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# Potentiometric and spectroscopic study of ternary complexes of copper(II), substituted 1,10-phenanthrolines and oxidised glutathione

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A series of ternary systems consisting of copper(II), oxidised glutathione (a S–S′ bonded hexapeptide) and five differently substituted 1,10-phenanthrolines has been studied in aqueous solvent in the range pH 3–8. The stability constants of the complexes formed, together with the relevant distributions as a function of pH, have been evaluated by elaboration of data from acid–base potentiometric titrations. Electron paramagnetic resonance and electronic spectroscopy have been used to identify the chromophore in the 1:1:1 complexes, *i.e.* the ternary species are in all cases the predominant ones at pH close to the physiological values. The data from the spectroscopic measurements, when considered together with the trend in stability constant values, allowed reasonable hypotheses about the effect of the substituents on the phenanthroline ring on the stability and configuration of the complexes.

The tripeptide glutathione (L-γ-glutamyl-L-cysteinylglycine) is one of the naturally most abundant non-proteic thiols; it participates in redox reactions involving the $Cu^{II}$–$Cu^{I}$ couple.[1] Usually, the fast oxidation of the sulfhydryl group is catalysed by traces of metal ions such as copper(II).[2] Some complexes also show catalytic activity; for example, chelation of copper(II) by 1,10-phenanthroline (phen) strongly enhances the catalytic ability with respect to the oxidation.[3,4] As a part of our studies on the co-ordination of copper with ligands of biological interest we reported a study on the ternary system copper(II)-oxidised glutathione–1,10-phenanthroline.[5] In the present paper we extend that study to differently substituted 1,10-phenanthrolines, bearing one or more substituents with different electronic effects on the aromatic system and, consequently, on the basicity of the nitrogen atoms, but also with different possible steric hindrances with respect to the co-ordination with copper ion.

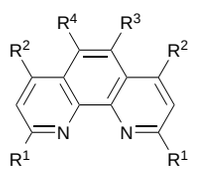
The main goal was to ascertain how the nature of the substituent(s) on the phenanthroline moiety affects the stability of the resulting ternary complex, as well as to collect information about the spectroscopic and structural modifications induced. The substituents have been suitably chosen, in order to be able to make appropriate comparisons based on electronic and steric arguments. Potentiometric acid–base titrations have been performed and elaborated in order to calculate the composition of the systems at varying pH of the solution and to evaluate the stability constants of the complexes formed. The EPR and UV/VIS spectra have been recorded in order to acquire structural information on the complexes of interest. The studies have been carried out in aqueous solutions, in the range pH 3–8.

## Experimental

### Materials, instrumentation and methods

The methods followed and the instrumentation used both in potentiometric and in spectroscopic measurements have been described.[5] 2,9-Dimethyl-, 4,7-dimethyl-, 5,6-dimethyl-, 5-methyl- and 5-nitro-1,10-phenanthroline were all from Aldrich (99% purity). Oxidised glutathione was a Sigma product (99% purity). Stock solutions of the phenanthrolines were standardised by acid–base titrations,[5] those of the metal [$Cu(NO_3)_2 \cdot 3H_2O$, Fluka] by common analytical procedures.[6]

The experimental procedures followed in the acid–base potentiometric titrations performed to evaluate the stability constants have also been described.[5] The metal-to-phenanthroline ratio varied from 2:1 to 1:4 in the binary copper–substituted phenanthroline systems, and was equal to 1:1:1 in the ternary systems. The concentrations were about $10^{-3}$ mol $l^{-1}$. The temperature was controlled at 25.0 ± 0.1 °C and the ionic strength of the solutions was 0.1 mol $l^{-1}$ ($KNO_3$). The computer program SUPERQUAD[7] was employed to elaborate the results of the potentiometric titrations.




