Electrochemical properties of copper complexes with unsubstituted and substituted 1,10-*o*-phenanthrolines in *N*,*N*-dimethylformamide solvent

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Abstract

The electrochemical reduction of a series of copper(II) complexes with 1,10-*o*-phenanthrolines, namely the 1:1 and 1:2 metal:ligand complexes with 2,9-dimethylphenanthroline, 4,7-dimethylphenanthroline and unsubstituted phenanthroline, respectively, has been studied in *N*,*N*-dimethylformamide using platinum electrodes. As to the 1:2 complexes, the effect of the presence of substituents with different electronic and steric effects on the phenanthroline ligands has been studied with the aim of rationalizing the different values of the standard potentials which have been measured. Furthermore, the possibility of electrogenerating neutral species, with a formally zerovalent copper centre, exhibiting different stability depending on the nature of the ligands, has been ascertained. In our solvent medium, 1:1 complexes have been found to be in equilibrium with the corresponding 1:2 complexes. A scheme for the reduction of solutions of these compounds, including the different equilibria associated to the electrode charge transfers, has been outlined.

Introduction

As a part of a study devoted to the physicochemical characterization of complexes containing the copper–phenanthroline core, our first goal was to define the electrochemical behaviour of a series of binary complexes of copper with differently substituted or unsubstituted phenanthrolines in a medium also suitable for studying a number of additional copper coordination compounds we had recently synthesized or we were going to synthesize. In addition to the 1:1 and 1:2 compounds with the unsubstituted 1,10-*o*-phenanthroline ($[Cu(OP)]^{2+}$ and $[Cu(OP)_2]^{2+}$), we have investigated the analogous complexes with methyl substituents in the 4 and 7 ($[Cu(4,7\text{-}DMP)]^{2+}$ and $[Cu(4,7\text{-}DMP)_2]^{2+}$), as well as in the 2 and 9 positions ($[Cu(2,9\text{-}DMP)]^{2+}$ and $[Cu(2,9\text{-}DMP)_2]^{2+}$). While in the two last compounds the electronic effect due to the presence of the methyl groups is coupled with a marked steric hindrance attributable to the same substituents [1], the latter effect can be disregarded in those complexes where methyls are in the positions 4 and 7. The resulting strong differences in the standard potentials of the copper(II)/copper(I) redox couples are of particular interest in defining the best ligand environments for copper to be effective in the cleavage of DNA [2], which accounts for the antineoplastic properties of similar complexes. Our attention has also been attracted by the ascertained possibility of electrogenerating formally zerovalent copper complexes [3], which form at rather negative potential values, however inside the potential window of the medium employed by us, i.e. *N*,*N*-dimethylformamide solvent containing 0.1 M tetraethylammonium tetrafluoroborate.

Experimental

The synthesis of the different complexes studied was carried out according to well established procedures, by mixing methanol solutions of copper(II) nitrate and of the proper phenanthroline [4]. The two reagents were in relative stoichiometric amounts when the 1:2 derivatives were prepared, while an excess of copper(II) salt was used in order to lead to the corresponding 1:1 complexes. Elemental analysis (C,H,N), conductivity measurements in 5×10^{-4}

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M, *N*,*N*-dimethylformamide solutions, as well as magnetic susceptibility data at room temperature resulted in agreement with the reported formulae.

N,*N*-Dimethylformamide (DMF) (Aldrich, anhydrous, 99 + %, Gold Label, water content < 0.005%, packaged under nitrogen) was used as the electrochemical solvent, without any further purification. Tetraethylammonium tetrafluoroborate (Fluka) supporting electrolyte was dried for 48 h at 50 °C under reduced pressure before use.

Voltammetric tests were performed with an analog home-made three-electrode voltammograph consisting of a potentiostat, a function generator and a voltmeter. The resulting cyclic voltammograms were recorded on an AMEL model 863 XY recorder. In controlled potential coulometric tests an AMEL model 552 potentiostat in conjunction with an AMEL model 558 integrator was used. In these latter experiments an H-shaped cell, with a sintered glass disk interposed between working and auxiliary electrode compartments, was used. The working electrode was a platinum gauze, the auxiliary electrode was a mercury pool, and the reference electrode was an aqueous saturated calomel electrode (SCE). Cyclic voltammograms were recorded using the same cell, with a platinum disk (about 2 mm diameter) as the working electrode and the platinum gauze inside the same compartment as the auxiliary electrode. A stream of 99.99% pure nitrogen flowed continuously during the experiments in order to purge the space above the solution.

