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Cyclic voltammetric studies of copper(II) complexes with some bis(imidazole)bis(thioether) ligands. The X-ray crystal structure of (1,6-bis-(5(4)-imidazolyl)-2,5-dithiahexane)dichlorocopper(II)

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Abstract

A variety of copper coordination compounds with an N_2S_2 donor set, composed of tetradentate bis(imidazole)bis(thioether) ligands, have been synthesized and characterized. The starting solid complexes have the general formula Cu(L)XY, in which X and Y are monoanions: Cl^- (both X and Y) or $[BF_4]^-$ (Y), and the ligands L are bidhx (1,6-bis-(5-methyl-4-imidazolyl)-2,5-dithiahexane), bhdhx (1,6-bis-(5(4)-imidazolyl-2,5-dithiahexane) and bidhp (1,7-bis-(5-methyl-4-imidazolyl)-2,6-dithiaheptane). These ligands differ only in the length of the bridge between the S atoms and in the presence or absence of a methyl substituent on the imidazole group. The cyclic voltammetric behaviour of four of those complexes, viz. $[Cu(bidhx)Cl(BF_4)]$ (**A**), $[Cu(bhdhx)Cl][BF_4]$ (**B**), $[Cu(bhdhx)Cl_2]$ (**C**) and $[Cu(bidhp)Cl_2]$ (**D**), in dimethyl sulfoxide solution under different conditions is described in detail. It was found that $[Cu(bidhp)Cl_2]$ decomposes so quickly in solution that its cyclic voltammograms became meaningless. A possible interpretation of the experimental results of the other three complexes, including the influence of coordinated $[BF_4]^-$, will be presented and compared with previous results on similar complexes. For these three complexes, half-wave potentials from +8 to +120 mV versus SCE (+250 to +360 mV versus SHE) were found, which are within the lower range of redox potentials for blue copper proteins. The compound $[Cu(bhdhx)Cl_2]$ (**C**) crystallizes in the orthorhombic space group *Pbca* with $a = 12.738(3)$, $b = 17.218(4)$, $c = 13.894(7)$ Å, $V = 3047(2)$ Å^3, $Z = 8$ and consists of molecular units with a $[CuN_2S_2Cl_2]$ chromophore. Distances in the distorted octahedral geometry are: Cu–N = 1.96, Cu–S = 2.52 and 2.84, and Cu–Cl = 2.37 and 2.59 Å.

Introduction

Synthesis and characterization of low-molecular weight analogs for the active sites of metalloproteins is receiving increasing attention of a very large number of workers and research groups. As possible models for type-I copper proteins, many copper complexes with ligands containing the N_2S_2 set of donor atoms have been reported, and the results recently reviewed [1, 2].

In a recent publication [3] it was shown that reduction of copper(II) to copper(I) in azurin, isolated from *Alcaligenes denitrificans*, involves minimal structural changes in the copper protein, one of the requirements for fast electron transfer. This would be a feature of great interest for the success of a synthetic analog in mimicking the blue sites of natural copper proteins, even though it is generally accepted that low-molecular weight compounds cannot reproduce properties that arise from the protein backbone [4].

The expansion of bioinorganic chemistry in the last decades gave a strong impetus to the development of copper coordination chemistry, and an enormous number of new complexes, with very interesting structures and properties, have been prepared. As a rule, their redox properties have been investigated by electrochemical techniques, especially the cyclic voltammetry of solutions in appropriate solvents.

It is obvious that the ideal solvent should be chemically inert towards the copper complex but, in practice, such a solvent may not be found, and then the electrochemical studies are carried out in non-ideal solvents. If the

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reaction between the solvent and the complex is sufficiently slow, at least the first voltammograms will not be irrevocably affected by this reaction.

In the present paper we report our work on the electrochemical behaviour, as studied by cyclic voltammetry, of four copper(II) complexes, viz. [Cu(bidhx)Cl(BF_4)] (**A**), [Cu(bhdhx)Cl][BF_4] (**B**), [Cu(bhdhx)Cl_2] (**C**) and [Cu(bidhp)Cl_2] (**D**) in dimethyl sulfoxide solution. This study was undertaken with the purpose of investigating how differences in organic ligands (length of bridge between the two sulfur atoms and presence or absence of methyl substituents) and in the (non-)coordinating monoanions would affect their redox properties in comparison with similar complexes, previously studied [5]. Consequently, the same solvent, dimethyl sulfoxide, had to be used in spite of its non-inertness towards copper complexes.

We also report the X-ray crystal structure of [Cu(bhdhx)Cl_2] (**C**) as a representative example of a new N_2S_2 compound, and compare it to the ones known from our previous work. Used ligand abbreviations are: bidhx = 1,6-bis-(5-methyl-4-imidazolyl)-2,5-dithiahexane; bidhp = 1,7-bis-(5-methyl-4-imidazolyl)-2,6-dithiaheptane; bhdhx = 1,6-bis-(5(4)-imidazolyl)-2,5-dithiahexane.

