EPR and electrochemical study of copper complexes with phenanthrolines and cinnamate ligands

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Abstract

Solid state and solution EPR and electrochemical studies have been carried out on a series of complexes of copper(II) with differently substituted phenanthrolines and cinnamate ligands. Spectra were recorded on binary complexes with cinnamate ligand and on a series of ternary complexes with the same anion and 1,10-*o*-phenanthroline, 2,9-dimethyl-1,10-*o*-phenanthroline or 4,7-dimethyl-1,10-*o*-phenanthroline additional ligands, respectively. The electrochemistry of the same copper complexes was studied in *N,N*-dimethylformamide solvent. The results of both EPR and electrochemical experiments can be correlated with electronic and steric effects attributable to the methyl substituents on the phenanthroline ligand.

Introduction

We have recently devoted attention to different physicochemical properties of complexes containing the copper(II)–1,10-*o*-phenanthroline core. In particular, an EPR study in aqueous solution [1] allowed us to evidentiate structural changes which can be observed by passing from unsubstituted bis-phenanthroline to sterically hindered bis-2,9-dimethyl-phenanthroline complexes. On the other hand, the electrochemistry of copper complexes has been extensively studied, in order both to get information of a merely thermodynamic nature, and to study structural reorganizations accompanying redox changes [2]. Studies on copper(II)–phenanthroline complexes in different solvents have also been reported [3–7]. In our previous electrochemical investigation on bis-phenanthroline, bis-2,9-dimethyl- and bis-4,7-dimethylphenanthroline copper compounds in dimethylformamide solvent, the electronic and steric effects of the methyl substituents on the redox properties of the complexes, both in terms of standard redox potential and of stability of the formed low valent metal species, have been discussed [8]. Structural and redox properties of copper–

phenanthroline systems are of particular interest in a biological context, since the copper(I)–phenanthroline core is supposed to play a role in the reduction of hydrogen peroxide in intracellular solution, to form hydroxyl radicals that are capable of damaging nucleic acid [9].

In the present paper we report on EPR and electrochemical studies of copper ternary complexes with unsubstituted or substituted phenanthroline ligand and 2,5-dimethoxycinnamate anion. These complexes have been synthesized by us [10] with the aim of inducing electronic and structural changes in derivatives retaining the copper–phenanthroline core. The main goal is to ascertain whether the difference in the position of methyl groups can still be related to structural variety and redox properties.

An additional interesting aspect has been evidentiated in our previous electrochemical study of the binary copper–phenanthroline complexes [8]. The stable copper(I) solutions, in fact, can be further reduced, leading to formation of copper complexes, which can be reoxidized to the corresponding starting compounds via a two-electron process. In this context, the study of the stability of formally zerovalent copper complexes, with partially changed ligand sets with

respect to those previously studied, constitutes a further object of the work reported in the present paper.

Within the series of compounds examined, the copper(II)–cinnamate ligand complex has also been included. The study of this species seemed interesting to us in order to complete the transition from binary copper(II)–phenanthroline to ternary copper(II)–phenanthroline–cinnamate, and finally to binary copper(II)–cinnamate complexes, as well as in view of the properties acknowledged to species of this type, which also play a biological role in inhibiting the growth of different microbial strains [11].

Experimental

Synthesis and characterization of the complexes studied were performed as described in ref. 10.

Magnetic susceptibility measurements were carried out at 298 K on a Bruker B-MB$_4$ Faraday system with a Cahan 1000 electrobalance, using Hg[Co(SCN)$_4$] as a standard and correcting for diamagnetism with the appropriate Pascal constants [12].

The solutions for the EPR experiments were prepared by dissolving the solid complexes in N,N-dimethylformamide (DMF) (Fluka) to a 3×10^{-3} M concentration. The solvent was used without further purification. X-band EPR spectra were obtained with a Bruker ER 200D-SRC spectrometer equipped with a high sensitivity ER 4108 TMH cavity and a 100 KHz field modulation. Temperature was calibrated with an ER 4111 VT accessory thermocouple and microwave frequency was measured with an EIP 301 counter. The spectrometer was interfaced with a PS/2 Technical Instrument Hardware computer equipped with a Intel 80386 microprocessor. The data were acquired and evaluated using the EPR data system CS-EPR produced by Stelar Inc. Mede, Italy. The computer program for the simulation of EPR spectra of fast tumbling copper complexes in an isotropic environment is described in a previous paper [13].

