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SYNTHESIS AND CHARACTERIZATION OF 2,6-BIS(CARBOXYETHYL SULFANYLMETHYL)-4-METHYL PHENOL AND ITS MONO AND BINUCLEAR COMPLEXES WITH Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}

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ABSTRACT. After the synthesis of the ligand 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol (H_3L), which has two sites for metal ion coordination, we prepared mononuclear, MLH (M = Mn, Co, Ni, Cu, Zn) and FeLHCl, homobinuclear, M_2LOAc (M = Mn, Co, Ni, Cu, Zn), and heterobinuclear complexes, CuM'LOAc (M' = Ni, Zn). The UV spectra in methanol show d→d transitions for the complexes as well as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorptions attributed to the ligand. The absence of a free C=O vibration in the infrared spectra of the solids indicates intermolecular interactions between the complexes. In the binuclear complexes the metallic centers are linked through the phenolic oxygen and the acetate is in a syn-syn configuration. The cyclic voltammetry studies of the binuclear complexes show that there are interactions between the metal ions. The high value of K_{com} (comproportionation) indicates that the complexes are of "class III" in the Robin and Day series. This work shows interplay between the metallic centers and the absence of decomplexation.

INTRODUCTION

Since Shulman and Dwyer [1] have shown that metal ion chelation exists in many biological processes, the chemistry of polynuclear complexes containing two or more metal ions, identical or not, has been widely investigated. Studies dealt with selective coordination [2-5] modeling of metal ion-containing biomolecules [6-10] and the use of such complexes as potential catalysts [11, 12].

Two ways for the preparation of complexes are essentially used in the literature. The first one involves condensation of ketoprecursors with polyamines by a template route [13-20] and in the other one first the ligand is prepared and then the complexes [21-26].

In our previous studies, we have used both routes: Gaye and Sall [27] used the template route to prepared complexes from 2,6-diformyl-4-chlorophenol as ketoprecursor and 2,6-diaminopyridine as polyamine. They also used 2,2'-dihydroxy-3,3'-diacetyl-5,5'-dichloro-diphenyl methane as ketoprecursor [28] as well as a polyamine with a long aliphatic chain ($C_{16}H_{33}$-), to solubilize the complexes [29] in organic solvents. The second way of preparation was investigated by preparing the ligand 2,6-bis(carboxymethyl sulfanylmethyl)-4-methyl phenol and its complexes [30-31].

In this work we described the preparation of the ligand 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol (H_3L). This ligand has two sites for metal ion coordination. Using this ligand, we prepared mononuclear complexes, MLH (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and FeLHCl, homobinuclear complexes, M_2LOAc (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}),

and heterobinuclear copper complexes, CuM'LOAc with Ni^{2+} or Zn^{2+}. We have put much emphasis in this study on polynuclear complexes, especially those of copper. In fact, it is now well known that many proteins and enzymes contain copper of "types III" [32-34].

EXPERIMENTAL

Synthesis of 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol (H_3L). To 60 mL of 20% NaOH (0.3 mol), *p*-cresol (10.8 g, 0.1 mol) was added and stirred for 15 min. Then mercaptopropionic acid (21.33 g, 0.2 mol) was added under nitrogen. To this mixture formaldehyde (15.16 g, 0.22 mol) was slowly added over a period of 30 min. The solution was heated under reflux during 20 hours under nitrogen atmosphere. The mixture was cooled and acidified to pH 1 with 2 M HCl. We obtained an oil which was extracted with ethyl acetate (3 x 50 mL). The extracted product was dried with anhydrous sodium sulfate. After filtration and evaporation of ethyl acetate under rotavapor, a yellow oil was obtained, treated with water and kept in the refrigerator over night. The resulting yellow product was collected by filtration, washed with cool water and dried under vacuum over P_4O_{10}.