Experimental

Starting materials

[Cu(bidhx)Cl(BF_4)] (**A**), [Cu(bhdhx)Cl][BF_4] (**B**), [Cu(bhdhx)Cl_2] (**C**) and [Cu(bidhp)Cl_2] (**D**) were prepared and characterized as previously described [6–8]. Dimethyl sulfoxide (Aldrich, 'anhydrous grade', less than 0.005% H_2O), tetraethylammonium perchlorate, TEAP (GFS Chemicals, polarographic grade), tetraethylammonium chloride, TEACl (BDH) and tetraethylammonium tetrafluoroborate, $TEABF_4$ (Pfalz & Bauer) were used as received.

Electrochemical measurements

Cyclic voltammograms were obtained, as previously described [5], at several scan rates on freshly prepared solutions, *in situ*, about 10^{-3} M (**A** and **B**) or 10^{-4} M (**C** and **D**) in complex. The solid complexes were brought into solution, as quickly as possible; this was achieved by addition of the solid complex to the solvent, with supporting electrolyte (0.1 M in TEAP), already in the cell, while bubbling deoxygenated dinitrogen through. All potentials are quoted versus SCE, with the salt bridge, and are uncorrected for liquid junction potentials and *IR* drop. Peak currents were corrected for background currents, whenever relevant.

X-ray diffraction and structure determination

Crystals of the compound Cu(bhdhx)Cl_2 were obtained from ethanol through slow evaporation. X-ray measurements were made on a crystal 0.18×0.22×0.10 mm. Crystal data for Cu(bhdhx)Cl_2, $M=388.57$, are: orthorhombic space group *Pbca* with $a=12.738(3)$, $b=17.218(4)$, $c=13.894(7)$ Å, $V=3047(2)$ Å^3, $Z=8$, green plate form crystals, μ(Mo Kα)$=20.4$ cm^{-1}, $F(000)=1576$, λ(Mo Kα)$=0.71069$ Å, $D_{calc}=1.694$ g cm^{-3}. Data collection: Nicolet P3 diffractometer with ω-scan mode. Data collection range $4.0<2\theta<54.0°$,$0<h<16$, $0<k<21$, $0<l<17$. A total of 3478 reflections was measured, of which 2263 were used in the refinement ($I>3\sigma(I)$). The data were corrected for Lorentz and polarization effects and absorption from empirical Φ-scan data. Structure refinement: the structure was solved by direct methods of the SHELXS-86 program [9] and refined with anisotropic temperature factors for non-hydrogen atoms using the SHELX-76 program [10]. Hydrogen atoms with $U=0.06$ Å^2 were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Final values for R and R_w with $w=1/\sigma^2(F_0)$ are 0.035 and 0.041, respectively, for 173 variables. Residual electron density was within ±0.43 e Å^{-3} and largest Δ/δ was 0.19. Scattering factors and anomalous dispersion corrections were taken from ref. 11. Calculations were performed on a VAX 8650 computer. Final coordinates and U_{eq} values for the non-hydrogen atoms and bond lengths and angles are listed in Tables 1 and 2, respectively. See also 'Supplementary material'.

TABLE 1. Fractional atomic coordinates ($\times10^4$) and thermal parameters for Cu(bhdhx)Cl_2

Atom	x	y	z	U_{eq} (Å^2)[a]
Cu	1542(1)	1740(1)	1156(1)	0.033
Cl(1)	−26(1)	2688(1)	1310(1)	0.051
Cl(2)	2975(1)	2614(1)	1046(1)	0.045
S(4)	252(1)	645(1)	1401(1)	0.058
S(7)	2897(1)	467(1)	750(1)	0.038
N(11)	2184(3)	1698(2)	4049(2)	0.049
N(13)	1700(2)	1624(2)	2552(2)	0.035
N(21)	811(3)	1702(2)	−1723(2)	0.045
N(23)	1381(2)	1621(2)	−239(2)	0.033
C(12)	2420(3)	1898(2)	3148(3)	0.040
C(14)	971(3)	1231(2)	3104(3)	0.042
C(15)	1281(4)	1273(3)	4040(3)	0.053
C(10)	17(3)	874(3)	2647(3)	0.056
C(5)	1132(4)	−184(3)	1526(3)	0.060
C(6)	1869(4)	−240(2)	660(3)	0.058
C(20)	3042(3)	842(2)	−455(3)	0.049
C(22)	634(3)	1905(2)	−794(3)	0.038
C(24)	2062(3)	1213(2)	−834(2)	0.040
C(25)	1700(3)	1263(2)	−1747(3)	0.049

[a] $U_{eq}=1/3(U_{11}+U_{22}+U_{33})$.