Characteristics of the DMF solvent and of the supporting electrolyte (tetraethylammonium tetrafluoroborate) used in the electrochemical tests, of the instrumentation and cell employed, as well as of the procedures followed in these experiments, are illustrated in ref. 8. Cyclic voltammetry and controlled potential coulometry were the electrochemical techniques employed. In some instances, either due to very fast irreversible chemical reaction following the electrode charge transfer, or owing to the irreversible nature of the charge transfer, in cyclic voltammetric tests no backward anodic peak directly associated

to the forward cathodic one could be recorded. In this case, peak potential values ($E_{p,c}$), rather than half-wave potentials ($E'_{1/2}$) are reported [14]; although the former quantities lack in thermodynamic significance, they give a rough indication of the reduction potential of the species studied.

Results and discussion

EPR experiment

The complex formed by copper(II) with 2,5-dimethoxycinnamate (2,5-DMC) possesses at 298 K a magnetic moment of 1.35 BM, a value lower than that evaluable for the only spin contribution (1.73 BM) and also lower than the typical value of 1.8–2.2 BM usually found for mononuclear compounds. The EPR spectrum of a polycrystalline sample affords complementary information to the susceptibility results. Figure 1(a) shows the X-band EPR spectrum obtained for a polycrystalline sample of this binary complex, at 298 K. Three transitions, that confirm a strong copper–copper antiferromagnetic interaction, are clearly detected: a moderately strong absorption at 343 G, a weak absorption at 5870 G
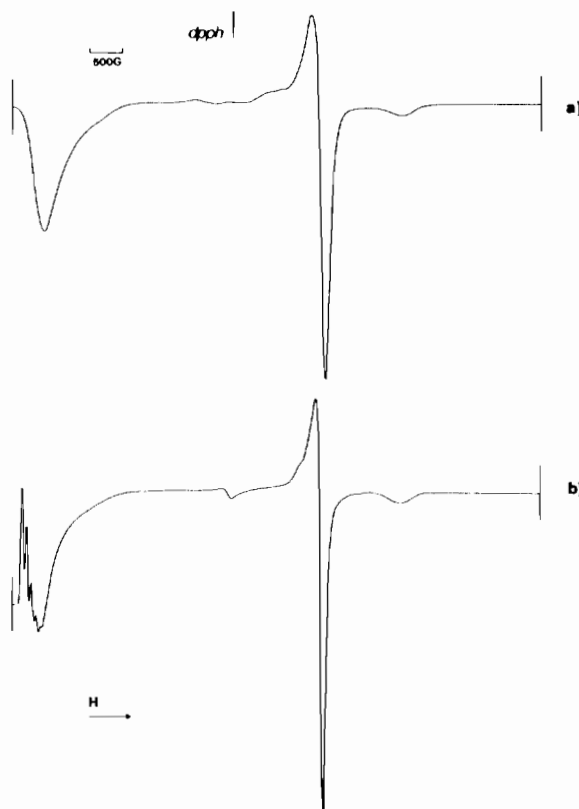

Fig. 1. EPR spectrum of [Cu(2,5-DMC)$_2$]$_2$ at 298 K (a) and 125 K (b).

(parallel $H_{\parallel 1}$ and $H_{\parallel 2}$ components, respectively), and a strong absorption at 4657 G (perpendicular component $H_{\perp 2}$). Using these measured positions for the triplet $S=1$ state and the available literature methods [15], we find $D=0.35$ cm^{-1}, $g_{\parallel}=2.40$ and $g_{\perp}=2.09$. These values are in agreement with those found for binuclear copper(II) carboxylate complexes having a populated spin-triplet state. At 125 K on the $H_{\parallel 1}$ it was possible to calculate $A_{\parallel}=71.4$ G, due to hyperfine splitting from the two equivalent copper nuclei, although only five of the expected seven lines can be seen (Fig. 1(b)). The very weak band at about 3200 G present in the 125 K EPR spectrum is attributed to non-dimeric (doublet-species) copper(II). On these bases the formulation [Cu(2,5-DMC)$_2$]$_2$ can be proposed for the binary complex species.

