Redox Properties of Five-coordinate and Six-coordinate Chlorobis(imidazole)-bis(thioether)copper(II) complexes

M. F. CABRAL, J. DE O. CABRAL

Laboratorio Ferreira da Silva, Faculdade de Ciências, 4000 Porto (Portugal)

E. BOUWMAN, W. L. DRIESSEN and J. REEDIJK

Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

Abstract

Two different solid complexes were obtained from the same starting materials in solution, i.e. a six-coordinate complex, $[Cu(bidhx)Cl_2]$, and, in the presence of some extra water, a five-coordinate complex, $[Cu(bidhx)Cl]Cl(H_2O)_2$. These solid complexes have been previously characterized, by chemical analyses, X-ray structure, and spectroscopic properties. Their cyclovoltammetric behaviour and solution spectra in dimethyl sulfoxide are now described. It was found that two waves were observed in the case of the six-coordinate complex, but only one for the five-coordinate. It was also found that these waves were quite dependent on the nature of the supporting electrolyte, on addition of extra chloride ion and on addition of water. A possible interpretation of these experimental results is presented and compared with earlier obtained results. Under these experimental conditions the redox potentials of $[Cu(bidhx)Cl_2]$ and $[Cu(bidhx)Cl]Cl(H_2O)_2$ are about +0.26 and −0.02 V versus SCE (+0.50 and +0.22 V versus NHE) respectively. The first value is close to those found for the blue copper proteins.

Introduction

The quest for model compounds of the active site in blue copper proteins has been the focus of attention of a very large number of workers and research groups. Whatever the measure of success of the numerous model compounds synthesized in mimicking the properties of the natural proteins, the studies have yielded at least very interesting copper coordination compounds [1].

Some of such model compounds have medicinal uses. There are even cases in which they proved to be more effective than the natural enzymes, for example, in protecting cells from damage by ionizing radiation [2].

Important biological functions of copper proteins involve cycles of redox processes of the type Cu(II)–Cu(I)–Cu(II), sometimes with relatively high redox potentials in comparison with common Cu(II) compounds. As such, it is not surprising that a large number of electrochemical studies of this kind of model compounds appears in the literature.

Cyclic voltammetry and differential pulse polarography have been used, as, for instance, in the case of mononuclear and dinuclear complexes with macrocyclic Schiff base ligands [3–7] and with azole-derived ligands [8–10].

In the so-called Type 1 copper proteins the intense blue colour is generally accepted to originate from the CuN_2S_2 chromophore and in particular from a $Cu(II)–(SR)^-$ charge-transfer band. Consequently, model compounds have been synthesized with this chromophore by using nitrogen-donor ligands, such as pyridine, pyrazole and imidazole, and sulfur-donor ligands, such as thioketones, thiols and thioethers [11].

As a contribution to model compounds for these blue copper proteins, the synthesis of imidazole-thioether containing ligands and their coordination compounds was undertaken. The ligand 1,6-bis-(5-methyl-4-imidazolyl)-2,5-dithiahexane (abbreviated as bidhx), a potentially tetradentate N_2S_2 ligand, was used in the synthesis of copper coordination compounds [12–15]. Starting from a solution of hydrated copper(II) chloride and a suspension of the ligand, bidhx, two different coordination compounds were isolated: $[Cu(bidhx)Cl_2]$ (**A**), with six-coordinate copper(II), and, on addition of some extra water, $[Cu(bidhx)Cl]Cl(H_2O)_2$ (**B**) with five-coordinate copper(II) [14]. Their molecular structures are redrawn in Figs. 1 and 2.