| | |
|---|---|
| $R^1 = R^2 = R^3 = R^4 = H$ | 1,10-phenanthroline (phen) |
| $R^1$ = Me, $R^2 = R^3 = R^4 = H$ | 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen) |
| $R^2$ = Me, $R^1 = R^3 = R^4 = H$ | 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen) |
| $R^3 = R^4$ = Me, $R^1 = R^2 = H$ | 5,6-dimethyl-1,10-phenanthroline (5,6-dmphen) |
| $R^3$ = Me, $R^1 = R^2 = R^4 = H$ | 5-methyl-1,10-phenanthroline (5-mphen) |
| $R^3 = NO_2$, $R^1 = R^2 = R^4 = H$ | 5-nitro-1,10-phenanthroline (nphen) |

X-Band EPR spectra were obtained on a Varian E-9 spectrometer equipped with a standard low-temperature apparatus, under the same conditions as those employed in the potentiometric measurements. The microwave frequency was calibrated against diphenylpicrylhydrazyl (dpph) powder ($g = 2.0036$). Spin-Hamiltonian parameters were obtained by simulating experimental EPR spectra by means of a revised version of the MONOCLIN program.[8] Estimated errors in the reported $g$ and $A$ values are ±0.01 and about $\pm 2 \times 10^{-4}$ $cm^{-1}$, respectively. Electronic absorption spectra of the ternary systems were recorded on a JASCO Uvidec 610 spectrophotometer, under conditions analogous to those of the pH-metric and EPR measurements.

## Results and Discussion

### Potentiometry

For reader's convenience, we summarise in two tables the literature data on the formation constants of adducts between oxidised glutathione or substituted phenanthrolines and proton(s) or copper(II) ions, in aqueous solution: the protonation con-

stants of the hexapeptide oxidised glutathione, as well as of the different substituted phenanthrolines, are in Table 1, the formation constants of the complex species in the binary systems copper–oxidised glutathione and copper–substituted phenanthroline in Table 2.

It is evident that the trend in the values of the protonation constants reflects the presence in the phenanthroline ligand of one or more electron donors or electron-withdrawing substituents. Analogously, trends consistent with the different basicity of the phenanthroline nitrogen atoms are found for the binary 1:1, 1:2 and 1:3 metal:phenanthroline complexes, with the significant exception of the 2,9-dimethylphenanthroline. In this case, steric effects play the major role, not allowing the formation of a stable 1:3 complex and causing a distortion in the planar configuration of the 1:2 and 1:1 complexes, with consequent decrease in the relevant stability, much lower than that of the corresponding complexes with unsubstituted phenanthroline.

The ternary systems copper–substituted phenanthroline–oxidised glutathione were studied in solutions at 1:1:1 molar ratios, in the range pH 3–8. We did not use higher metal:ligand molar ratios, eventually capable of leading to significant concentrations of dinuclear species in the solution, since the main goal of the study was a comparison of 1:1:1 substituted and unsubstituted ternary complexes,[5] with particular attention to the relevant biological activity. Table 3 reports the log β values for the different ternary complexes identified. They all are 1:1:1 complexes, with different protonation levels of the peptide moiety. It is evident from Table 3 that the steric hindrance of the methyl substituents in positions 2 and 9 of the phenanthroline ring plays a major role also in conditioning the stability of these ternary complexes, since all the four complexes with differently protonated peptide ligands are much less stable than the corresponding ones with unsubstituted phenanthroline.[5] On the other hand, the electronic effects of the substituents on the ring are much less evident in the ternary complexes than in the binary ones.

Fig. 1 reports the distribution diagram of the species in the ternary system with the metal in the presence of oxidised glutathione and of 2,9-dmphen as a function of pH. Qualitatively similar trends are obtained for the other systems and can be easily computed on the basis of the data in Table 3.

