The Redox Properties of (1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane) Chlorocopper(II) Chloride as Studied by Cyclic Voltammetry

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Received November 5, 1983

Cyclic voltammetry in acetonitrile has been used to study the redox properties of the compound [Cu(BBDH)Cl] Cl under various conditions. The nature of the species in solution was studied with the aid of ligand-field spectra and ESR spectra. It appears that in CH_3CN solution two Cu(II) species are predominating, viz. $[Cu(BBDH)(CH_3CN)_x]^{2+}$ and Cu(BBDH)-Cl^+. Minor species are dimeric in nature, such as $[(BBDH)CuCl_2Cu(BBDH)]^{2+}$, as easily seen from ESR. The relative amount of the two major species was varied using added LiCl, allowing us to determine the nature of both species. The redox potential of the species $[Cu(BBDH)Cl]^+$ appeared to be 0.62 V (against a normal hydrogen electrode), which is very high for a Cu(II) compound and in the same area as found for the blue copper proteins. Re-oxidation of $Cu(BBDH)^+$ in the presence of LiCl shows that Cl^- slowly recoordinates after reoxidation.

Introduction

Apart from their fascinating electronic properties, such as the small parallel hyperfine splitting and the high molar extinction of the visible absorption band, blue copper proteins show a remarkably high redox potential, compared with copper(II) coordination compounds [1]. In mimicing the structure of the active site of blue copper proteins, several workers have given attention to the chromophore CuN_2S_2, with nitrogen donor ligands such as pyridine, pyrazole and imidazole and sulfur donor ligands such as thioketone and thioether [2–6]. Previous investigations with benzimidazole–thioether chelating ligands such as BBDH (1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane) and BBDHp (1.7-bis(benzimidazol-2-yl)-2,6-dithiaheptane) have shown that the copper(II) compounds with these ligands are easily reduced to the Cu(I) state in certain solvents [3, 7]. In a subsequent study it was found that this reduction is enhanced by the action of visible light [8]. Therefore it was considered useful to study the electrochemical reduction in order to determine the redox potential and to compare it with other compounds and with the metalloproteins. The ligand BBDH was selected because this system has been most extensively studied by spectroscopic methods and by photo-redox reactions. To avoid complications with redox reactions in the solvent, acetonitrile was used as the solvent for the cyclic voltammetry studies. The ligand structure is depicted in Fig. 1, together with a schematic structure of $[Cu(BBDH)Cl]^+$.

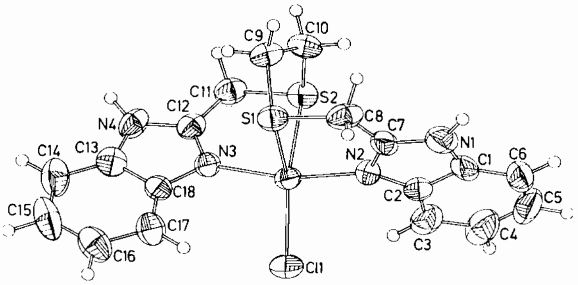


Fig. 1. Drawing of the ligand in the schematic structure of $Cu(BBDH)Cl^+$ (after ref. 3).

Experimental

Starting Materials

$Cu(BBDH)Cl_2$, $Cu(BBDH)(ClO_4)$ and BBDH were prepared as described previously [3, 8]. CH_3CN (Merck *p.a.*), tetraethylammonium perchlorate and chloride (Pfalz & Bauer, research chemicals), and lithium chloride (Merck *p.a.*) were used as received.

Electrochemical Measurements

Cyclic voltammograms were obtained with a PAR model 174 polarographic analyzer, a PAR model 175 universal programmer and a Houston Omnigraph 2000 X–Y recorder. A Metrohm electrolysis cell

0020-1693/84/$3.00

TABLE I. Electrochemical Parameters of Cyclic Voltammetry on Cu–BBDH Species. (Acetonitrile, oxygen-free solutions, *ca.* 10^{-3} *M* in copper compound, at 25 °C; potentials in mV *vs.* SCE, uncorrected for liquid junction potentials; scan rates, S.R., in mV s^{-1}).