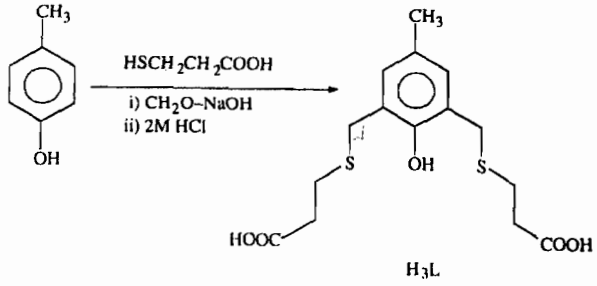
Synthesis of complexes. The mononuclear, homobinuclear and heterobinuclear complexes were obtained by neutralizing the ligand with lithium hydroxide, partially or completely, and by adding the salts of the metal ions of first transition series in the stoichiometries 1:1, 1:2, and 1:1:1, respectively.

Physical measurements. Microanalytical data were obtained from the Microanalytical Service of the University of Padova (Italy). The melting points were measured with Büchi 530 melting point apparatus. The UV spectra (of saturated methanol solution of complexes) were recorded with a UV spectrophotometer model Jasco 5800 with double beam and quartz cells. The IR spectra were recorded on a Perking Elmer 580 B FTIR spectrophotometer as nujol mulls using CsI windows or KBr pellets. The ^1H NMR spectra were recorded on a Jeol FX90 spectrometer in DMSO-d_6 solution. The mass spectra were obtained on a VG Micromass 16 F spectrometer.

The electrochemical data were obtained by a potentiostat-galvanostat model DEA-1 composed IMT 101, Electrochemical INTERFACE and DEA 332 Digital Electrochemical Analyser. The cyclic voltammetry studies were carried out in a cell equipped with a platinum electrode by using acetonitrile solutions of the $M^{II}M^{II}LOAc$ ($M^{II} = Cu^{2+}$, Ni^{2+}) complexes; 0.1 M TBAP (tetrabutyl ammonium perchlorate) was used as supporting electrolyte; the scan rate was 50 mV/s.

RESULTS AND DISCUSSIONS

Studies of 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol (H_3L). The ligand 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol (H_3L) was obtained in a single step following the procedure of Massy and McKillop [35] as indicated in the scheme 1:



Scheme 1

The elemental analyses (Table 1) and mass spectra match the proposed structure for the ligand. The mass spectrum, in addition to the principal fragmentation peaks, shows strong M+ peak at m/z value corresponding to the formula weight of the ligand. The ^{1}H NMR spectrum in DMSO-d_6 shows the following absorption peaks: δ 2.29 (s,3H, $ArCH_3$), δ 2.20 (m, 8H, $ArCH_2SC\underline{H}_2C\underline{H}_2$), δ 3.80 (s, 4H, $ArC\underline{H}_2SCH_2$), δ 7.20 (m, 2H, H_2Ar) and δ 11.00 (br, 3H, COOH+ArOH). The integration peak areas are in agreement with this assignment.

Table 1. Elemental analyses, yields and melting points of the ligand and the complexes.

Compounds	Calculated			Found			Yield	m.p.
	%C	%H	%S	%C	%H	%S	%	°C
$C_{15}H_{20}S_2O_5(H_3L)$	52.18	5.97	18.24	52.30	5.85	18.61	69	68
$MnC_{15}H_{18}S_2O_5.2H_2O$	41.26	4.49	14.41	41.57	5.11	14.79	74	>250
$CoC_{15}H_{18}S_2O_5.2H_2O.1/4MeOH$	39.64	4.31	14.20	39.53	4.97	14.65	57	>250
$NiC_{15}H_{18}S_2O_5.5/2H_2O$	40.21	4.46	14.20	40.38	5.19	14.37	63	>250
$CuC_{15}H_{18}S_2O_5$	44.41	4.61	14.18	44.37	4.46	15.79	78	210 (d)
$ZnC_{15}H_{18}S_2O_5.2H_2O$	40.66	4.36	13.90	40.59	4.99	14.44	65	223
$FeC_{15}H_{18}S_2O_5Cl.2\ EtOH.1/6H_3L$	47.83	6.02	13.34	47.15	6.13	13.65	41	243
$Mn_2C_{17}H_{20}S_2O_7.H_2O$	38.13	4.24	12.01	38.65	4.20	12.14	82	220 (d)
$Co_2C_{17}H_{20}S_2O_7.MeOH$	39.18	4.36	11.23	39.31	4.39	11.66	74	>250
$Ni_2C_{17}H_{20}S_2O_7.4H_2O$	34.10	4.26	11.04	34.58	4.74	10.84	81	>250
$Cu_2C_{17}H_{20}S_2O_7.H_2O$	37.33	3.96	12.01	37.42	4.06	11.75	87	194
$Zn_2C_{17}H_{20}S_2O_7.1/6H_3L$	39.18	4.36	13.61	39.79	3.99	12.70	49	245
$CuNiC_{17}H_{20}S_2O_7.3H_2O$	36.00	4.34	10.52	35.40	4.54	11.12	64	170
$CuZnC_{17}H_{20}S_2O_7.7/2H_2O$	34.93	4.14	9.66	34.46	4.59	10.82	56	240 (d)