The different systems exhibit quite a number of similarities, the differences being, in turn, qualitatively in accord with the expectations based on the electronic but, even more, on the steric effects of the substituents present on the phenanthroline ring. The most stable species in the systems are, over a wide pH range, the ternary complexes $[Cu(HL)L']^-$. In particular, the last complexes are the most stable at pH > 4, up to pH ⩾ 8, in all systems except for those bearing 2,9- and 5,6-dmphen. The relative weakness of chelation of the metal centre by the 2,9-dmphen ligand, already evidenced and discussed with respect to the corresponding binary complexes, causes the predominant species at pH > 7 to be the 1:1 complex with the oxidised glutathione. More surprisingly, a similar trend is observed for the system with 5,6-dmphen: the ternary complexes are not stable enough to compete with the particularly stable binary copper–oxidised glutathione complex.[11]

The acidic strength of the ternary complexes can also be computed; the relevant $pK_a$ values are reported in Table 4.

Useful information can be obtained by considering equilibrium (1) where L′, as seen in the Tables, indicates a generic phenanthroline ligand.

$$[CuL']^{2+} + [Cu(HL)]^- \rightleftharpoons [Cu(HL)L']^- + Cu^{2+} \quad (1)$$

$$\log K_{eq1} = \log \beta_{[Cu(HL)L']^-} - \log \beta_{[CuL']^{2+}} - \log \beta_{[Cu(HL)]^-} \quad (2)$$

Equation (2) follows a criterion suggested by Sigel and coworkers[13,14] to account for the stability of a ternary complex with respect to the corresponding binary ones. In a comparison

**Table 1** Protonation constants of oxidised glutathione and substituted phenanthrolines. Standard deviations in parentheses

| Species | log β[a] | Species | log β |
|---|---|---|---|
| $HL^{3-}$ | 9.59 (0.01) | $Hphen^+$ | 4.88[b] |
| $H_2L^{2-}$ | 18.65 (0.01) | $H(2,9\text{-dmphen})^+$ | 5.85[c] |
| $H_3L^-$ | 22.64 (0.03) | $H(4,7\text{-dmphen})^+$ | 5.95[d] |
| $H_4L$ | 26.07 (0.02) | $H(5,6\text{-dmphen})^+$ | 5.60[d] |
| $H_5L^+$ | 28.53 (0.04) | $Hmphen^+$ | 5.28[e] |
| $H_6L^{2+}$ | 30.87 (0.08) | $Hnphen^+$ | 3.57[b] |

$H_4L$ = oxidised glutathione. [a] From ref. 5 (0.1 mol $l^{-1}$ $KNO_3$). [b] From ref. 9 (0.1 mol $l^{-1}$ KCl, 25 °C). [c] From ref. 12 (0.1 mol $l^{-1}$ KCl, 25 °C). [d] From ref. 11 (0.1 mol $l^{-1}$ KCl, 25 °C). [e] From ref. 10 (0.1 mol $l^{-1}$ KCl or $KNO_3$, 25 °C).

**Table 3** Formation constants of ternary complexes $[Cu(H_nL)L']^{(n-2)+}$

| L′ | *n* | log β |
|---|---|---|
| phen* | 0 | 17.91 (0.04) |
| | 1 | 27.04 (0.01) |
| | 2 | 31.21 (0.02) |
| | 3 | 34.44 (0.04) |
| 2,9-dmphen | 0 | 17.24 (0.10) |
| | 1 | 24.73 (0.03) |
| | 2 | 28.65 (0.03) |
| | 3 | 31.92 (0.07) |
| 4,7-dmphen | 0 | 18.41 (0.08) |
| | 1 | 27.57 (0.05) |
| | 2 | 31.62 (0.05) |
| | 3 | 35.10 (0.06) |
| 5,6-dmphen | 1 | 26.74 (0.03) |
| | 2 | 30.68 (0.04) |
| | 3 | 33.66 (0.10) |
| mphen | 1 | 26.72 (0.02) |
| | 2 | 30.76 (0.04) |
| | 3 | 33.93 (0.07) |
| nphen | 0 | 17.62 (0.09) |
| | 1 | 25.93 (0.02) |
| | 2 | 30.25 (0.02) |

* From ref. 5 (0.1 mol $l^{-1}$ $KNO_3$, 25 °C).