It can, therefore, be assumed that both compounds coexist in solution, the formation of the five-coordinate hydrated complex being favoured by addition of more water than that from the hydrated copper(II) chloride.
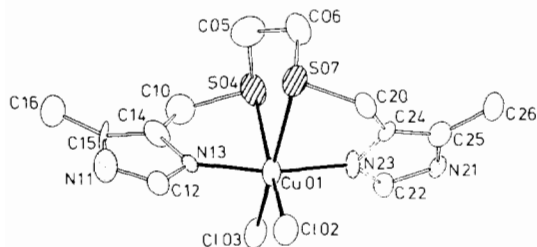
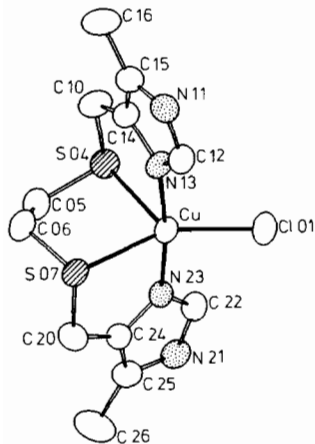Fig. 1. ORTEP projection and atomic labelling of [Cu(bidhx)-Cl$_2$]. For clarity the hydrogen atoms are omitted (after ref. 14).

Fig. 2. ORTEP projection and atomic labelling of the cation [Cu(bidhx)Cl]$^+$. For clarity the hydrogen atoms are omitted (after ref. 14).

This paper describes mainly the electrochemical behaviour of both compounds, studied by cyclic voltammetry, with the purpose of not only checking the possible coexistence of the two compounds in solution but especially how the difference in coordination of copper(II) with the same ligands would affect the redox potential in comparison with other compounds and with the copper proteins.

Experimental

Starting Materials

[Cu(bidhx)Cl$_2$], [Cu(bidhx)Cl]Cl(H$_2$O)$_2$ and bidhx were prepared as previously described [12, 14]. Dimethyl sulfoxide, Me$_2$SO (Aldrich, anhydrous), tetraethylammonium perchlorate, TEAP (GFS chemicals, polarographic grade), and tetraethylammonium chloride, TEACl (BDH), were used as received.

Electrochemical Measurements

Cyclic voltammograms were obtained, with the instruments previously described [8] at 25.00 ± 0.01 °C, in dry Me$_2$SO, under O$_2$-free conditions. The three electrode system consisted of: a clean platinum bead (c. 9.1 mm^2 in area), as working electrode; a

clean platinum spiral, as counter electrode; a Metrohm EA 441/1 saturated calomel, as reference electrode (SCE).

The SCE was connected to the cell through a salt bridge composed of a 0.1 mol dm^{-3} NaNO$_3$ aqueous solution, in contact with the calomel electrode. The salt bridge and cell solutions were separated by a Vycor tip. To minimize leakage of water from the salt bridge into the cell solution, the SCE and salt bridge were removed after each run, carefully dried, and reused in the following run.

Both TEAP and TEACl were used as supporting electrolytes (0.1 M in Me$_2$SO). From a number of preliminary experiments it was found that the best results were obtained at a scan rate of 20 mV s^{-1}. At higher (50, 100, 200, 500 mV s^{-1}) or lower (5, 10 mV s^{-1}) scan rates the cyclic voltammograms were either less well defined or even seriously distorted.

All further experiments were carried out at this scan rate, always with freshly prepared solutions, about 10^{-3} M in complex.

Under these experimental conditions, the Fc$^+$/Fc (Fc = Ferrocene) couple gave $E_{1/2}$ = +0.315 V (ΔE_p = 90 mV), in the presence of TEAP, and $E_{1/2}$ = +0.380 V (ΔE_p = 80 mV), in the presence of TEACl. These results were used in two ways: criterion for electrochemical reversibility, and number of electrons involved; test on the reliability of the behaviour of the reference system (SCE and salt-bridge), by the occasional check on the reproducibility of the values of the Fc$^+$/Fc couple.

All potentials are quoted versus SCE, with the salt-bridge, and are uncorrected for liquid junction potentials and iR drop.

Spectroscopic Measurements

Ligand field spectra of the solids (300–2000 nm) and of the solutions in Me$_2$SO with supporting electrolytes (450–1500 nm) were taken on a Perkin-Elmer 330 spectrometer equipped with a data station. EPR spectra of the solids and of the frozen solutions in Me$_2$SO with the respective supporting electrolytes were obtained on a Varian E-3 instrument operating at X-band frequencies.