The UV spectrum of the ligand shows two intense absorption bands at 220 nm and 280 nm. Three bands are expected for the aromatic moiety, i.e. two intense ones at 180 nm and 220 nm and a medium one at 260 nm [36]. The absorption at 220 nm is attributable to the $\pi \rightarrow \pi^*$ transition of the aromatic ring, whereas the weaker absorption at 260 nm corresponds to the third transition, i.e. the $n \rightarrow \pi^*$ transition. In fact this absorption became very weak after complexation, which confirms our attribution. The IR data are reported in Table 2. Next to the stretching frequencies of the aromatic rings, we note bands of the carboxylic acid groups with peaks at 1727 cm^{-1}; 1693 cm^{-1} and 1252 cm^{-1}. The band at 1727 cm^{-1} is assigned to the stretching vibration of νC=O free. The band at 1693 cm^{-1} resulting from νC=O shows the

existence of an intermolecular hydrogen bond [37,38]. The νC-O carboxylic band has a peak at 1252 cm^{-1}. The νC-O phenolic band appears as doublet at 1332 cm^{-1} and 1284 cm^{-1} [39]. The absence of a band at 2500 cm^{-1}, which would correspond to the stretching vibration νS-H, and the presence of bands at 753 cm^{-1} and 707 cm^{-1}, which are attributed to $\nu_{as}S\text{-}C_2$ and $\nu_sS\text{-}C_2$, respectively, prove that sulfanyl propionic acid is fixed by the sulfur on the aromatic ring via "CH_2"group.

Table 2. IR spectral data of the ligand (H_3L).

Characteristic bands	IR frequencies
νOH	3380 w
νC=CH (Ar)	3080 vw, 3020 vw
νC-H	2920 vw, 2860 vw, 2740 vw, 2670 vw
νC=O	1727 vs, 1693 vs
νC=C	1605 sh
Aromatic skeleton vibration	1510 vw, 1432 s
δ_{as}C-H	1481 s
δOH+δCH aromatic skeleton	1432 s
δ_sC-H (CH_3)	1389 m
νC-O (phenol)	1332 s, 1284 m
νC-O (acid)	1252 s
CH_2 vibrations	1226 vs, 1214 vs
δC-H (Ar)	1053 m, 1014 vw, 992 m
ωC-H	960 m
ωO-H	906 m
Substituted aromatic ring deformations (1,2,4)	877 m
Substituted aromatic ring deformations (1,4)	864 w, 812 w
ρCH_2	766 m
$\nu_{as}SC_2$	753 m
ν_sSC_2	707 w
ωCOOH	599 w

w: weak; vw: very weak; s: strong; vs: very strong; m: medium; sh: shoulder.

Studies of the complexes. The UV results are reported in Table 3. We note the d→d transitions beyond the absorpitons peaks at 220 nm and 280 nm due to the ligand. The UV spectrum of the heterobinuclear copper-nickel complex shows, in addition to the absorptions at 210 nm and 290 nm, which are attributed to the ligand, other absorptions at 245 nm, 342 nm, 400 nm and also a sharp absorption centered at 700 nm. The comparison with the data of the homobinuclear complexes enables us to assign the absorptions at 342 nm, 400 nm and 700 nm to d→d transitions of the Cu^{2+} whereas the absorption at 245 nm corresponds to a charge transfer.