System	S.R.	Ep, c	Ep, a	ΔEp	
$Cu(BBDH)Cl_2$	50	+350	+475	125	Peak potentials of first wave practically independent of scan rate. Second wave much less reversible
		+85	+225	140	
	100	+350	+475	125	
		+80	+230	150	
	200	+345	+475	130	
		+65	+250	185	
$Cu(BBDH)Cl_2$ + added LiCl	50	+335	+425	90	Improved reversibility of first wave. Predominance of unsolvated Cu(II) species.
		+30	+180	150	
$Cu(BBDH)(ClO_4)$ + added LiCl	100	+340	+400	60	First wave becomes reversible.
		+60	+180	120	Formation of the solvated and unsolvated Cu(II) species.
$Cu(BBDH)Cl_2$ + large excess Cl^- by TEACL	50	+240	+370	130	Formation of new, probably dimeric species.
		+40	–	–	

[a] On addition of LiCl there was an evolution of peak currents and potentials with time. Figures in the Table are the final values detected. [b] Addition of BBDH did not affect the first wave but the second became almost totally irreversible (no anodic counterpart). [c] In the cyclic voltammograms potentials were estimated to ±5 mV.

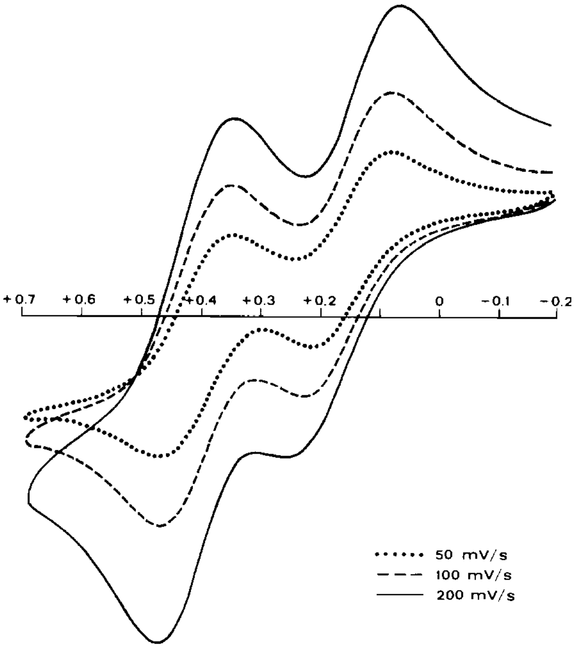


Fig. 2. Cyclic voltammograms of $CuCl_2(BBDH)\cdot H_2O$ *ca.* 10^{-3} *M* in CH_3CN at different scan rates (supporting electrolyte: tetraethylammonium perchlorate in 0.1 *M* concentration; potentials *vs.* SCE).

model EA 876/5 was used, with a three-electrode system: a platinum bead as working electrode, a platinum spiral as counter electrode and a Metrohm EA 441/1 saturated calomel electrode were used as reference. Potentials are reported *vs.* SCE and are uncorrected for liquid junction potentials. Experiments were carried out at 25.0 ± 0.1 °C in solutions previously degassed with oxygen-free nitrogen. The inert gas was presaturated with a blank solution of supporting electrolyte in CH_3CN to avoid evaporation on degassing. During the experiments the solutions were kept under a blanket of oxygen-free nitrogen.

Spectroscopic Measurements

Ligand-field spectra were recorded as solids and in CH_3OH and CH_3CN solution on a Beckman DK-2A ratio recording spectrophotomer in the 500–1500 nm region. ESR spectra of frozen solutions in CH_3CN, CH_3OH, toluene/ethanol mixtures were obtained on a Varian E-3 instrument operating at X-band frequencies.