Results and Discussion

General

All voltammograms were started in the cathodic direction and run between +700 or +600 mV and −400 mV versus the SCE system, to prevent the oxidation of chloride ions and the deposition of metallic copper on to the platinum bead. At least within this potential range the ligand is electrochemically inactive.

The experimental results are summarized in Table 1. Typical voltammograms are shown in Figs. 3, 4 and 5.

TABLE 1. Electrochemical data for the copper complexes in Me$_2$SO solution[a]

Supporting electrolyte	Compound added		$E_{p,c}$ (mV)	$E_{p,a}$ (mV)	ΔE_p (mV)	$E_{1/2}$ (V)
Compound: [Cu(bidhx)Cl$_2$]						
0.1 M TEAP		I	+200	+320	120	+0.260[b]
		II	−30	+85	115	+0.023[b]
	TEACl (solid)	I	+220	+340	120	+0.280
		II	−90	+70	160	−0.010
		I	+170	+330	160	+0.250
		II	−140	+50	190	−0.045
	H$_2$O	I	+245	+320	75	+0.283
		II	0	+70	70	+0.035
0.1 M TEACl		I	+180	+330	150	+0.245
		II	−130	+60	190	−0.035
	H$_2$O	I	+260	+340	80	+0.300
		II	−20	+100	120	+0.040
Compound: [Cu(bidhx)Cl]Cl(H$_2$O)$_2$						
0.1 M TEAP			−50	+65	115	+0.008
	TEACl (solid)		−80	+140[c]	220	+0.030
	H$_2$O		−20	+85	105	+0.033
0.1 TEACl			−140	+110[c]	250	−0.015
	H$_2$O		−40	+125	165	+0.043

[a]Potentials vs. SCE, uncertainty ±10 mV, scan rate 20 mV s^{-1}; all solutions were freshly prepared, about 10^{-3} in complex.
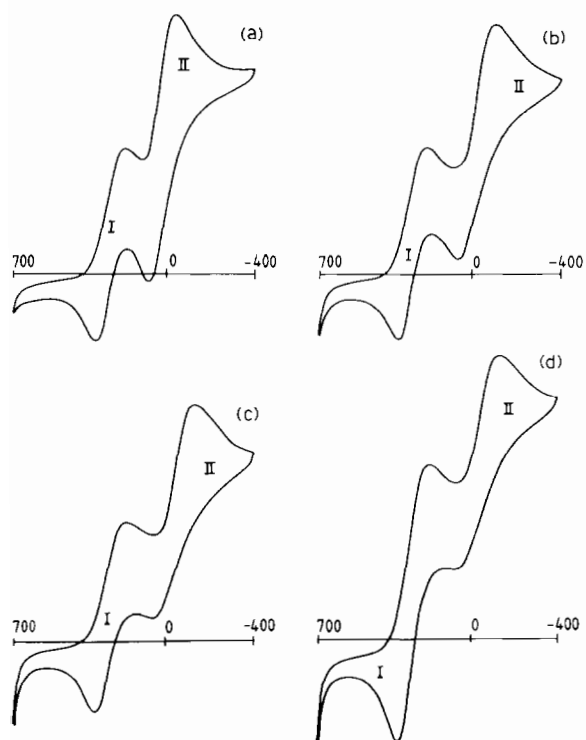[b]$i_{p,a}/i_{p,c} \cong 1$.   [c]Poorly defined.