In the case of voltammetric responses relative to either reversible or quasi-reversible charge transfers uncomplicated by any coupled chemical reaction, $E_{1/2}{}^{r}$ for the redox couple involved could be computed as the half-sum of forward and directly associated backward peak potentials [5].

X-band ESR spectra were recorded on frozen solutions (120 K) with a Bruker ER 220D SRC spectrometer.

Results and discussion

1:2 Complexes

Figure 1 reports the voltammetric behaviour exhibited by a copper(II)-bis(2,9-dimethyl-1,10-*o*-phenanthroline)([$Cu^{II}(2,9\text{-}DMP)_2]^{2+}$), DMF solution, at a Pt electrode. A first, reversible, cathodic–anodic peak system (A/B), is detectable at quite positive potentials ($E_{1/2}{}^{r} = +0.580$ V, Table 1), confirming the high oxidizing power of this complex, previously measured in aqueous [6, 7] and non-aqueous [8] solvents. Two additional reversible peak systems (C/D and E/F) are recorded at rather negative potentials.

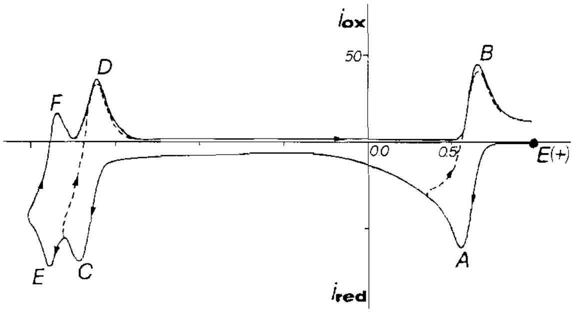


Fig. 1. Cyclic voltammetric curves recorded on a 4×10^{-3} M $[Cu(2,9\text{-}DMP)_2](NO_3)_2$, 0.1 M tetraethylammonium tetrafluoroborate, DMF solution. Pt working electrode; 0.2 V s^{-1} potential scan rate; room temperature. ● Starting potential for the initially cathodic scan. Potential (*E* expressed in V) is referred to SCE. Current (*i*) in μA.

TABLE 1. $E_{1/2}{}^{r}$ values (V vs. SCE) for the indicated redox couples

L	$[CuL_2]^{2+}/[CuL_2]^{+}$	$[CuL_2]^{+}/[CuL_2]^{0}$
OP	+ 0.135	− 1.530
4,7-DMP	+ 0.075	− 1.695
2,9-DMP	+ 0.580	− 1.600

In controlled potential coulometric tests at 0.000 V it can be ascertained that one mol of electrons per mole of starting complex is spent in the first reduction process: the solution turns from pale green to orange colour and the voltammetric curves recorded on these reduced solutions look like those reported in Fig. 1. Of course, as to the A/B peak system, the anodic peak B is now recorded on a direct anodic scan starting at the electrolysis potential. ESR spectra recorded on reduced solutions frozen at 120 K reveal the disappearance of the signals recorded on the starting compound. By anodic reoxidation at + 0.850 V the initial species is regenerated to an almost quantitative yield. The wide potential range between peak systems A/B and C/D gives a measure of the high thermodynamic stability of the + 1 oxidation state for the copper in this complex. Furthermore, the results of coulometric and associated voltammetric tests also support a high kinetic stability of this species.

The cyclic voltammetric curves reported in Fig. 1 suggest that the species formed at peak C as a consequence of the reduction of the copper(I) complex arising at peak A is not particularly short-lived, as proved by the height of the directly associated backward anodic peak D. Controlled potential coulometric tests at peak C (− 1.700 V as working potential), when carried out on both the starting copper(II) and on the previously electrogenerated copper(I) complex solutions, reveal that one additional electron is involved in this second reduction process. The solution becomes deep brown in colour, a fine solid is suspended, and the part of the platinum gauze working electrode which was dipped inside the solution is bright brown. Cyclic voltammetric curves recorded on these further reduced solutions do not show the peak system E/F any more, and anodic scans starting from the potential of this second electrolysis only lead to the recording of ill-defined responses, an irreversible anodic process being evidentiated at about -0.5 V.

Attempts have been made to record ESR spectra of these further reduced solutions, but the high reactivity of the compound formed prevents spectra being obtained that are detailed enough to allow a reliable discussion about the distribution of the electron density inside the metal–ligand system.