We report the IR data of the complexes in Table 4. The infrared spectra of the different complexes are nearly the same. A comparison between the IR spectra of the ligand and of the complexes shows that νC=O present as a very strong band at 1727 cm^{-1} in the ligand is significantly affected by the coordination of the metal ion. A remarkable shift is observed when going from the free ligand to the monouclear complexes while the inrtroduction of the second metal ion causes no further shifts. We note two strong bands in the region 1600-1500 cm^{-1} and 1500-1400 cm^{-1} assigned to $\nu_{as}COO^-$ and ν_aCOO^-, respectively. This shows that all the acetate moieties are involved in the coordination. In agreement with the literature, we have

assigned the bands in the region 760-700 cm^{-1} in the free ligand to the νC-S stretching mode. We have noted a shift to lower frequencies of this band in the complexes. We also note the decrease of the νC-O phenolic band.

Table 3. Electronic spectral data of the prepared ligand and complexes.

Compound	Transition $\pi \rightarrow \pi^*$	Transition $\pi \rightarrow \pi^*$	Transition $d \rightarrow d^*$	Charge transfer
H_3L	220 nm	280 nm		
FeHLCl	220 nm	287 nm	340 nm, 415 nm	
Mn_2LOAc	220 nm	290 nm	255 nm, 315 nm, 415 nm	
Ni_2LOAc	210 nm	290 nm		
Cu_2LOAc	210 nm	290 nm	345 nm, 400 nm, 685 nm	
Zn_2LOAc	210 nm	290 nm		
CuNiLOAc	210 nm	290 nm	342 nm, 400 nm, 700 nm	245 nm
CuZnLOAc	230 nm	282 nm	345 nm, 400 nm	255 nm

Table 4. IR spectral data (main bands) of the complexes.

Compound	ν_{as}COO-	ν_sCOO-	νC-O (phenol)	ν_{as}S-C_2	ν_sS-C_2
$MnHL.2H_2O$	1570 vs	1425 vs	1310 m, 1270 m	680 vs	630 vw
$FeHLCl.2EtOH.1/6H_3L$	1593 vs	1438 vs	1313 w, 1273 w	679 s	618 sh
$CoHL.2H_2O.1/4MeOH$	1580 vs	1420 vs	1310 s, 1270 s	680 w	620 w
$NiHL.5/2H_2O$	1580 vs	1420 vs	1310 s, 1270 s	680 w	620 w
CuHL	1565 vs	1430 vs	1310 m, 1280 sh	680 w	630 w
$ZnHL.2H_2O$	1510 vs	1420 vs	1310 m, 1280 sh	680 w	630 w
$Mn_2LOAc.H_2O$	1563 vs	1420 vs	1307 s, 1271 s	663 s	616 m
$Co_2LOAc.MeOH$	1580 vs	1420 vs	1310 m, 1270 m	670 w	620 w
$Ni_2LOAc.4H_2O$	1577 vs	1421 vs	1309 m, 1270 m	680 m	620 w
$Cu_2LOAc.H_2O$	1465 vs	1420 vs	1307 w, 1260 m	680 w	621 w
$Zn_2LOAc.1/6H_3L$	1578 vs	1424 vs	1307 m, 1278 m	681 w	617 w
$CuNiLOAc.3H_2O$	1570 vs	1422 vs	1308 w, 1264 w	678 w	621 w
$CuZn_2LOAc.7/2H_2O$	1590 vs	1404 vs	1306 s, 1269 s	681 s	620 w

w: weak; vw: very weak; s: strong ; vs: very strong; m: medium; sh: shoulder.

It appears that in the mononulclear complexes and in the binuclear complexes there is no free νC=O. Thus both acetate moieties are involved in metal coordination. If for the mononuclear complexes many structures are possible, for the binuclear ones we proposed the structure shown in Figure 1. Two metal centers are bridged by the phenolic oxygen and an acetate moiety. The involvement of the other oxygen of the acetate residue of the ligand can be explained by its interaction with the metal in trans configuration. The gap between the stretching vibration of acetate corroborates a syn-syn conformation [40] supporting the proposed structure. The comparison of the infrared spectra of the free ligand with those of the homobinuclear complexes shows a decrease of the νC-O phenolic band. This clearly indicates that the phenolic oxygen is involved in metal ion coordination, as is the COO^- moiety, the sulfur of the ligand and the bridging acetate group. X-Ray studies by Benzekri and *et al.* [41] of binuclear complexes of 2,6-bis-(4-(-2-benzimidazolyl)-2-thiobutyl)-4-methyl phenol revealed a structure similar to our proposed structure with a bridge by phenolic oxygen and by chloride, hydroxide or azide.