Fig. 3. Cyclic voltammograms of [Cu(bidhx)Cl$_2$]: (a) in TEAP; (b) in TEAP with addition of TEACl; (c) in TEAP with further addition of TEACl; (d) in TEACl. Horizontal scale in mV.
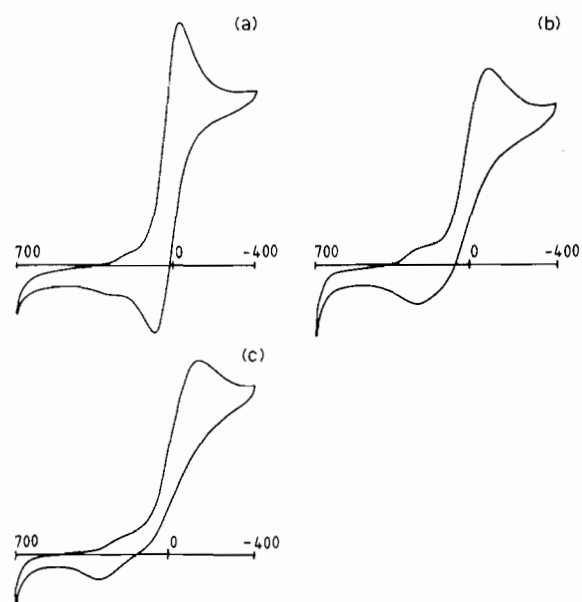

Fig. 4. Cyclic voltammograms of [Cu(bidhx)Cl]Cl(H$_2$O)$_2$: (a) in TEAP; (b) in TEAP with addition of TEACl; (c) in TEACl. Horizontal scale in mV.

It can easily be seen that the electrochemical behaviour of the two complexes is not only very different, but also quite dependent on the nature of the supporting electrolyte. On addition of water it
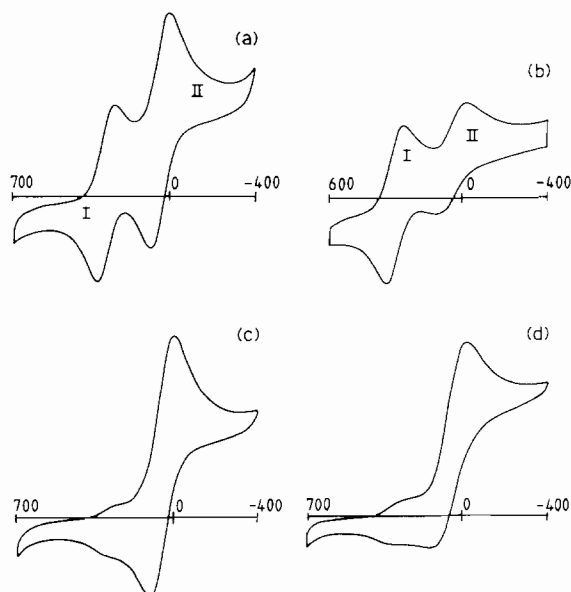
Fig. 5. Effect of addition of water on the cyclic voltammograms: (a) [Cu(bidhx)Cl$_2$] in TEAP; (b) [Cu(bidhx)Cl$_2$] in TEACl; (c) [Cu(bidhx)Cl]Cl(H$_2$O)$_2$ in TEAP; (d) [Cu(bidhx)Cl]Cl(H$_2$O)$_2$ in TEACl. Horizontal scale in mV.

appears that for both cases practically the same electroactive species is formed in solution.

There are also striking differences between the spectra of the solid compounds and of their solutions in Me$_2$SO, which show that the absorbing species are different (Table 2).

Freshly prepared solutions in Me$_2$SO were always used, since decomposition reactions appear to occur within a few hours.

[Cu(bidhx)Cl$_2$] (A)

With TEAP as supporting electrolyte two nearly reversible waves, I and II, were observed at 20 mV s^{-1} (see Table 1). On addition of successive amounts of solid TEACl, Fig. 3(b) and (c), there is a noticeable loss of reversibility and a displacement of wave II towards more negative potentials, approaching the values when TEACl is the supporting electrolyte, Fig. 3(d).