**Table 2** Overall formation constants for the species present in the binary systems copper(II)–hexapeptide and –substituted 1,10-phenanthroline. Standard deviations in parentheses

| | | | log β | | |
|---|---|---|---|---|---|
| Species | log β[a] | L′ | $[CuL']^{2+}$ | $[CuL'_2]^{2+}$ | $[CuL'_3]^{2+}$ |
| $[CuL]^{2-}$ | 14.34 (0.01) | phen[b] | 9.08 | 15.8 | 21.00 |
| $[Cu(HL)]^-$ | 18.72 (0.01) | 2,9-dmphen | 6.01 (0.13) | 11.8 (0.08) | — |
| $[Cu(H_2L)]$ | 22.43 (0.01) | 4,7-dmphen[c] | 8.76 | 16.0 | 22 |
| $[Cu(H_3L)]^+$ | 25.51 (0.02) | 5,6-dmphen[c] | 8.71 | 15.7 | 21.1 |
| $[Cu_2L]$ | 17.39 (0.02) | mphen[d] | 8.55 | 15.02 | 20.12 |
| | | nphen[b] | 8.00 | 13.47 | 17.61 |

L′ = Phenanthroline ligand. [a] From ref. 5 (0.1 mol $l^{-1}$ $KNO_3$, 25 °C). [b] From ref. 9 (0.1 mol $l^{-1}$ KCl, 25 °C). [c] From ref. 11 (0.1 mol $l^{-1}$ KCl, 25 °C). [d] From ref. 10 (0.1 mol $l^{-1}$ KCl or $KNO_3$, 25 °C).

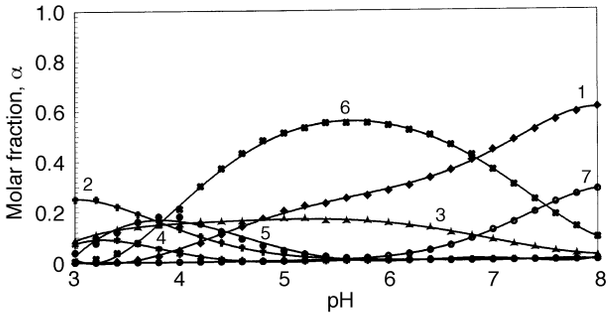



**Fig. 1** Distribution diagram of the species in the ternary system Cu : L : 2,9-dimethyl-1,10-phenanthroline. **1**, $[CuL]^{2-}$; **2**, $[Cu(2,9\text{-}dmphen)]^{2+}$; **3**, $[Cu(2,9\text{-}dmphen)_2]^{2+}$; **4**, $[Cu(H_3L)(2,9\text{-}dmphen)]^{+}$; **5**, $[Cu(H_2L)(2,9\text{-}dmphen)]$; **6**, $[Cu(HL)(2,9\text{-}dmphen)]^{-}$; **7**, $[CuL(2,9\text{-}dmphen)]^{2-}$

**Table 4** $pK_a$ Values of the ternary complexes: $pK_{a,1}$ refers to $[Cu(H_3L)L']^{2+}$, $pK_{a,2}$ to $[Cu(H_2L)L']$, $pK_{a,3}$ to $[Cu(HL)L']^{-}$

| L′ | $pK_{a,1}$ | $pK_{a,2}$ | $pK_{a,3}$ |
|---|---|---|---|
| phen * | 3.23 (0.05) | 4.17 (0.03) | 9.13 (0.04) |
| 2,9-dmphen | 3.27 (0.08) | 3.92 (0.04) | 7.49 (0.10) |
| 4,7-dmphen | 3.48 (0.08) | 4.05 (0.07) | 9.16 (0.09) |
| 5,6-dmphen | 2.98 (0.10) | 3.94 (0.05) | — |
| mphen | 3.17 (0.08) | 4.04 (0.04) | — |
| nphen | — | 4.32 (0.03) | 8.31 (0.09) |