TABLE 2. Interatomic distances (Å) and angles (°) for $[Cu(bhdhx)Cl_2]$

Cu–Cl(1)	2.589(1)	N(13)–Cu–Cl(1)	93.5(1)
Cu–Cl(2)	2.371(1)	N(13)–Cu–Cl(2)	92.8(1)
Cu–S(4)	2.523(1)	N(13)–Cu–S(4)	81.8(1)
Cu–S(7)	2.845(1)	N(13)–Cu–S(7)	93.2(1)
Cu–N(13)	1.961(3)	N(23)–Cu–Cl(1)	93.8(1)
Cu–N(23)	1.960(3)	N(23)–Cu–Cl(2)	94.8(1)
		N(23)–Cu–S(4)	89.3(1)
N(13)–C(12)	1.323(5)	N(23)–Cu–S(7)	77.7(1)
C(12)–N(11)	1.332(5)	S(4)–Cu–S(7)	81.2(1)
N(11)–C(15)	1.364(6)	S(4)–Cu–Cl(1)	87.5(1)
C(15)–C(14)	1.361(5)	S(7)–Cu–Cl(2)	90.5(1)
C(14)–N(13)	1.381(4)	Cl(1)–Cu–Cl(2)	101.5(1)
C(14)–C(10)	1.502(6)	N(13)–Cu–N(23)	168.2(1)
C(10)–S(4)	1.800(4)		
S(4)–C(5)	1.824(5)	C(15)–C(14)–C(10)	131.3(4)
C(5)–C(6)	1.530(7)	C(14)–N(13)–C(12)	107.1(3)
C(6)–S(7)	1.792(4)	N(13)–C(14)–C(10)	120.6(3)
S(7)–C(20)	1.803(4)	C(14)–C(10)–S(4)	111.2(3)
C(20)–C(24)	1.499(5)	C(10)–S(4)–C(5)	100.5(2)
C(24)–N(23)	1.388(5)	C(5)–C(6)–S(7)	110.5(3)
N(23)–C(22)	1.319(4)	C(6)–S(7)–C(20)	104.6(2)
C(22)–N(21)	1.355(4)	S(7)–C(20)–C(24)	113.2(3)
N(21)–C(25)	1.362(5)	C(20)–C(24)–N(23)	121.8(3)
C(25)–C(24)	1.353(5)	C(20)–C(24)–C(25)	129.8(4)
N(11)...Cl(2)^a	3.180(2)	C(25)–C(24)–N(23)	108.3(3)
N(21)...Cl(1)^b	3.116(2)	C(24)–N(23)–C(22)	106.9(3)
N(13)–C(12)–N(11)	109.8(4)	N(23)–C(22)–N(21)	109.9(3)
C(12)–N(11)–C(15)	108.7(3)	C(22)–N(21)–C(25)	107.7(3)
N(11)–C(15)–C(14)	106.4(4)	N(21)–C(25)–C(24)	107.1(3)
C(15)–C(14)–N(13)	108.0(4)		

^{a}Symmetry operation: $x, \frac{1}{2}-y, \frac{1}{2}+z$. ^{b}Symmetry operation: $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