On the other hand, taking into account the experimental errors, Table 1 and Fig. 3 show that the half-wave potential of wave I remains virtually unaffected by the addition of solid TEACl, in spite of a slight shift of the peak potentials in direction of the values found with TEACl as supporting electrolyte.
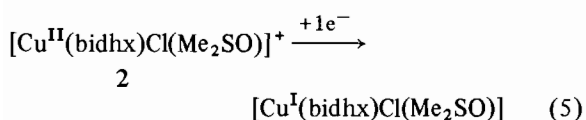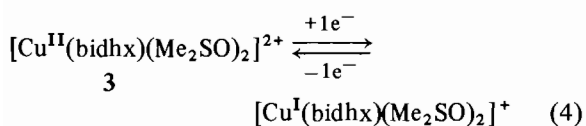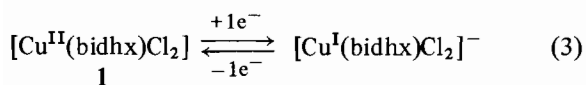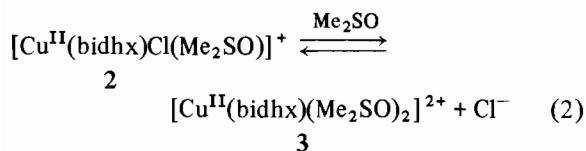
These results clearly indicate that, on dissolving [Cu(bidhx)Cl$_2$] in Me$_2$SO, two electroactive Cu(II) species coexist in solution, one of which probably is the initial complex and the other some product of a solvation reaction. This is not entirely unusual, as a similar behaviour has been reported for a related ligand [8], although in another solvent.

A tentative interpretation of these experimental results is based on the assumption of the following sequence of events.

TABLE 2. Spectroscopic data for the solid compounds and their solutions in Me$_2$SO[a]

	LF maxima (10^3 cm^{-1})	EPR parameters (at 77 K)
Compound: Cu(bidhx)Cl$_2$		
Solid (diff. refl.)	13.7; 8.6	$g_\perp = 2.20$ $g_{\parallel} = 2.02$
Me$_2$SO 0.1 M TEAP	14.0; 12.3	$g_\perp = 2.10$ $g_{\parallel} = 2.30$
		$A_{\parallel} = 150$ Gauss
0.1 M TEAP + H$_2$O	15.0; 12.2	2 species: (1) [Cu(H$_2$O)$_6$]$^{2+}$
		(2) complex
0.1 M TEACl	15.4(sh); 12.6	$g_\perp = 2.10$ $g_{\parallel}$ $A_{\parallel}$ visible
		but not resolved
0.1 M TEACl + H$_2$O	14.8; 12.2	2 species: (1) Cu(H$_2$O)$_6^{2+}$
		(2) complex
Compound: [Cu(bidhx)Cl]Cl(H$_2$O)$_2$		
Solid (diff. refl.)	16.3; 11.5	$g_1 = 2.15; g_2 = 2.11; g_3 = 2.03$
Me$_2$SO 0.1 M TEAP	14.8; 12.6(sh)	$g_{iso} = 2.10$
0.1 M TEAP + H$_2$O	15.4; 12.5(sh)	$g_1 = 2.23; g_2 = 2.10; g_3 = 2.02$
		$A_1 = 100$ Gauss
0.1 M TEACl	15.4(sh); 13.0	$g_{\parallel} = 2.20; g_\perp = 2.09$
		$A_{\parallel} = 110$ Gauss
0.1 M TEACl + H$_2$O	14.8; 12.8(sh)	$g_1 = 2.22; g_2 = 2.10; g_3 = 2.02$
		$A_1 = 110$ Gauss

[a] All solution spectra were taken of somewhat aged solutions, due to the poor solubility of the complexes. The spectra are taken of 10^{-2} M solutions which were made by sonification (at least a few hours).