Figure 2 shows the EPR spectra of polycrystalline samples of ternary complexes of copper with 2,5-DMC and 4,7-dimethylphenanthroline (4,7-DMP): Cu(2,5-DMC)$_2$(4,7-DMP) (a) and with 2,5-DMC and 2,9-dimethylphenanthroline (2,9-DMP): Cu(2,5-DMC)$_2$(2,9-DMP) (b), both recorded at 125 K. It seems evident from the spectra that the dimeric species evidenced in the binary system copper(II)–cinnamic acid is not present in these cases
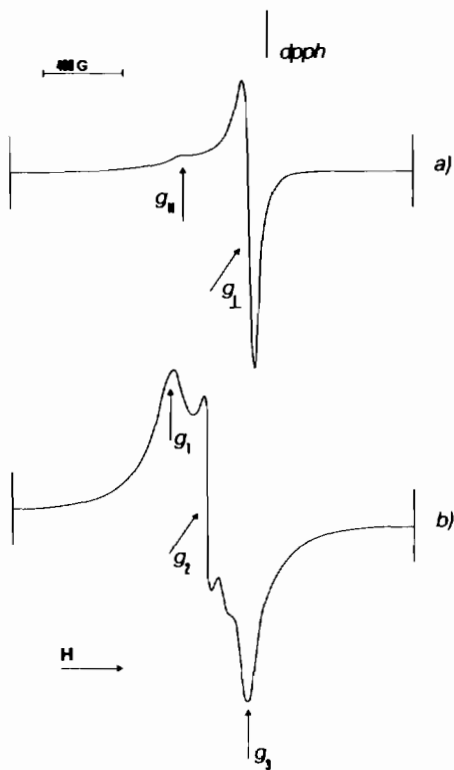
and that new copper ternary monomer compounds are responsible for the relevant EPR signals. The EPR spectrum in Fig. 2(a) is of the axial type ($g_{\parallel}=2.28$; $g_{\perp}2.06$) and the values $g_{\parallel}>g_{\perp}>2.04$ suggest a d$_{x^2-y^2}$ ground state, characteristic of an essentially square planar stereochemistry. On the contrary, the spectrum in Fig. 2(b) is clearly of the rhombic type with $g_1=2.31$, $g_2=2.17$ and $g_3=2.02$: it shows a striking deviation from planar configuration. The difference in structure is attributable to the presence of methyl groups in the 2 and 9 positions on the phenanthroline moiety, close to the coordination sites, while methyl groups in further 4 and 7 positions do not affect the coordination around the metal.

Figure 3(a) and (b) shows the EPR spectra obtained for the same compounds in DMF solution at 298 K. Although the spectra are in this case less informative, because magnetic anisotropies are averaged out by Brownian fast motion, still the two EPR features appear qualitatively very different from each
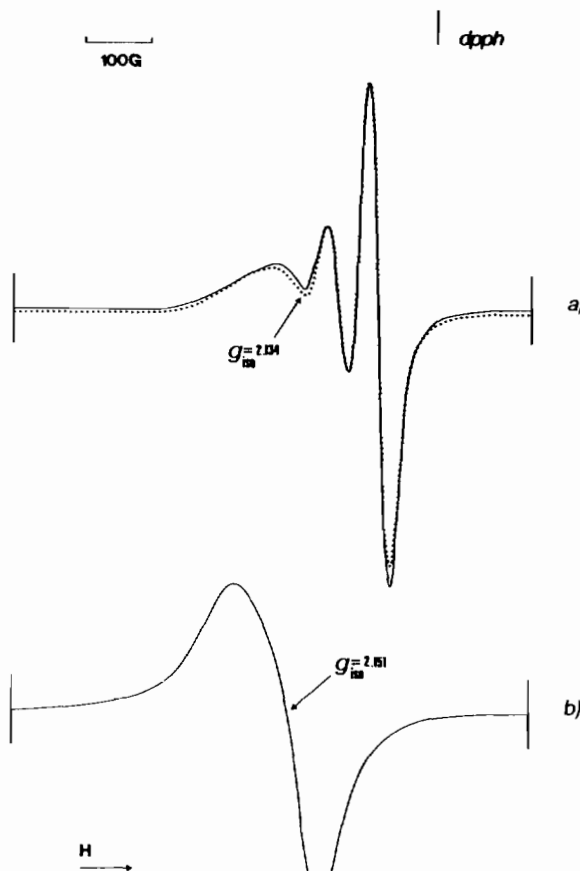