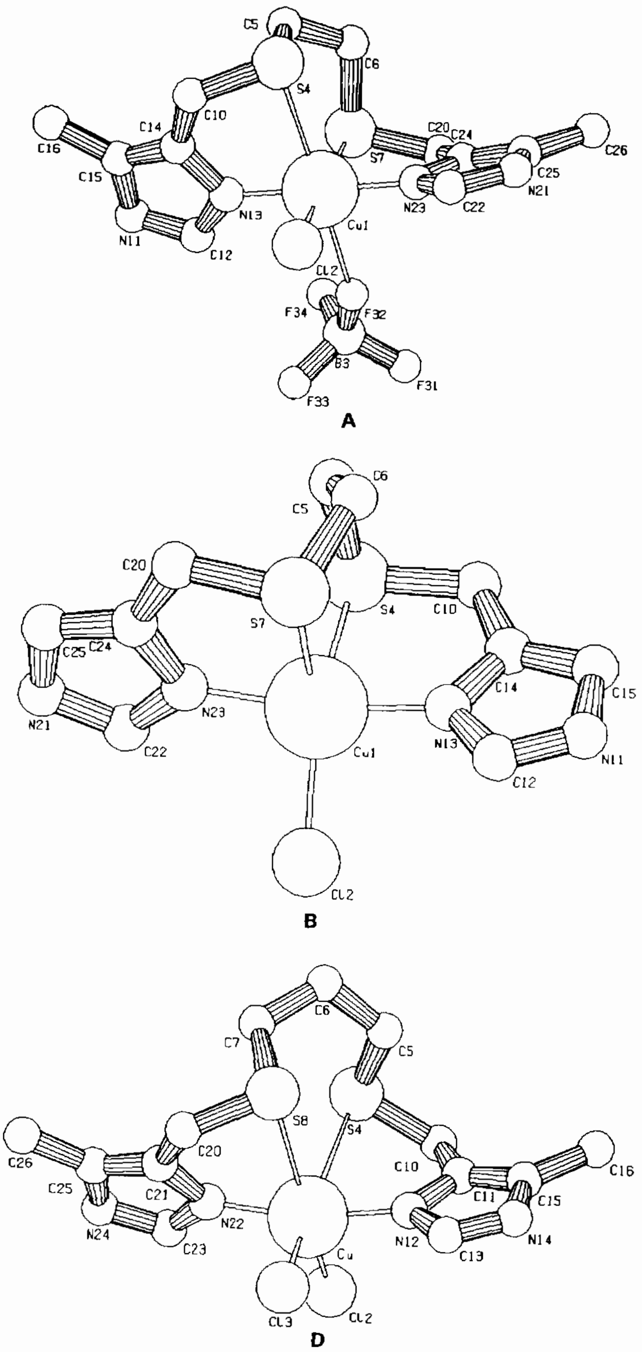
Results and discussion

General

The molecular structures of the solid complexes **A**, **B** and **D** are redrawn in Fig. 1. Figure 2 depicts a projection [12] of the new structure **C**, determined in the present study and to be discussed below in detail (bond distances in Table 2). A stereo packing diagram is depicted in Fig. 3, including H-bonding interactions.

Table 3 summarizes experimental electrochemistry results, and typical voltammograms are depicted in Fig. 4, all obtained immediately after complete dissolution of the complexes.

The three organic ligands, bidhx, bhdhx and bidhp, are not electrochemically active, at least within the potential range used for the complexes. Whenever peak currents could be reasonably measured, it was found that they increased linearly with the square root of scan rates, a characteristic of a diffusion-controlled electrochemical process. Values of ΔE and the peak currents ratios are typical for one-electron, quasi-reversible redox processes for complexes **A**, **B** and **C**.



A

B

D

Fig. 1. PLATON drawing of the structures of compounds **A**, **B** and **D**, based on the coordinates in the original publications. In case of **B** the BF_4^- counterion has been omitted for clarity.

It has already been reported [8] that complex **D** decomposes in ethanol solution. This complex also quickly decomposes in Me_2SO solution as shown by the fact that, in about one hour, an initially clear greenish solution becomes turbid with a suspension of a fluffy whitish material. Thus, the behaviour of complex **D** will not be further discussed, despite its interesting solid state structure.

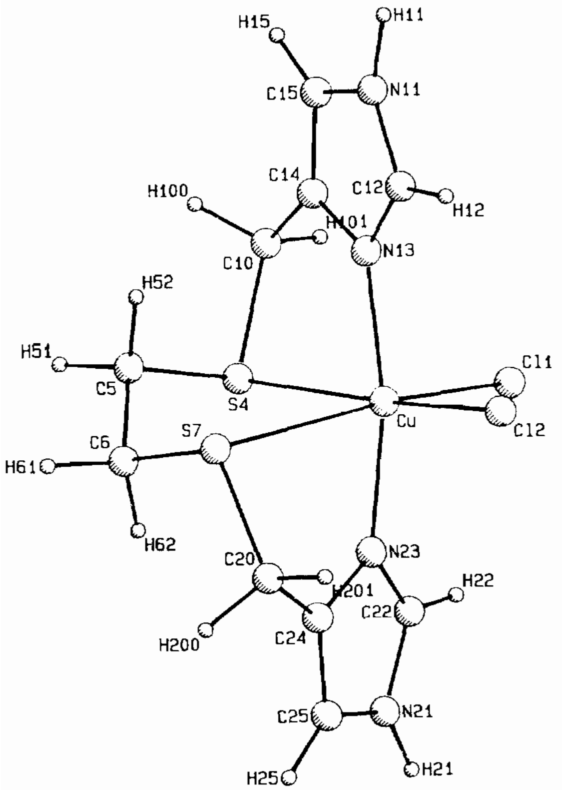


Fig. 2. Projection of the structure of compound **C**, [Cu(bhdhx)Cl_2], drawn after ref. 12.

Solvation by dimethyl sulfoxide is not an unusual phenomenon for copper(II) complexes, and it may become dominant in cyclic voltammetry, as was recently reported [13]. We noticed that solvation of the complexes **A**, **B** and **C** proceeded practically to completion within hours.

The crystal structures of the complexes **A**, **B** and **C** (Figs. 1 and 2) show that copper(II) is at the apex of a system of three consecutive, five-membered chelate rings, which appears to make that part of the complexes more resistant to solvation than at the site of the anionic ligands, as has been observed previously [5, 13].

Before going into more detailed individual discussions, it must be reported that addition of solid TEACl to solutions with TEAP as supporting electrolyte in all cases had the same effect, i.e. serious distortion of the voltammograms, which became electrochemically irreversible. We had already reported [5] similar effects with [Cu(bidhx)Cl_2] and [Cu(bidhx)Cl]Cl$(H_2O)_2$, and interpreted them in terms of formation of monochloro-copper(II) species, which would be irreversibly reduced to the corresponding copper(I) compounds. It is considered possible that an analogous interpretation also applies here and, thus, no further discussion will need to be provided.