* From ref. 5 (0.1 mol $l^{-1}$ $KNO_3$, 25 °C).

involving different phenanthrolines and a single $HL^{3-}$ species, the stability of the ternary complex can be related to that of the 1 : 1 metal–phenanthroline adduct. The log $K_{eq1}$ values found for the different phenanthrolines are −0.76,[5] 0.0, +0.09, −0.69, −0.55, −0.79 for phen, 2,9-, 4,7-, 5,6-dmphen, mphen and 5-nphen, respectively. This series reveals that equilibrium (1) is significantly shifted towards the formation of the ternary complex; the stability of such a species, with respect to the corresponding 1 : 1 copper–phenanthroline complex, is the highest for 2,9- and for 4,7-dmphen.

As suggested in our previous work,[5] a different equilibrium (3) could be proposed to account for the tendency of oxidised

$$[CuL'_2]^{2+} + [Cu(HL)]^{-} \rightleftharpoons [Cu(HL)L']^{-} + [CuL']^{2+} \quad (3)$$

$$\log K_{eq2} = \log \beta_{[Cu(HL)L']^{-}} + \log \beta_{[CuL']^{2+}} - \log \beta_{[Cu(HL)]^{-}} - \log \beta_{[CuL'_2]^{2+}} \quad (4)$$

glutathione to substitute a phenanthroline ligand. The following log $K_{eq2}$ [see equation (4)] values are obtained: L′ = phen, 1.6;[5] 2,9-dmphen, 0.22; 4,7-dmphen, 1.61; 5,6-dmphen, 1.03; mphen, 1.53; nphen, 1.74. In view of these data, the inadequacy of such an equilibrium to give suitable indications is evident, since the listed values mainly reflect the strength of the resulting binary Cu–L′ complexes. Interestingly, the value of log $K_{eq2}$ for nphen is quite high, despite the low stability of the Cu–nphen complex.

In the context of a comparison in stability among the members of the series studied, equilibrium (5) can also be proposed.

$$[CuL'_2]^{2+} + HL^{3-} \rightleftharpoons [Cu(HL)L']^{-} + L' \quad (5)$$

By trivial combination of log β computed for the ternary and for the binary complexes, the following log $K_{eq3}$ values are obtained: L′ = phen, 11.24; 2,9-dmphen, 12.93; 4,7-dmphen, 11.57; 5,6-dmphen, 11.04; mphen, 11.70; nphen, 12.46. It is once more evident that the different affinity of the various phenanthrolines for the metal centre plays the predominant role, the highest values found for 2,9-dmphen and for nphen being in agreement with the easiest release of phenanthroline ligands by the relevant 1 : 2 metal–ligand binary complexes.

A sound confirmation that the nature of the phenanthroline moiety constitutes the most important factor in conditioning the relative stability within this series of compounds is given by the values found for the constants of equilibrium (6), simply

$$[CuL']^{2+} + HL^{3-} \rightleftharpoons [Cu(HL)L']^{-} \quad (6)$$

accounting for the tendency of the binary 1 : 1 Cu–L′ complexes to add an oxidised glutathione ligand to form the ternary complex. The following values are found for log $K_{eq4}$: L′ = phen, 17.96; 2,9-dmphen, 18.72; 4,7-dmphen, 18.81; 5,6-dmphen, 18.03; mphen, 18.17; nphen, 17.93. Quite significantly, there are no remarkable differences within this series.