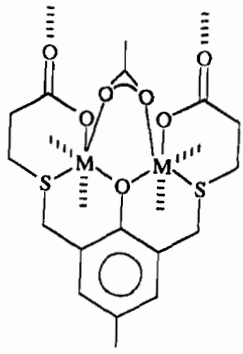


Figure 1. Proposed structure for binuclear complexes.

Cyclic voltammetry studies of Ni_2LOAc, Cu_2LOAc, CuNiLOAc and CuZnLOAc. Some cyclic voltammograms are shown in Figures 2 and 3. The values of the various redox potentials are reported in Table 5. The voltammograms show two waves in oxidation and two waves in reduction. For the homobinuclear nickel complex, we have observed two redox potentials in acetonitrile. The two corresponding peaks enable us to consider a two-step redox process with a monoelectron transfer, i.e. one electron per Ni(II) according to Scheme 2:

$$Ni^{II}Ni^{II}LOAC \underset{+e}{\overset{E_0^1\ -e}{\rightleftharpoons}} Ni^{I}Ni^{II}LOAC \underset{+e}{\overset{E_0^2\ -e}{\rightleftharpoons}} Ni^{I}Ni^{I}LOAc$$

Scheme 2

Table 5. Electrochemical data of the complexes from voltammetry studies.

Compound	Solvent	E_{red}(V)	E_{ox}(V)	E_0^1	E_0^2	$\Delta E = E_0^2 - E_0^1$	K_{com}
Cu_2LOAc	CH_3CN	-0.42 -1.40	+0.15 -0.65	-0.13	-1.05	-0.92	3.55×10^{15}
	CH_3OH	+0.30 -0.85	+0.68 +0.68	+.49	-0.38	-0.87	5.07×10^{14}
Ni_2LOAc	CH_3CN	-0.40 -1.36	+0.13 -0.46	-0.13	-0.92	-0.79	2.26×10^{13}
	CH_3OH	-0.84 -	+0.12 -0.86	-0.36	-	-	-
CuNiLOAc	CH_3CN	-0.25 -1.16	+0.21 -0.31	-0.02	-0.735	-0.725	1.22×10^{12}
	CH_3OH	+0.18 -0.84	+0.76 -0.16	+0.4 7	-0.5	-0.97	2.49×10^{16}
CuZnLOAc	CH_3CN	- -	- -	- -	-	-	-
	CH_3OH	- -1.00	+0.72 +0.12	- -	-0.44	-	-

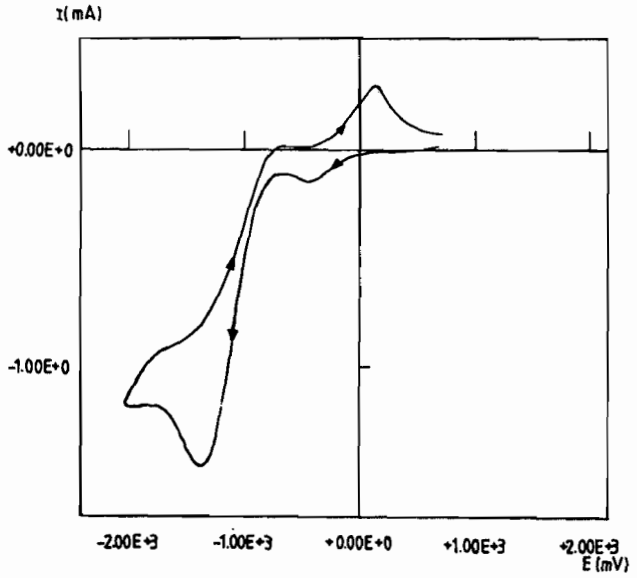


Figure 2. Cyclic voltammogram of Cu_2LOAc in CH_3CN.