Results and Discussion

Initial observations on cyclic voltammetry of $CuCl_2(BBDH)\cdot H_2O$ in CH_3CN showed two quasi-reversible processes to occur, as depicted in Fig. 2. Blank experiments showed that BBDH itself is electrochemically inert, at least between +1.0 and –0.4 V (*vs.* saturated calomel, SCE). Reduction to the Cu(0) state was considered as highly unlikely, since deposition of metallic copper only took place at much more negative potentials. Therefore two Cu(II) species must be present in CH_3CN solutions

TABLE II. ESR and UV Spectral Data of Cu(BBDH)Cl$_2$ under Various Conditions.

Species	LF maximum[c]		$g_\parallel$	$A_\parallel$	$g_\perp$	Comments
Cu(BBDH)Cl$_2$	15.4 (390)	11.4[c] (260)	2.22	130	2.06	MeOH/dmso 3:1 77 K
		14.9(w)[b]	2.19[a]	130[a]	2.07[a]	CH$_3$CN, toluene, EtOH (45/45/10)
		11.2(st)[b]	2.34	115	2.07	
Cu(BBDH)Cl$_2$ + extra Cl$^-$ (5 eq Bu$_4$NCl)	–		2.19	130	2.07	CH$_3$CN, toluene, EtOH (45/45/10)
			2.34[a]	115[a]	2.07[a]	

[a] The most abundant species. [b] Solid state diffuse reflectance data, wave numbers in 10^3 cm^{-1}. [c] Solution spectrum under ESR conditions; in parentheses relative intensities or extinction coefficients (in l mol^{-1} cm^{-1}).

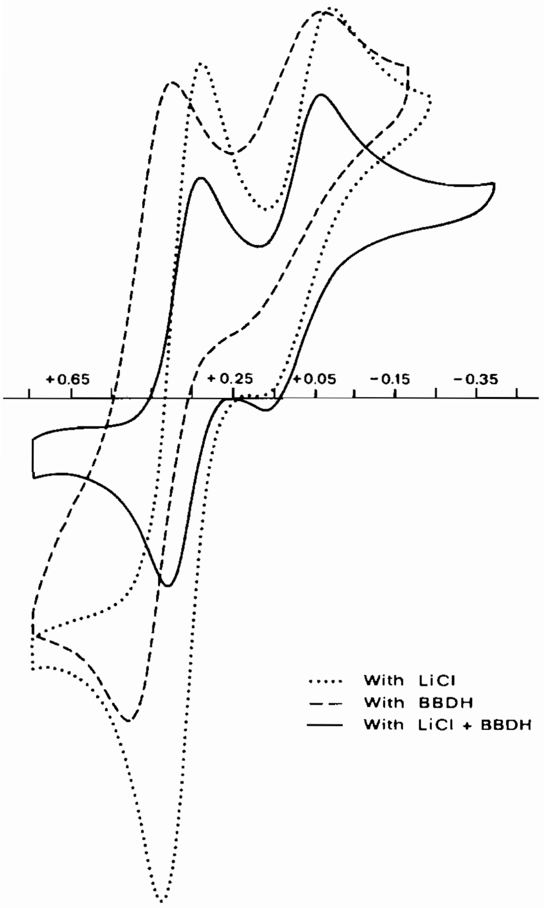


Fig. 3. Cyclic voltammogram of *ca.* 10^{-3} *M* CuCl$_2$(BBDH)·H$_2$O in CH$_3$CN with added LiCl (supporting electrolyte: tetraethylammonium perchlorate in 0.1 *M* concentration; scan rate: 50 mV s^{-1}; potentials *vs.* SCE).

under our conditions (*i.e.* in the presence of 0.1 molar tetraethylammonium perchlorate). To investigate the nature of these species, cyclic voltammetry was applied in the presence of an excess of LiCl. The result is depicted in Fig. 3. It now appears that one species is reduced in concentration and that the other species is increased in concentration. The peak potentials of both species are listed in Table I, together with some other electrochemical parameters.