For a better understanding of the differences in the compounds with only chloride as a monoanion, a crystal structure determination was felt necessary. The structure determination of compound **C** was therefore undertaken and is described below, together with a detailed comparison with the earlier determined X-ray structures of compounds **A**, **B** and **D**.

X-ray structure description of [Cu(bhdhx)Cl] (C) and comparison with that of complexes A, B and D

The structure of compound **C**, depicted in Fig. 2, for which bond length and angle information is given in Table 2, is not unusual and very much resembles the earlier determined structure **D** [8] and the structure of the related compound [Cu(bidhx)Cl_2 [7]. The six-coordination for Cu(II), compared to the five-coordination in compound *B* [6], results in rather long (and asymmetric) Cu–S and Cu–Cl distances, generating a rhombic symmetry. As a matter of fact the asymmetry of Cu–Cl and Cu–S in compound **C** is larger than in **D**, as seen from the Cu–S distances (2.523 and 2.845,

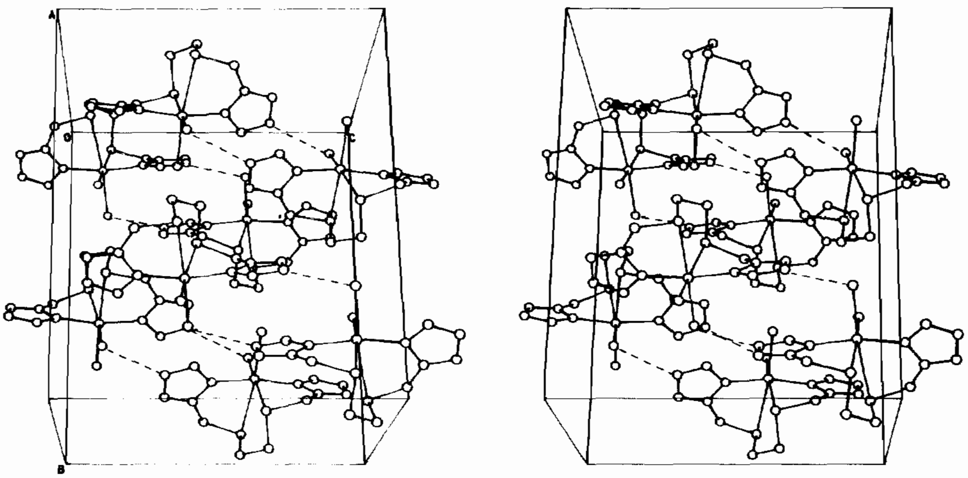


Fig. 3. Stereodrawing of the packing of compound **C**; N..Cl contacts are indicated by dashed lines.

TABLE 3. Electrochemical data for the copper(II) complexes in Me_2SO solution, 0.1 M in TEAP[a]

Compound		Scan rate (mV s^{-1})	$E_{p,c}$ (mV)	$E_{p,a}$ (mV)	ΔE_p (mV)	$E_{1/2}$ (mV)	$i_{p,a}/i_{p,c}$
[Cu(bidhx)Cl(BF_4)]	**(A)**	10	+50	+130	80	+90	0.92
		20	+50	+130	80	+90	0.87
		50	+50	+140	90	+95	0.79
		100	+40	+150	110	+95	0.79
[Cu(bhdhx)Cl][BF_4]	**(B)**	10	+70	+150 +270	80	+110[b]	0.81
		20	+70	+150 +270	80	+110[b]	0.72
		50	+70	+160 +270	90	+115[b]	0.62
		100	+70	+180 +255	100	+120[b]	0.61
[Cu(bhdhx)Cl_2]	**(C)**	10	−55	+70	125	+8	0.71
		20	−60	+80	140	+10	0.68
		50	−90	+115	205	+13	0.61
		100	−120	+200	320	+40	0.50
[Cu(bidhp)Cl_2]	**(D)**	20	+130[c]	+210			
			−70	+110	180[d]	+20[d]	
		50	+80[c]	+210			
			−90	+125	215[d]	+18[d]	
		100	+30[c]	+250			
			−145	+155[c]			
		200	−145	+250	390[d]	+50[d]	

[a] Potentials vs. SCE, uncertainty ±10 mV; all solutions freshly prepared *in situ*, about 10^{-3} M (**A** and **B**) or 10^{-4} M (**C** and **D**) in complex. [b] Assumed correspondence between the cathodic and the less anodic peaks. [c] Poorly defined. [d] Lack of reasonable correspondence between cathodic and anodic peaks.

compared to 2.88 and 2.97 Å in **D**) and the Cu–Cl distances (2.371 and 2.589, compared to 2.45 and 2.40 Å in compound **D**).

It should be noted that compounds **A** and **B** have a five-coordinate geometry (tetragonal pyramidal for **A**, with an additional long 2.59 Å Cu–FBF_3 contact) and trigonal bipyramidal for **B** (with non-coordinating BF_4 counterions). In compounds **C** and **D** both anions are coordinated to copper, yielding a six-coordinate structure. As will become clear from the electrochemical studies in solution, the coordination number of Cu in the solid state does not contribute much to the stabilization of the solution structure. The Cu–N distances (Table 2) are comparable to other Cu imidazole chelate compounds [2, 6–8].