In order to determine the amount of copper complex which does not decompose to electrodeposited metal, for this, as well as for the other complexes studied, different reoxidation procedures have been followed. The electrodeposited copper on the platinum electrode used for reduction was either directly reoxidized inside the solution, or previously anodized in fresh DMF. The nature of the species formed could be checked by cyclic voltammetry and the relevant amounts could be computed from the number of Coulombs spent in the different electrolyses. As to the 2,9-DMP derivative, about 20% of the copper is found to have deposited on the electrode and about 60% of the starting amount of copper(II) complex is formed by anodic reoxidation at $+0.800$ V after oxidizing the electrodeposited copper in a fresh solution. On the other hand, anodizing the copper-covered platinum gauze at $+0.800$ V directly inside the electrolysis solution leads to the regeneration of the starting copper(II) complex with a yield of about 80%. It must also be noted that by anodization of the electrode in fresh DMF after the first exhaustive one-electron reduction it can be verified that no copper deposition takes place during this process. In any case, visible spectra were recorded to support the voltammetric data in checking the formation of the starting complex by reoxidation of both the one-electron and the two-electron reduced species.

These results allow some conclusions about the second reduction process to be drawn. It should involve the formation of a complex with the copper in formally zero oxidation state; this complex only forms in part, to an extent which we could ascertain to depend on the nature of the ligands (*vide infra*). Dissociation of the adduct is possible either at the electrode surface (very fast), when the copper(I) metal centre of the electroactive species acquires a further electron from the electrode leading to copper metal electrodeposition, or as a result of a slower decomposition of the reduced complex in the bulk of the solution. In this latter case the complex must be considered irreversibly decomposed: regeneration of the starting compound may occur either by direct oxidation of the neutral complex with the metal in formally zero oxidation state or by oxidation of electrodeposited copper metal in the presence of the ligands. Furthermore, a relatively slow, deep rearrangement of the neutral $[Cu(2,9\text{-}DMP)_2]^0$ compound, with respect to the configuration of the parent copper(I) complex, should be admitted in order to explain the fact that the reduced complex is anodically reactive only at much more positive potentials than those of peak D in Fig. 1, which is not present in the voltammograms recorded on the reduced solutions. This rearrangement also gives a reason for the concomitant disappearance of the peak system E/F. However, by cyclic voltammetry, $E_{1/2}^r$ for the $[Cu(2,9\text{-}DMP)_2]^+/[Cu(2,9\text{-}DMP)_2]^0$ redox couple can be computed. This value, as well as those for the other redox couples studied in this paper, is reported in Table 1.

The first voltammetric cathodic–anodic peak system for the copper(II) complexes bearing two 4,7-DMP or two OP ligands shows the features proper to uncomplicated quasi-reversible one-electron processes ($\Delta E_p = 150$ and 400 mV at 0.2 V s^{-1} for the OP and 4,7-DMP derivatives, respectively). These complexes are both much less easily reducible to the corresponding copper(I) compounds than the analogous complex with the 2,9-DMP ligand [9]. $E_{1/2}^r$ values for the relevant copper(II)/copper(I) couples are reported in Table 1: also in these cases a first one-electron reduction process leads to the corresponding copper(I) complex, and the starting compound is quantitatively regenerated by anodic reoxidation of the reduced solution. Anodization of the working electrode in a fresh solution does not reveal any significant decomposition of these complexes. In both cases no ESR signal is detectable on the one-electron reduced solution.

Cyclic voltammograms recorded on solutions of these compounds, with the metal in both $+1$ and $+2$ oxidation states, also show peak systems corresponding to C/D and E/F in Fig. 1. One additional mol of electrons per mole of substance is used in controlled potential electrolyses at the second reduction process (peak C); neither a peak like D nor peaks like E and F are recorded on the resulting solutions, suggesting that the electrogenerated $[Cu(OP)_2]^0$ and $[Cu(4,7\text{-}DMP)_2]^0$ species should irreversibly evolve to more stable configurations. However, also in these cases the reaction following the charge transfer is slow enough to allow $E_{1/2}{}^{r}$ values for the cationic form/neutral form redox couples to be computed (see Table 1). Also for these reduced compounds any attempt to record reliable enough ESR spectra failed.