Fig. 2. EPR spectra at 125 K of polycrystalline compounds Cu(2,5-DMC)$_2$(4,7-DMP) (a) and Cu(2,5-DMC)$_2$(2,9-DMP) (b).

Fig. 3. 298 K EPR spectrum of Cu(2,5-DMC)$_2$(4,7-DMP) paired with the simulated spectrum (▶▶▶▶) (a) and of Cu(2,5-DMC)$_2$(2,9-DMP) (b) in 3×10^{-3} M DMF solution.

other. Furthermore, from the spectrum in Fig. 3(a), relative to the 4,7-DMP derivative, $g_{iso} = 2.134$, consistent with the average value calculated for the polycrystalline state, and, from the spectrum in Fig. 3(b), $g_{iso} = 2.151$. In Fig. 3(a) three of the four components predictable for a typical copper(II) complex in solution are clearly distinguishable, allowing a precise evaluation of the copper hyperfine coupling constant ($A_{Cu} = 66$ G) and, through computer simulation, of the rotational correlation time ($\tau_c = 1.6 \times 10^{-10}$ s). The simulated spectrum obtained is also reported in Fig. 3(a). All these findings are in agreement with the square planar stereochemistry already proposed from solid phase data at 125 K. Unfortunately, the results obtained for Cu(2,5-DMC)$_2$(2,9-DMP) in solution do not allow any quantitative analysis, the computer simulation being prevented. However, it is reasonable to state that the striking differences detected in Fig. 2(a) and (b) for the solid compounds are not contradicted by findings inferred from the solution EPR spectra in Fig. 3(a) and (b). A possible explanation for the difficulty in getting a best fit in the simulation of the spectrum in Fig. 3(b) is actually related to the deviation from planarity of the Cu(2,5-DMC)$_2$(2,9-DMP) complex. Solid state X-ray measurements on this compound have evidenced a five-coordination of ligands around the metal in a square-based pyramid [10].

Examination of the spectra obtained on the copper complex with 2,5-DMC and unsubstituted phenanthroline (OP), Cu(2,5-DMC)$_2$(OP), allows conclusions completely similar to those for the corresponding 4,7-DMP derivative to be drawn out.

Electrochemical experiments

Typical cyclic voltammetric curves recorded on a Cu(2,5-DMC)$_2$(OP), DMF solution, are reported in Fig. 4. A first reduction process takes place in correspondence to peak A, to which a backward anodic peak, B, is directly associated. The cathodic–anodic process, which clearly suffers from a high degree of irreversibility, should involve poisoning adsorption on the electrode, since cycling the potential in the region where the response is recorded causes progressive lowering and broadening of both peaks. Cleaning of the electrode surface, that only allows reproducible responses to be recorded, is possible by polarizing the electrode at potentials high enough to involve solvent oxidation. As Fig. 4 shows, additional cathodic processes (peaks C and E) are recorded at more negative potentials. The reduction of free OP, and of the other phenanthroline ligands, has been checked to occur at even more negative potentials.