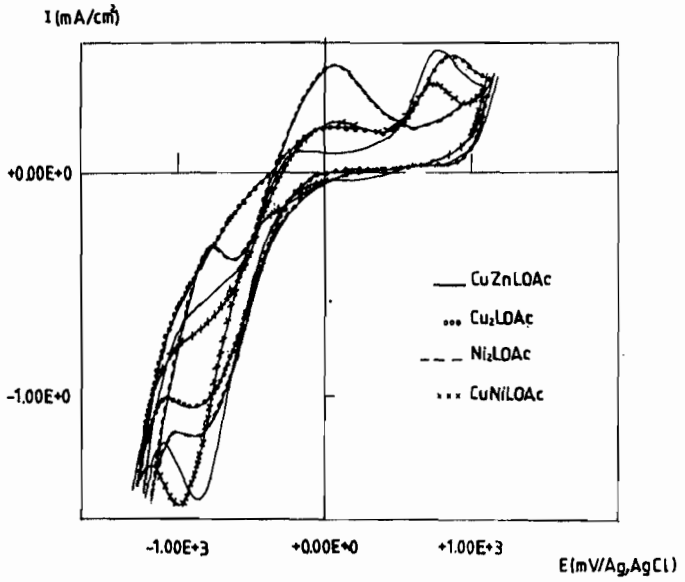


Figure 3. Cyclic voltammograms of Cu_2LOAc, CuZnLOAc, Ni_2LOAc, and CuNiLOAc binuclear complexes in CH_3OH.

This two steps process is often described in the literature [42-44] and indicates a coupling between the two metal centers. This interaction between the two metal ions can be elucidated by the comproportionation constant (K_{com}) which can be correlated with the extent of delocalization in the mixed valent species, according to the Robin and Day classification [45]:

$$K_{com} = e^{-(F\Delta E/RT)} \text{ with } \Delta E = E_0^{\,2} - E_0^{\,1}$$

where K_{com} is the constant for the following equilibrium:

$$M^{II}M^{II}LOAc + M^{I}M^{I}LOAc \rightleftharpoons 2\,M^{II}M^{I}LOAc$$

According to this classification the homobinuclear copper complex with the high value of $K_{com} = 3.55 \times 10^{15}$ and the nickel complex with $K_{com} = 2.26 \times 10^{13}$ belong into the completely delocalized "class III". The high value of $K_{com} = 2.49 \times 10^{16}$ for the heterobinuclear complex CuNiLOAc puts it also in "class III", indicating an interaction between the two metal centers.

Comparison of the cyclic voltammograms of the homobinuclear and heterobinuclear complexes enabled us to assign the first reduction and the second oxidation to copper, i.e. the nickel reduction is obtained after the reduction of the copper [46]. The second reduction and the first oxidation occur with the second metal ion. The reaction proposed is a monoelectronic process as shown in Scheme 3:

$$Cu^{II}Ni^{II}LOAc \underset{+e}{\overset{E_0^1\ -e}{\rightleftharpoons}} Cu^{I}Ni^{II}LOAc \underset{+e}{\overset{E_0^2\ -e}{\rightleftharpoons}} Cu^{I}Ni^{I}LOAc$$

Scheme 3

The high value of $K_{com} = 2.49 \times 10^{16}$ for the complex CuNiLOAc shows that this complex is of the delocalized "class III" and clearly indicates an interaction between metal centers. We have measured E_p-$E_{p/2}$ (E_p and $E_{p/2}$ were the potentials of peaks and half peaks). The fact that the obtained values are all higher than 100 mV shows that a quasi reversible reduction process occurs. This is confirmed by the ratio of anodic peak current to cathodic peak current different from unity. It is well known that for a reversible system, these values are constants and are: E_p-$E_{p/2}$ = 59 mV and $I_{pa}/I_{pc} = 1$ at 25 ^{0}C [47]. The difference between the equilibrium potential of steps 2 and 1 ($\Delta E = E_0^{\,2} - E_0^{\,1}$) is very large and results in a high value of the comproportonation constant which explains the high thermodynamic stability of the complexes. The expression of K_{com} from the following reaction

$$M^{II}M^{II}LOAc + M^{I}M^{I}LOAc \rightleftharpoons 2\,M^{II}M^{I}LOAc$$

showing high values of K_{com} indicates a high stability of the $M^{II}M^{I}$ species.