$$[Cu^{II}(bidhx)Cl_2] \xrightleftharpoons{Me_2SO}$$
$$\mathbf{1}$$
$$[Cu^{II}(bidhx)Cl(Me_2SO)]^+ + Cl^- \quad (1)$$
$$\mathbf{2}$$

$$[Cu^{II}(bidhx)Cl(Me_2SO)]^+ \xrightleftharpoons{Me_2SO}$$
$$\mathbf{2}$$
$$[Cu^{II}(bidhx)(Me_2SO)_2]^{2+} + Cl^- \quad (2)$$
$$\mathbf{3}$$

$$[Cu^{II}(bidhx)Cl_2] \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}} [Cu^{I}(bidhx)Cl_2]^- \quad (3)$$
$$\mathbf{1}$$

$$[Cu^{II}(bidhx)(Me_2SO)_2]^{2+} \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}}$$
$$\mathbf{3}$$
$$[Cu^{I}(bidhx)(Me_2SO)_2]^+ \quad (4)$$

$$[Cu^{II}(bidhx)Cl(Me_2SO)]^+ \xrightarrow{+1e^-}$$
$$\mathbf{2}$$
$$[Cu^{I}(bidhx)Cl(Me_2SO)] \quad (5)$$
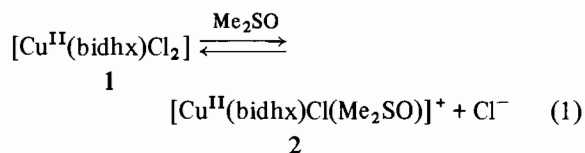
Equations (1) and (2) represent two successive solvation equilibria. As the best results were obtained at a low scan rate (20 mV s^{-1}) with fresh solutions, the establishment of these equilibria would be relatively slow. Nevertheless, given sufficient time dissociation could proceed to a much greater extent, giving rise to the above-mentioned decomposition.

If, in the absence of added chloride ion, **1** and **3** are the predominant species, **1** would be responsible for wave I, and **3** for wave II, as expressed by eqns. (3) and (4), respectively. Given the nearly reversible behaviour of these two waves, it can be assumed that the amount of **2** present is not significant; otherwise the influence of the irreversible process (5) would clearly affect the behaviour.

As such, on addition of solid TEACl to the solution with TEAP, the amount of **2** would increase at the expense of **3**, but this addition would have little effect on that of **1**. This effect is mostly reflected on the behaviour of wave II, which will increasingly change to a mixture of the redox processes (4) and (5), losing reversibility (ΔE_p increases), sharpness of anodic peaks, and approaching the potentials observed when TEACl was the supporting electrolyte.

It has been known for many years that copper(II) halides have a strong tendency to coordinate with Me$_2$SO [16]. Thus, it is not unreasonable to assume that solvation in fact is just a competition between the solvent Me$_2$SO and Cl$^-$ in the coordination sphere of the Cu(II) complex, on the hypothesis that bidhx remains very tightly bound.

This interpretation finds some support in previously reported results [14]. In the crystalline solid there are two Cu–Cl bond lengths, that is, one bond is stronger than the other; then, it would be acceptable that solvation takes place in two successive steps. Also, the EPR spectra of a frozen solution of [Cu(bidhx)Cl$_2$] in Me$_2$SO revealed the existence of two species, which is consistent with the presence of **1** and **3**, not **2**, owing to the absence of any extraneous source of chloride ions.
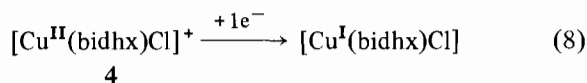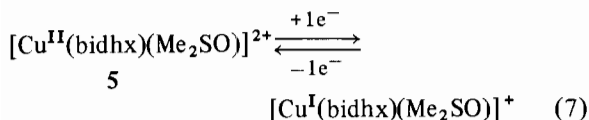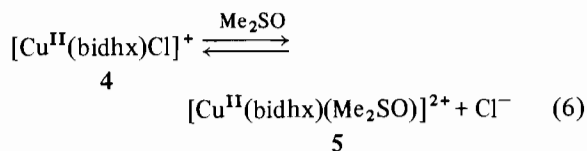
As mentioned before, there is also a striking difference between the ligand field spectra of [Cu(bidhx)Cl$_2$] in the solid state and in solution in Me$_2$SO with added TEAP. In the solid state (see Table 2) there are three clear absorption bands, one sharp band at 28 500 cm^{-1}, probably a LMCT, a broader band at 13 700 cm^{-1}, and a very broad band at 8600 cm^{-1}, characteristic of a highly distorted octahedral coordination of copper(II). In solution, practically only one, very weak, extremely broad band (from c. 19 000 cm^{-1} to more than 8000 cm^{-1}) is observed, with two barely discernible maxima in the region of 14 000 and 12 300 cm^{-1}. This broadness is not unusual for copper complexes (see e.g. ref. 6) and shows that there are two or more weakly absorbing species in solution whose bands overlap to such an extent that they become undistinguishable. Consequently, although these spectra confirm severe dissociation, they do not provide any information on the nature of the species in solution.