## EPR and UV/VIS spectroscopy

The EPR spectra of the ternary systems of copper(II) with the different substituted phenanthrolines and oxidised glutathione were recorded at room temperature as well as in frozen solution, under the same conditions as those employed for the potentiometric measurements. In the EPR spectra the presence of various complex species, in addition to the binary copper–phenanthroline complexes, can be evidenced at low pH values. At pH > 4 the signal of a single species progressively increases and it is finally the only one present up to pH 7–8. From the EPR data, as already reported for the ternary system with unsubstituted phenanthroline,[5] at increasing pH a decrease in $g_{\parallel}$ values and a corresponding increase in $A_{\parallel}$ values are observed; moreover, a corresponding blue shift in the $\lambda_{max}$ value is evidenced in the electronic spectra, suggesting an involvement in the co-ordination to the metal ion of the donor atoms from the hexapeptide molecule. The distribution diagrams computed from the potentiometric data were employed in order to evaluate the pH values of the solution at which the complex $[Cu(HL)L']^{-}$ is largely predominant. These values were quite close to those characterising the physiological pH.

The electronic absorption spectra at pH ≈ 6 exhibit peaks consistent with $CuN_2O_2$ or $CuN_3O$ chromophores and an essentially square-planar or octahedral arrangement[15,16] ($\lambda_{max}$ = 610 nm for the ternary complex with 5-methylphenanthroline, 615–620 nm with 4,7-dimethyl-, 5,6-dimethyl- and 5-nitrophenanthroline, and 640 nm with 2,9-dimethylphenanthroline). The higher $\lambda_{max}$ value found for the ternary system with 2,9-dimethylphenanthroline may be accounted for by a higher distortion of the copper square plane.[17,18]

The room-temperature EPR spectra are essentially isotropic. The good correlation between $g_{iso}$ and $g_m$ obtained from room-temperature and frozen-solution spectra, respectively, suggests that no changes in the co-ordination occur on passing from aqueous solution at 298 K to water–glycol (5 : 1) at 110 K. The frozen-solution EPR spectra obtained close to the physiological pH are quite similar for all the ternary systems and can be described by an axial spin Hamiltonian, in accord with an octahedral arrangement having tetragonal distortion. This does not hold for the Cu–L–2,9-dmphen complex, which is of rhombic type, in agreement with a distortion of the copper square plane.

As an example, in Fig. 2(*a*) and 2(*b*) the frozen-solution EPR spectra of the $[Cu(HL)(nphen)]^{-}$ and of the $[Cu(HL)(2,9\text{-}dmphen)]^{-}$ complexes, respectively, are reported.

As shown by the data in Table 5, the presence of methyl groups on the phenanthroline ring in positions far from the co-ordination sites does not change the EPR parameters significantly. The differences found for the $[Cu(HL)(2,9\text{-}dmphen)]^{-}$ complex can be ascribed to differences in the arrangement of the ligand around the metal centre in this unique compound.

In the perpendicular part of the spectra a poorly resolved structure was evidenced; however, seven lines attributable to the