The packing of the molecules of compound in the lattice is determined by van der Waals forces and by relatively strong N–H..Cl hydrogen bonds. The molecules form hydrogen bonds in the *c* direction of the crystal, linking molecules 2 by 2 through single N–H...Cl bonds, which are almost linear. The contact distances and angles are 3.180 Å and 159.4° (for N(11)...Cl(2) and N–H–Cl) and 3.116 Å and 149.2° (for N(21)– –Cl(1) and N–H–Cl). Symmetry operations are given in Table 2. A stereo drawing of the packing showing the hydrogen-bond contacts is given in Fig. 3. In addition to the H bonding a weak stacking between imidazole rings occurs in the *b* direction (closest contacts are N11–C(22) 3.12, N(21)–C(12) 3.17, N(23)–N(11) 3.22, C(15–C(22) 3.25, C(25)–C(12) 3.30, C(12)–C(22) 3.40 Å).

Cyclic voltammetry

[Cu(bidhx)Cl(BF_4)] (A)

It was observed that, within about two hours, the voltammograms started to become increasingly distorted with time, most probably as a result of decomposition by solvation. Nevertheless, the results were entirely reproducible when freshly prepared solutions were used.

Since [Cu(bidhx)Cl(BF_4)] and [Cu(bidhx)Cl_2] only differ in one anionic ligand, and $[BF_4]^-$ is generally, but not always [14], a poorer ligand than Cl^-, it might reasonably be expected that solvation would proceed according to the following scheme

$$\underset{\textbf{1}}{[Cu(bidhx)ClBF_4]} \xrightarrow[+Me_2SO]{-BF_4^-} \underset{\textbf{2}}{[Cu^{II}(bidhx)Cl(Me_2SO)]^+}$$

$$\underset{\textbf{2}}{[Cu^{II}(bidhx)Cl(Me_2SO)]^+} \xrightarrow[+Me_2SO]{-Cl^-} \underset{\textbf{3}}{[Cu^{II}(bidhx)(Me_2SO)_2]^{2+}}$$