The results obtained by anodic reoxidation of these solutions are similar for both of these compounds. By following the different procedures described for the 2,9-DMP derivative, in both cases about 10% of copper was recovered as electrodeposited metal, the starting complex could be regenerated from a solution-soluble reduced form to an extent of about one third with respect to the starting quantity, and the final solution looked turbid, owing to a fine suspension that accounts for the 60% missing copper. These findings suggest a much lower stability of the $[Cu(OP)_2]^0$ and $[Cu(4,7\text{-}DMP)_2]^0$ complexes with respect to $[Cu(2,9\text{-}DMP)_2]^0$.

A look at the data in Table 1 allows interesting comparisons to be made. Electronic effects of the methyl substituents on the phenanthroline–copper system account for the difference between the potentials computed for the OP and the 4,7-DMP derivatives, both as regards the $[CuL_2]^{2+}/[CuL_2]^{+}$ and the $[CuL_2]^{+}/[CuL_2]^{0}$ redox couples. On the other hand, it is evident that different factors are to be taken into account in order to rationalize the values of the standard potentials of the 2,9-DMP derivative, particularly as regards the copper(II)/copper(I) couple. An explanation for the high value estimated for this derivative lies in the steric hindrance of the methyl groups close to the coordinating nitrogen atoms, which induces destabilization of the copper(II) complex and progressive distortion towards tetrahedral coordination [3, 6]. On the other hand, copper(I) can very easily form tetrahedral bonds with $4s4p^3$ orbitals, where bulky α-substituents can be arranged [10]. This factor seems to play a much less important role in the subsequent further reduction, which should involve less significant changes in the steric environment. This can be attributed to the reduced steric hindrance in the $[Cu(2,9\text{-}DMP)_2]^{+}$ complex and to the delocalization of the additional electron inside the whole of the metal–ligand system in any $[CuL_2]^0$ complex.

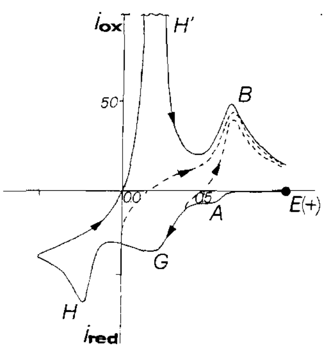


Fig. 2. Cyclic voltammetric curves recorded on a 4×10^{-3} M $[Cu(2,9\text{-}DMP)](NO_3)_2$ solution. Experimental conditions as in Fig. 1.

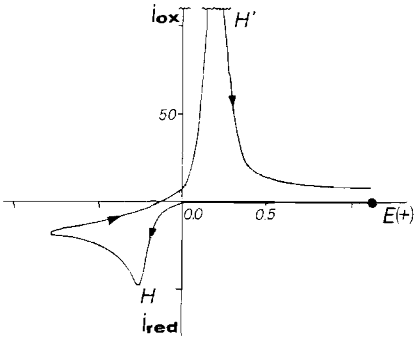


Fig. 3. Cyclic voltammetric curve recorded on a 4×10^{-3} M $Cu(NO_3)_2$ solution. Experimental conditions as in Fig. 1.

1:1 Complexes

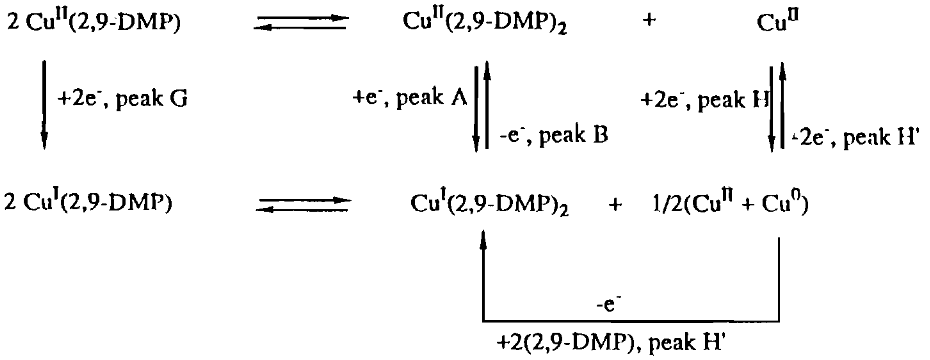
The cathodic behaviour of copper(II)(2,9-dimethyl-1,10-o-phenanthroline) ($[Cu(2,9\text{-}DMP)]^{2+}$), copper(II)(4,7-dimethyl-1,10-o-phenanthroline) ($[Cu(4,7\text{-}DMP)]^{2+}$) and copper(II)(1,10-o-phenanthroline) ($[Cu(OP)]^{2+}$) has also been investigated. Cyclic voltammetric curves recorded on a solution of the first complex are reported in Fig. 2. For the sake of comparison, the voltammetric behaviour of a $Cu(NO_3)_2$ solution is reported in Fig. 3. It shows clearly that copper(I) is not stable over a wide enough potential range in this medium, the disproportionation equilibrium