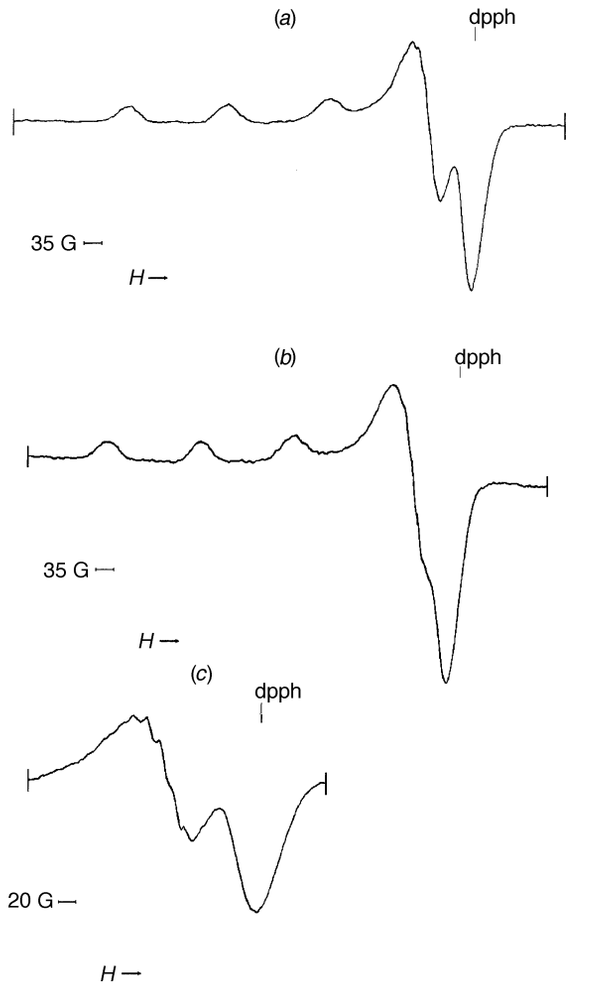



**Fig. 2** X-Band EPR spectra of (*a*) [Cu(HL)(nphen)]$^-$ (110 K, pH 6), (*b*) [Cu(HL)(2,9-dmphen)]$^-$ (110 K, pH 5.5) and (*c*) [Cu(HL)(5,6-dmphen)]$^-$ (110 K, pH 6, perpendicular region). G = $10^{-4}$ T

**Table 5** The EPR parameters for selected ternary systems obtained at pH 6

| Compound | *T*/K | $g_{xx}$ | $g_{yy}$ | $g_{zz}$ | $10^4A_{zz}$/ cm$^{-1}$ | $10^4A_N$/ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| [Cu(HL)(phen)]$^-$ * | 110 | 2.06 | 2.06 | 2.24 | 182 | 12.67, |
| | 298 | 2.13 | 2.13 | 2.13 | 76 | 11.0 |
| [Cu(HL)(2,9-dmphen)]$^-$ | 110 | 2.09 | 2.04 | 2.27 | 177 | — |
| | 298 | 2.138 | 2.138 | 2.138 | 74.8 | |
| [Cu(HL)(5,6-dmphen)]$^-$ | 110 | 2.06 | 2.06 | 2.24 | 184 | 12.6 |
| | 298 | 2.13 | 2.13 | 2.13 | 76 | |
| [Cu(HL)(mphen)]$^-$ | 110 | 2.06 | 2.06 | 2.23 | 182 | — |
| | 298 | 2.13 | 2.13 | 2.13 | 76 | |

* From ref. 5 (0.1 mol l$^{-1}$ $KNO_3$).

interaction between the unpaired electron of copper and the nitrogen atoms of the ligands can be identified in the case of the [Cu(HL)(5,6-dmphen)]$^-$ and [Cu(HL)(4,7-dmphen)]$^-$ ternary complexes, giving $A_N \approx 12.6 \times 10^{-4}$ cm$^{-1}$ [Fig. 2(*c*)].

On the basis of the EPR results, any involvement of sulfur atoms from the hexapeptide molecule in the co-ordination to copper ion, as well as any antiferromagnetic coupling between copper atoms in a dimeric structure, can be excluded. Our results suggest that $CuN_3O$ is in all cases the chromophore close to the physiological pH, involving N and O donor atoms from only one glutamyl moiety of the hexapeptide ligand, the other two positions in the plane being occupied by the two nitrogen donor atoms from the phenanthroline ligands. In addition, stability data and EPR parameters obtained for the ternary systems are well comparable with those reported for similar copper–phenanthroline–amino acid complexes.[19–21]

In conclusion, the steric effects seem definitely to play a major role in determining the different chemical arrangements within this series of ternary complexes. Besides, it is noteworthy that the structural variety that can be found in the copper(II)–phenanthroline binary complexes[22] is preserved when passing to these ternary species, with oxidised glutathione as an additional ligand.

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