In controlled potential coulometric tests carried out on the first reduction process (working potential
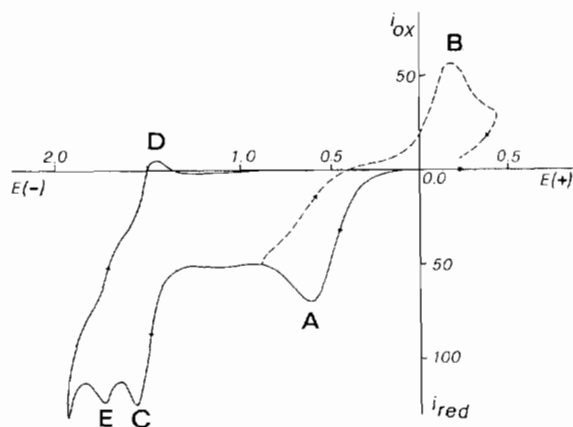

Fig. 4. Cyclic voltammetric curve recorded on a 3×10^{-3} M Cu(2,5-DMC)$_2$(OP), 0.1 M tetraethylammonium tetrafluoroborate DMF solution. Pt working electrode; 0.2 V s^{-1} potential sweep rate; ● starting potential for the initially cathodic scans. E in V (vs. SCE); i in μA.

equal to -1.0 V), 1 mol of electrons per mole of starting compound is used: the solution, initially pale green, turns to bright orange, and no EPR signal similar to that in Fig. 3(a) is detectable.

Cyclic voltammograms on the resulting solution are quite similar to those in Fig. 4; obviously, by starting an anodic sweep at the zero-current potential where the electrolysis has been performed, anodic peak B is first recorded, as a response attributable to the oxidation of the species present in the bulk of the reduced solution, while cathodic peak A is the directly associated backward peak. The more cathodic peaks shown in Fig. 4 are still well detectable. The quite good stability of the complex with copper in $+1$ oxidation state is confirmed by the possibility of obtaining the starting copper(II) compound, by anodic reoxidation of the reduced solution, to a yield higher than 80%.

Similar results are obtained with the Cu(2,5-DMC)$_2$(4,7-DMP), as well as with the Cu(2,5-DMC)$_2$(2,9-DMP) complexes, a significant difference lying in the $E^r_{1/2}$ values which can be computed for the relevant copper(II)/copper(I) redox couples. These parameters, together with the other redox potential values which have been evaluated for the complexes studied, are reported in Table 1.

For all of these compounds, in controlled potential electrolyses at the second cathodic peak (electrolysis potential of -1.57, -1.65 and -1.60 V for the OP, 4,7-DMP and 2,9-DMP compounds, respectively) one additional mol of electrons per mole of starting complex is spent. In any case, anodic reoxidation at $+0.7$ V leads to about 75% regeneration of the corresponding copper(II) starting compound; as proved by independent tests carried out anodizing

TABLE 1. $E'_{1/2}$ and $E_{p,c}$ values (in V vs. SCE)

		1st reduction process	2nd reduction process
$Cu^{II}(2,5\text{-}DMC)_2(OP)$	$E'_{1/2}$	-0.21^a	-1.54
	$E_{p,c}$	-0.58	-1.57
$Cu^{II}(2,5\text{-}DMC)_2(4,7\text{-}DMP)$	$E'_{1/2}$	-0.31^a	-1.64
	$E_{p,c}$	-0.70	-1.67
$Cu^{II}(2,5\text{-}DMC)_2(2,9\text{-}DMP)$	$E'_{1/2}$	$+0.16^a$	-1.60
	$E_{p,c}$	-0.34	-1.63
$Cu^{II}(2,5\text{-}DMC)_2$	$E_{p,c}$	-1.0	-1.70

$E'_{1/2} = (E_{p,c} + E_{p,a})/2$ in the likely hypothesis of $0.3 < \alpha < 0.7$ [14]. $^a E_{p,a} - E_{p,c}$ is near the value usually fixed for the limit between quasi-reversible and totally irreversible charge transfers.

the platinum gauze inside a fresh DMF solution, about one third of the copper(II) complex forms by oxidation of electrodeposited metal copper in the presence of the proper ligands, while two thirds are formed by direct oxidation of a solution-soluble reduced species. Similarly to what has been found for the binary phenanthroline complexes [8], peaks D and E cannot be detected in voltammetric responses recorded on these reduced solutions, which only show one anodic process occurring at more positive potentials. This fact once more suggests that the primary electrode product of the charge transfer occurring at peak C must undergo a very fast rearrangement.