$$2Cu^{I} \rightleftharpoons Cu^{II} + Cu^{0}$$

being shifted to the right to a significant extent [11]. Three subsequent cathodic peaks are detectable in Fig. 2 in the potential region from +0.8 to −0.4 V (peaks A, G and H). By comparison with authentic samples, peaks A and H can be attributed to the reduction of $[Cu^{II}(2,9\text{-}DMP)_2]^{2+}$ and of free copper(II) ions, respectively. Assuming that the equilibrium

$$2[Cu^{II}(2,9\text{-}DMP)]^{2+} \rightleftharpoons [Cu^{II}(2,9\text{-}DMP)_2]^{2+} + Cu^{II}$$

is slow enough on the time scale of a voltammetric experiment, peak G can be ascribed to the reduction of $[Cu^{II}(2,9\text{-}DMP)]^{2+}$. Anodic peak H', recorded by reversing the potential scan after traversing cathodic peak H, is attributable to the oxidation of electrodeposited copper metal, to give both free copper(II) ions and the $[Cu^{I}(2,9\text{-}DMP)_2]^{+}$ complex, which are



Scheme 1.

the thermodynamically stable species at those potentials. The latter species is further oxidized to $[Cu^{II}(2,9\text{-DMP})_2]^{2+}$ in correspondence to peak B.

In accord with the proposed reaction pathway, in controlled potential electrolyses at -0.7 V, 1.4 mol of electrons per mole of compound are used, and the resulting solution shows a voltammetric picture coincident with that of $[Cu^{I}(2,9\text{-DMP})_2]^+$. Scheme 1 accounts for the results found and agrees with the following overall reduction stoichiometry

$$2[Cu^{II}(2,9\text{-DMP})]^{2+} + 3e^- \longrightarrow [Cu^{I}(2,9\text{-DMP})_2]^+ + Cu^0$$

In agreement with these findings, directly anodizing the platinum gauze at $+0.900$ V the compounds present in the starting solution are quantitatively regenerated through the consumption of a number of Coulombs equal to those spent in the reduction. On the other hand, if the platinum gauze is previously oxidized in a fresh solution, about two thirds of the Coulombs spent in the reduction are used; one more third is spent in the subsequent oxidation of the reduction product, and both voltammetry and visible spectroscopy confirm that a solution containing $[Cu^{II}(2,9\text{-DMP})_2]^{2+}$ forms. Further reduction at the cathodic peak C of the previously reduced solution leads to results consistent with the reduction of $[Cu^{I}(2,9\text{-DMP})_2]^+$, discussed above.

Similar results are obtained for the two other 1:1 copper(II):phenanthroline complexes considered. As noted above, the redox potentials for the copper(II)/copper(I) couples in the 1:2 complexes are in these cases significantly cathodic with respect to that of the bis-2,9-DMP compound. Consequently, the relevant peak systems are so close to the peak involving the reduction of free copper(II) ions that the responses relative to the different reductions are much less resolved from one another. However, the results of coulometric tests are in agreement with an overall mechanism similar to that reported in Scheme 1, taking into account the closeness of the potentials at which any depicted electrode reaction takes place. Accordingly, for both the derivatives, cathodic reduction at -0.500 V involves the consumption of 1.45 mol of electrons per mole of substance. Coulometric reoxidation of these solutions confirms that one half of the copper has deposited as copper metal on the electrode and one half is present in the solution in the form of $[Cu^{I}L_2]^+$.

Conclusions

The results of the present study constitute a sound reason for performing additional work on the electrochemistry of this type of complex in organic solvent. On the one hand, it seems to us particularly interesting to study the redox properties of ternary phenanthroline complexes with the metal coordinated to different ligands, in order to change the electronic distribution inside the copper–phenanthroline system. On the other hand, the complete characterization of the formally zerovalent copper complexes deserves attention. To this purpose, the setting up of an electrochemical cell suitable for performing *in situ* ESR electrochemistry [12, 13] in our laboratories is in progress.

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