[Cu(bidhx)Cl]Cl(H$_2$O)$_2$ (B)

When TEAP is the supporting electrolyte, [Cu(bidhx)Cl]$^+$ shows only a clearly defined, quasi-reversible wave, Fig. 4(a). At more positive potentials there are signs of a barely discernible second wave, probably derived from some [Cu(bidhx)Cl$_2$]. On addition of solid TEACl, Fig. 4(b), the cathodic peak of that first wave shifts towards more negative potentials, approaching the value found with TEACl as supporting electrolyte, its anodic counterpart is practically non-existent, and the process becomes quite irreversible. As a matter of fact, with TEACl as the supporting electrolyte, Fig. 4(c), only a relatively broad, cathodic peak is clearly observed, the system becoming practically irreversible.

This electrochemical behaviour of the five-coordinate complex resembles what was observed with wave II of the six-coordinate; thus, it seems reasonable to assume that the electroactive species in solution must be similar to those from **A**, although not the same, and there will be analogies between the sequences of events.

For the five-coordinate complex the sequence might be the following:

$$[Cu^{II}(bidhx)Cl]^+ \xrightleftharpoons{Me_2SO}$$
4
$$[Cu^{II}(bidhx)(Me_2SO)]^{2+} + Cl^- \quad (6)$$
5

$$[Cu^{II}(bidhx)(Me_2SO)]^{2+} \xrightleftharpoons[-1e^-]{+1e^-}$$
5
$$[Cu^{I}(bidhx)(Me_2SO)]^+ \quad (7)$$

$$[Cu^{II}(bidhx)Cl]^+ \xrightarrow{+1e^-} [Cu^{I}(bidhx)Cl] \quad (8)$$
4

As a result of solvation, eqn. (6), an electroactive species **5** is formed, which will be predominant in solution, and will undergo a quasi-reversible redox process, eqn. (7), partially obscured by an irreversible process, eqn. (8), which takes place at about the same potential. On addition of solid TEACl, the amount of **4** increases and, as a consequence, the irreversibility of the redox process. With TEACl as supporting electrolyte, the amount of **5** becomes negligible and only the irreversible reduction of **4** is observed, although with some mixture of **5**. It cannot also be completely ruled on that, in the presence of a large excess of chloride ions, some **1** is formed in solution; this could account for the detected small wave at rather positive potentials.

The Cu—Cl bond length in solid **4** is significantly shorter than the shortest of the Cu—Cl bond lengths in **1** [14], and therefore stronger. Thus, the replacement of coordinated chloride ion by solvent molecules will be less energetically favourable, which might explain the greater effect of added TEACl on the voltammograms.

It must be assumed that **4** contains no coordinated Me_2SO, because it would then be the same as **2** and the cyclic voltammetric results do not support this point of view. Nevertheless, their electrochemical behaviour would be expected to be quite similar.

Species **5** and **3** are also very similar, but not the same. Whether the difference lies in the different number of assumed coordinated Me_2SO molecules or in the presence of water molecules introduced by $[Cu(bidhx)Cl]Cl(H_2O)_2$ cannot be said from the available experimental data.