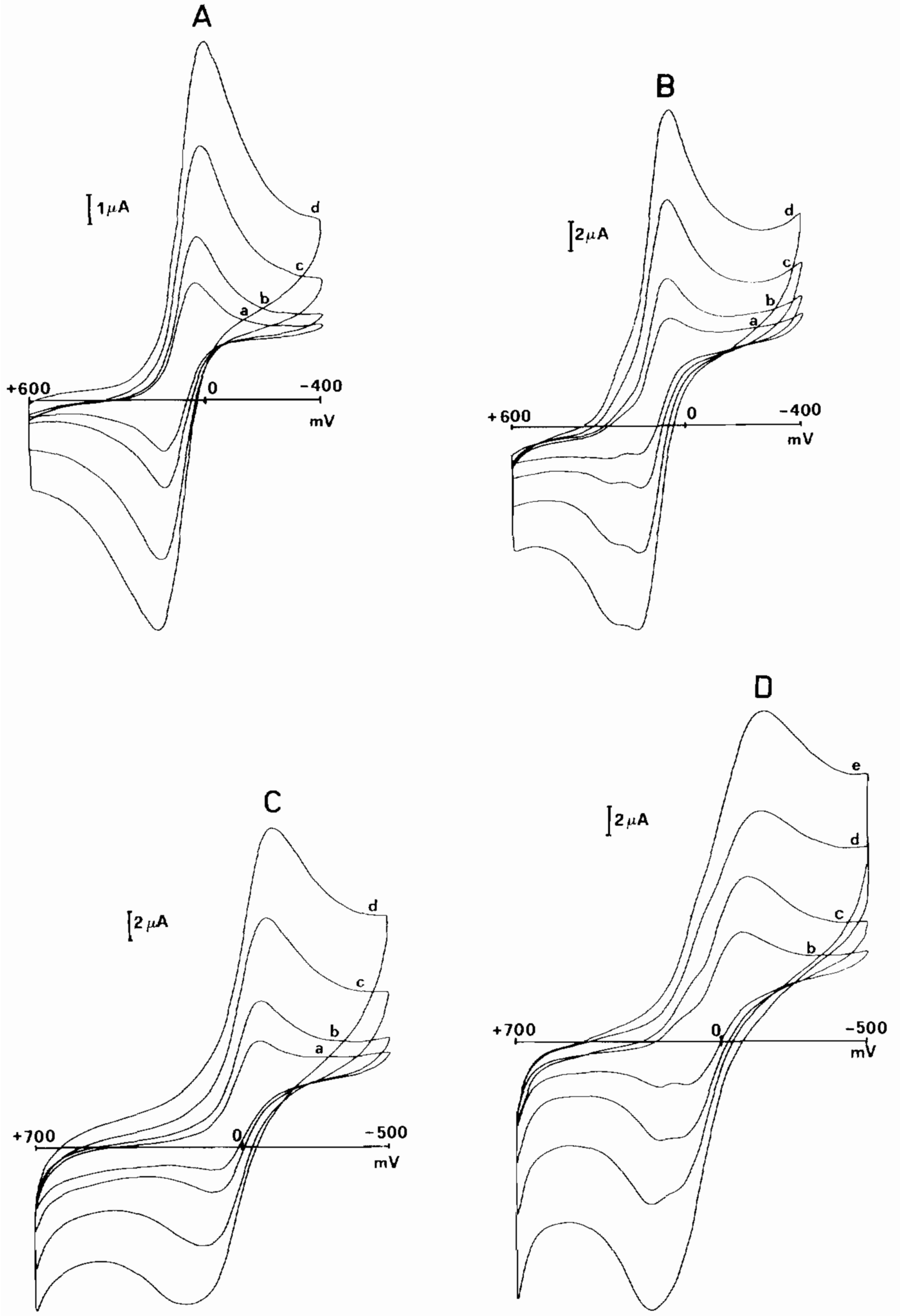


Fig. 4. Cyclic voltammograms of [Cu(bidhx)Cl(BF_4)] (**A**), [Cu(bhdhx)Cl][BF_4] (**B**), [Cu(bhdhx)Cl_2] (**C**) and [Cu(bidhp)Cl_2] (**D**) in Me_2SO with 0.1 M TEAP. Voltage range +700 or +600 mV to −440 or −500 mV vs. SCE. Scan rates: a, 10; b, 20; c, 50; d, 100 mV s^{-1}.

Nevertheless, this cannot be the case because, at 20 mV s^{-1} and with TEAP as supporting electrolyte, half-wave potentials of −10 mV for **2** and +23 mV for **3** have been observed [5], and, for [Cu^{II}(bidhx)Cl(BF_4)], a value of +90 mV was found (see Table 3).

Another, albeit apparently less probable, candidate is [Cu^{II}(bidhx)(BF_4)(Me_2SO)]$^+$, resulting from a different first step of solvation, in which the semi-coordinated BF_4^- initially remains coordinated, as suggested in the following scheme

$$\underset{\mathbf{1}}{[Cu(bidhx)ClBF_4]} \xrightarrow[+Me_2SO]{-Cl^-} \underset{\mathbf{4}}{[Cu^{II}(bidhx)(BF_4)(Me_2SO)]^+}$$

$$\underset{\mathbf{4}}{[Cu^{II}(bidhx)(BF_4)(Me_2SO)]^+} \xrightarrow[+Me_2SO]{-BF_4^-} \underset{\mathbf{3}}{[Cu^{II}(bidhx)(Me_2SO)_2]^{2+}}$$

with predominance of **4**, which would undergo the redox process

$$[Cu^{II}(bidhx)(BF_4)(Me_2SO)]^+ \underset{-1e^-}{\overset{+1e^-}{\longleftrightarrow}} [Cu^{I}(bidhx)(BF_4)(Me_2SO)]^0$$

responsible for the observed wave.

It can be assumed that the first solvation step, i.e. **1** into **4** is rather fast, and the second rather slow. This assumption finds some support in the observed differences between the electrochemical behaviour of $[Cu(bidhx)Cl(BF_4)]$ and that of $[Cu(bidhx)Cl_2]$: one wave in the first case (one electroactive species, a rather fast first solvation step), and two in the second (a relatively slow first solvation step); possibility of using a wide range of scan rates in the first case, but not in the second, meaning the existence of a more stable electroactive species in solution.

With the purpose of getting a clearer picture, a series of experiments were carried out in which solid $TEABF_4$ was added to solutions of the complex in Me_2SO, 0.1 M in TEAP. Immediately after addition the voltammograms shifted to less positive potentials but, after about 1 h, the voltammograms shifted to the more positive potentials they had before the addition. These observations might mean that, even if $[BF_4]^-$ is somewhat labile, it also re-coordinates much faster than it is displaced by Me_2SO, in other words, extraneous $[BF_4]^-$ reverses and slows the second solvation step of that scheme, i.e. **4** into **3**.

In spite of a certain lack of electrochemical reversibility, it is worth noting that, taking into account the experimental errors, $E_{1/2}$ can be considered essentially independent of scan rates.

[Cu(bhdhx)Cl][BF₄] (B)

The cyclic voltammograms of Fig. 4 show the existence of one well-defined cathodic peak and two anodic peaks. Both anodic peak potentials are practically independent of scan rates, as well as the cathodic peak potential. It seems, therefore, that at least two copper(I) species exist in solution after a reduction of copper(II) species. There are also barely discernible signs of a second reduction process, at positive potentials, which might be the cathodic counterpart of the more positive anodic peak. It was also observed that, scanning the same solution after keeping it in the cell for some time under a blanket of dinitrogen, the two anodic peaks tended to coalesce, becoming less distinguishable as the scan rate increased. This suggests the existence of a further slow process of solvation, better detectable at low scan rates.