Sweeping the speed between 200 mV/s and 20 mV/s (Figure 4) the number of potential peak remains the same, the form of the voltammograms are unchanged, showing that there is no decomposition of the complex [45]. In figure 5 we present the variation of peak current I_{pc} or I_{pa} according to the square root of the scan speed. We obtained a line with a correlation coefficient of 0.99 which shows a diffusion.

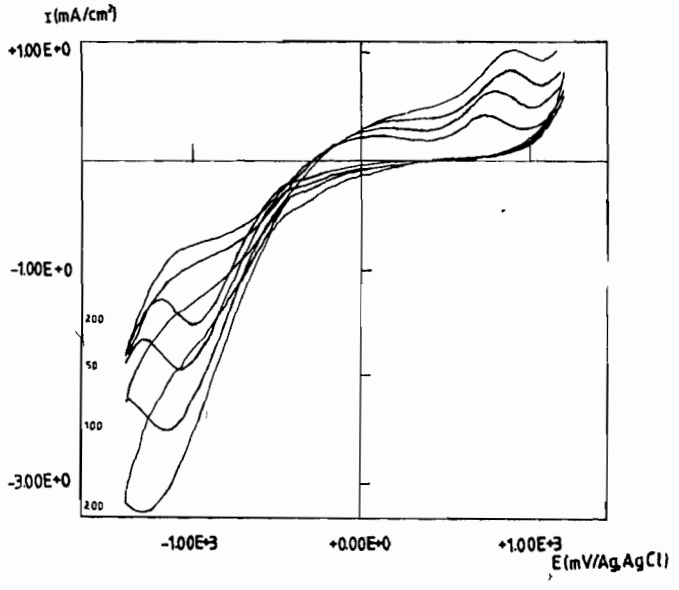


Figure 4. Cyclic voltammograms of CuZnLOAc in CH_3OH at variable speed (20 mV/s, 50 mV/s, 100 mV/s, and 200 mVs).

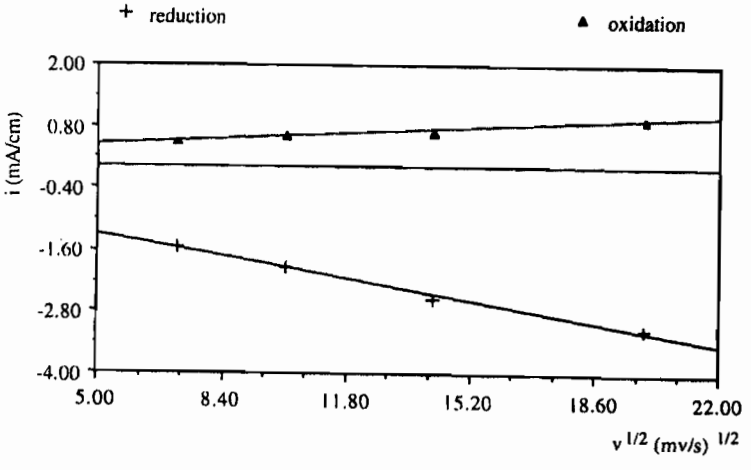


Figure 5. Variation of peak current I_{pc} or I_{pa} as function of the square root of the scan speed.

Comparison of the redox potential of the complexes with those of the free metal ions and some related complexes found in the literature show a difference. This is not surprising because the redox potential is a function of the environment of the meal ion, of the nature of the ligand, of the interaction between the metal centers and sometimes the solvent [42].

CONCLUSION

In this work we have prepared the ligand 2,6-bis(carboxyethyl sulfanylmethyl)-4-methyl phenol and its mononuclear, homobinuclear and heterobinuclear complexes. We have shown that an interaction occurs between the metal centers in the binuclear complexes.

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