As expected, the ligand field spectra of this complex in the solid state and in Me_2SO solution with added TEAP are very different, both in profile and position of peaks. In the solid state two relatively narrow absorption bands are observed, at 16 300 and 11 500 cm^{-1}. In solution, only a broad band is observed, with a maximum at 14 500 cm^{-1} and a shoulder at about 12 600 cm^{-1}. This difference in spectra reflects the effect of solvation with the formation of two or more absorbing species. Although the

absorption bands overlap to a great extent, it appears that in solution there is a predominant species, in agreement with what was suggested above: eqn. (6) and subsequently proposed sequence of events.

The Effect of Water Addition on the Cyclovoltammograms

Subsequent addition of the same amount of water to similar volumes of solutions of the complexes in Me_2SO changed their cyclic voltammograms, Fig. 5.

In the case of $[Cu(bidhx)Cl_2]$ with water, two almost reversible waves, Fig. 5(a) and (b), are still observed, with wave II being more affected than I. On the basis of the suggested sequence of events, it may be assumed that water competes with Me_2SO for the coordination sphere of the Cu(II) ion. Eventually $[Cu(H_2O)_6]^{2+}$ is seen in the frozen solution EPR spectra of A.

Similarly, when water is added to $[Cu(bidhx)Cl]-$ $Cl(H_2O)_2$ only one clear wave is observed, Fig. 5(c) and (d). This wave becomes more irreversible when TEACl is the supporting electrolyte, as was the case in the absence of added water.

The comparison of the half-wave potentials (see Table 1) reveals the interesting fact that, within the uncertainty of ± 10 mV, they are practically the same whatever the complex, for the same supporting electrolytes, viz.

	TEAP	TEACl
$[Cu(bidhx)Cl_2]$	+0.035	+0.040
$[Cu(bidhx)Cl]Cl(H_2O)_2$	+0.033	+0.043

from which it appears that the same electroactive species is present for all cases in solutions where water is added. This fact is consistent with what was found in the preparation of the complexes: the molecular complex, being less soluble, precipitates first; addition of water changes all unreacted starting materials into the same species which subsequently crystallizes out as the five-coordinate, hydrated complex.

The similarity of solution spectra of the two complexes when water is added to their solutions in Me_2SO further confirms that water converts both complexes into the same species, most likely initially a species $[Cu(bidhx)(H_2O)_2]^{2+}$, which upon aging or addition of extra water appears to degrade to even $[Cu(H_2O)_6]^{2+}$ in case of A.

Conclusions

The difference between the five-coordinate, $[Cu(bidhx)Cl]^+$, and the six-coordinate, $[Cu(bidhx)-Cl_2]$, copper(II) chlorocomplexes of the ligand bidhx becomes clearly evident in their redox behaviour, as

studied by cyclic voltammetry, when dissolved in Me_2SO with TEAP or TEACl as supporting electrolytes, and is quite dependent on the nature of this electrolyte. With the six-coordinate complex two waves are observed under all conditions. One of these is strongly affected by extraneous chloride ions (either by addition of a solid chloride to a solution with TEAP or from the supporting electrolyte TEACl itself). In contrast, $[Cu(bidhx)Cl]^+$ only yields one wave, also strongly affected by the presence of extraneous chloride ions.

These results may be interpreted in terms of controlled dissociation/solvation, in an extent related to the different strengths of the Cu—Cl bonds, as judged by their length.

When water is added to any of the four systems (two complexes and two supporting electrolytes), cyclic voltammograms suggest that a single species is formed in solution, which agrees with observations during the synthesis of the complexes.

One of the waves of $[Cu(bidhx)Cl_2]$, assigned to an unchanged complex, has a half-wave potential of about +0.26 V versus SCE (+0.50 V versus NHE) of the order of magnitude found for the redox potentials of the blue copper proteins [17].

For the other wave of $[Cu(bidhx)Cl_2]$ and the wave of $[Cu(bidhx)Cl]^+$ the half-wave potentials are of the order of +0.02 and −0.02 V versus SCE, respectively (+0.26 and +0.22 V versus NHE), well within the range of common Cu(II)/Cu(I) oxidation-reduction systems [18].

Acknowledgements

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