At attempted explanation of these observations is suggested below. The complex is ionic in the solid state and, as such, will ionize when dissolved, as expressed by

$$[Cu^{II}(bhdhx)Cl][BF_4] \longrightarrow [Cu^{II}(bhdhx)Cl]^+ + [BF_4]^-$$

This ionization would then be followed by a solvation equilibrium, relatively slow to be established, with the formation of two electroactive copper(II) species, in accordance with the following scheme

$$\begin{tikzcd}
\underset{\mathbf{5}}{[Cu^{II}(bhdhx)Cl]^+ + Me_2SO} \arrow[r, shift left] \arrow[d, shift left] & \underset{\mathbf{6}}{[Cu^{II}(bhdhx)(Me_2SO)]^{2+} + Cl^-} \arrow[l, shift left] \arrow[d, shift left] \\
{[Cu^{I}(bhdhx)Cl]^0 + Me_2SO} \arrow[r, shift left] \arrow[u, shift left] & {[Cu^{I}(bhdhx)(Me_2SO)]^+ + Cl^-} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

As a result of solvation, **6** would be predominant in solution and thus responsible for the less positive, quasi-reversible, stronger waves; the more positive, very weak waves could then be assigned to the small amount of **5** still existing shortly after dissolution.

[Cu(bhdhx)Cl₂] (C)

The relatively low solubility of this complex in Me_2SO and the relatively long time required to bring it into solution would favour decomposition by solvation, not only before starting the voltage scans but also during the few minutes involved in running successive voltammograms at four scan rates. As a result, a mixture of several electroactive species, such as: $[Cu(bhdhx)Cl_2]$, $[Cu(bhdhx)Cl(Me_2SO)]^+$, $[Cu(bhdhx)(Me_2SO)]^{2+}$, $[Cu(bhdhx)Cl]^+$ and $[Cu(bhdhx)(Me_2SO)_2]^{2+}$ might co-exist in solution, and make it almost impossible to attempt any interpretation of the electrochemistry of this complex.

The above-mentioned hypothesis finds some support in the electrochemical results, viz.

(i) the voltammograms (Fig. 4) show relatively sharp cathodic peaks, but rather broad anodic peaks, suggestive of mixture of species with close oxidation potentials;

(ii) $E_{1/2}$ values (Table 3) increase significantly with scan rate, which might be the result either from an uncertainty in assigning $E_{p,a}$ values, or from different times required to reach different solvation equilibria in solution, more perceptible at higher scan rates;

(iii) although $i_{p,a}$ and $i_{p,c}$ vary linearly with the square roots of scan rates, as mentioned before, their ratio greatly departs from unity and decreases as the scan rate increases.

Conclusions

The differences between the organic ligands bidhx, bhdhx and bidhp become clearly evident in the solution redox behaviour of these four complexes, irrespective of the fact that they are five- or six-coordinate copper(II) complexes in the solid state.

Increasing the length of the bridge between the S atoms on going from bidhx to bidhp dramatically affects the stability of similar complexes in solution. It appears that [Cu(bidhp)Cl_2] is highly strained in the solid state, and that this strain is relieved in solution, with decomposition of the complex.

To account for any differences resulting from the presence or absence of methyl substituents, i.e. between bidhx and bhdhx, the behaviour of [Cu(bidhx)Cl_2] (see ref. 5) and [Cu(bhdhx)Cl_2] (this work) can be compared, and the differences are obvious: two cathodic peaks in the case of bidhx, and one in the case of bhdhx. It appears, therefore, that the presence of the methyl substituents makes the complexes more resistant to solvation. Whether this is a consequence of steric, electronic or any other effect of the methyl substituents cannot be proved from the available experimental data.

The presence of $[BF_4]^-$ as one of the anionic ligands in a six-coordinate molecular complex posed an interesting problem: whether the first anionic ligand to be replaced by Me_2SO would be Cl^- or $[BF_4]^-$. Although far from a clear-cut case, the experimental evidence appears to favour the first hypothesis, unexpected as it may appear.

In solid [Cu(bhdhx)Cl][BF_4] the tetrafluoroborate anion is not coordinated, it is the counterion of a cationic, five-coordinate chlorocopper(II) complex. Thus, only the displacement of the anionic ligand, Cl^-, by Me_2SO is to be considered, and this is consistent with the experimental results. Most of the half-wave potentials found in this study, from +90 to +120 mV versus SCE (+330 to +360 mV versus SHE), are in the lower range of the known redox potentials for blue copper proteins [1].

The X-ray structure determination of compound **C** has made clear that the solid-state structures of the present group of compounds do not necessarily reflect the structures that may exist or may be formed in (nonaqueous) solutions, and care should be taken to extrapolate X-ray data to structural data in solution.

Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom parameters and values of F(obs) and F(calc) are available upon request from the authors.

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