_2$ complex

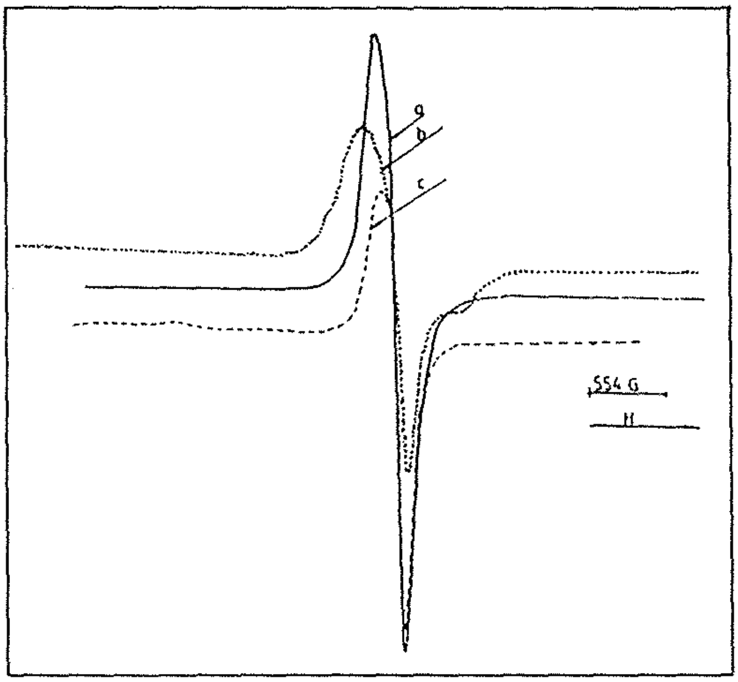


Fig. 4. ESR spectra of $Cu_2(L_1\text{-}4H)(H_2O)_2$ (a), $Cu_2(L_6\text{-}2H)Cl_2$ (b) and $Cu_2(L_3\text{-}2H)Cl_2$ (c) complexes

The assignments of the absorption bands from the electronic spectra of the complexes are reported in Table 3. The UV - VIS spectrum of the $Cu_2(L_1\text{-}4H)(H_2O)_2$ complex in the solid state is given in Figure 3. The spectra of the complexes exhibit a very strong and very broad band at about 440 - 488 nm. This band involves the $\sigma(S) \rightarrow d_{x^2-y^2}$ (Cu(II)) ligand → metal charge transfer transition[2,17]. This S (thioamide) → copper(II) transition appears at lower energy when the ligand field is weak (halogen donor atom) as compared to the case when the ligand field is strong (oxygen donor atom)[2]. The band at 606 - 638 nm is due to a d - d transition.. For $Cu_2(L\text{-}4H)(H_2O)_2$ complexes the wavelength of the d- d bands are fairly typical of square - planar stereochemistry with the $CuSNO_2$ cromophore[2]. The d - d bands observed in the spectra of $Cu_2(L'\text{-}2H)Cl_2$ complexes seem to indicate a square - planar symmetry around the Cu(II) ion[17].

ESR spectra of some of the complexes are shown in Figure 4. The g values for all complexes are given in Table 4. The powder ESR spectra of $Cu_2(L\text{-}4H)(H_2O)_2$ complexes exhibit an almost symmetrical signal. The g values are in agreement with literature data for similar complexes[1]. The g values of $Cu_2(L'\text{-}2H)Cl_2$ complexes are similar with literature data for other N,N' - disubstituted dithiooxamide complexes[18]. No $\Delta M_S = 2$ signal is detected, probably because of the very weak magnitude of the zero field splitting[1]. Considering the g values, a predominant $d_{x^2-y^2}$ ground state is indicated[18]. As the covalency increases, the energies of the excited states rise, so that the orbital contribution to g become less effective and g becomes closer to the free electron value[19].

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