Also for these ternary complexes the high reactivity of the two-electron reduction products prevents the recording of the EPR spectra clear enough to get reliable information about the electronic distribution inside the molecule, so that, on the basis of the results we have collected with the instrumentation which is available at this moment in our laboratories, we cannot be more specific about the exact nature of this potentially very interesting formally zerovalent copper species [8, 16].

The binary 1:2 copper(II)–cinnamate complex undergoes two subsequent totally irreversible one-electron reductions, as evidenced by cyclic voltammetry. Poor reproducibility of the relevant responses only allows a rough estimate of the parameters accounting for the location of the voltammetric peaks on the potential axis (see Table 1). The first process leads to a solution from which the starting compound can be regenerated in a good yield ($\simeq 80\%$) by one-electron anodic reoxidation; on the other hand, further one-electron reduction leads to quantitative deposition of metal copper on the platinum working electrode.

In conclusion, substitution of two cinnamate anions for one phenanthroline ligand [8] renders the reduction of the copper(II) complexes significantly more difficult. Even if the $Cu(2,5\text{-}DMC)_2(2,9\text{-}DMP)$ derivative undergoes reduction with marked irreversible character, leading to a relatively poor estimate of the relevant copper(II)/copper(I) redox potential, we can conclude for certain that it is the ternary complex with the highest oxidizing power. This datum agrees with the findings for the $[Cu(2,9\text{-}DMP)_2]^{2+}$ compound [8], and can be once more explained by the steric hindrance of the methyl substituents in the copper(II) complex. Electronic effects seem to play a minor role. On the other hand, these last factors become predominant in conditioning the potentials at which further reduction of the copper(I) complexes takes place.

References

1 Y. Young, R. Pogni and R. Basosi, *J. Chem. Soc., Faraday Trans. I, 85* (1989) 3995.

2 P. Zanello, in I. Bernal (ed.), *Stereochemical Control, Bonding and Steric Rearrangements, Stereochemistry of Organometallic and Inorganic Compounds 4*, Elsevier, Amsterdam, 1990, p. 181, and refs. therein.

3 I. V. Nelson and R. T. Iwamoto, *Anal. Chem., 35* (1963) 867.

4 G. S. Patterson and R. H. Hol, *Bioinorg. Chem., 4* (1975) 257.

5 A. G. Lappin, M. P. Youngblood and D. W. Marger, *Inorg. Chem., 19* (1980) 407.

6 N. Al-Shatti, A. G. Lappin and A. G. Sykes, *Inorg. Chem., 20* (1981) 1466.

7 C.-W. Lee and F. C. Anson, *Inorg. Chem., 23* (1984) 837.

8 M. I. Pilo, G. Manca, M. A. Zoroddu and R. Seeber, *Inorg. Chim. Acta, 180* (1991) 225.

9 E. Lickl, S. Chyi Chao and W. Chang Chang, *Free Rad. Res. Commun., 8* (1989) 37, and refs. therein.

10 L. P. Battaglia, A. Bonamartini-Corradi, M. A. Zoroddu, G. Manca, R. Basosi and C. Solinas, *J. Chem. Soc., Dalton Trans.*, in press.

11 M. A. Zoroddu and E. Berardi, *Transition Met. Chem., 14* (1989) 269.

12 E. A. Boudreaux and L. N. Mulay (eds.), *Theory and Applications of Molecular Paramagnetism*, Wiley, New York, 1976, p. 487.

13 R. Basosi, W. E. Antholine, W. Froncisz and J. S. Hyde, *J. Chem. Phys., 81* (1984) 4849.

14 G. Bontempelli, F. Magno, G. A. Mazzocchin and R. Seeber, *Ann. Chim. (Rome), 79* (1989) 103.

15 J. R. Wasson, C. I. Shyr and C. Trapp, *Inorg. Chem., 7* (1968) 469, and refs. therein.

16 A. M. Bond and M. A. Khalifa, *Inorg. Chem., 26* (1987) 413.