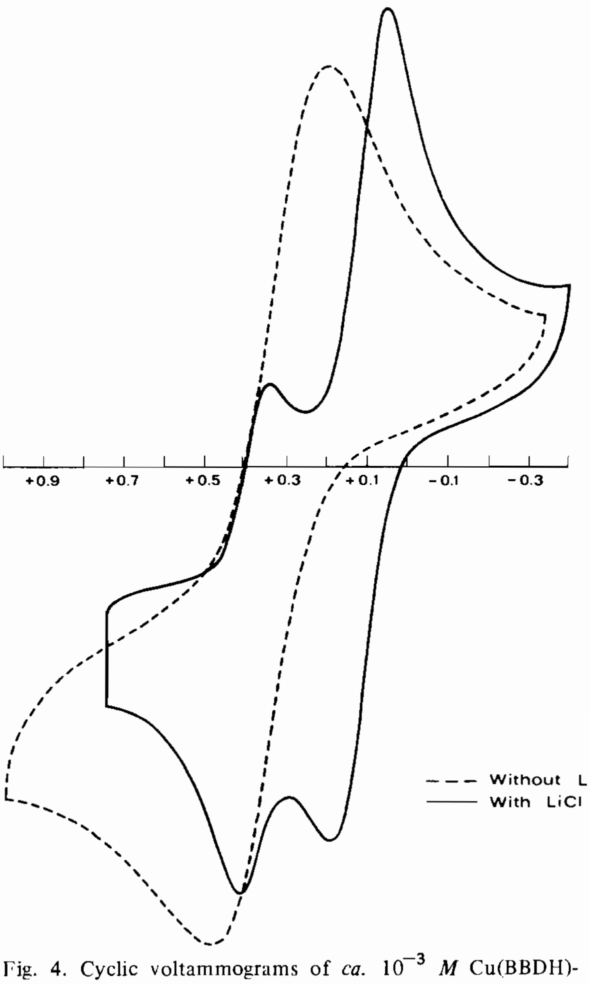
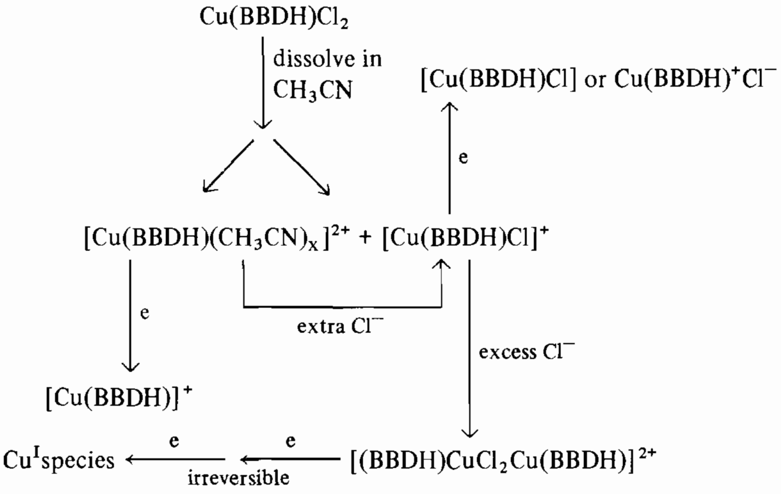


Fig. 4. Cyclic voltammograms of *ca.* 10^{-3} *M* Cu(BBDH)(ClO$_4$) in CH$_3$CN both in the absence and in the presence of LiCl (supporting electrolyte: tetraethylammonium perchlorate in 0.1 *M* concentration; scan rate: 100 mV s^{-1}; initial potentials: +1.0 and +0.8 V *vs.* SCE).



Scheme

It is likely from these results that one species contains chloride coordinated to copper (amount increases with added LiCl) and that the other species is a solvolysed product. To investigate the nature of this solvolysed product, cyclic voltammetry was applied to Cu(BBDH)ClO$_4$ with and without added LiCl. These results are shown in Fig. 4. The relevant parameters are given in Table I. The results show that in the presence of added LiCl the behaviour is essentially the same as when starting from Cu(BBDH)Cl$_2$, Without added LiCl, however, the process is much more irreversible and no firm conclusions about the structures can be drawn.

In order to obtain information about the species present in solution (in the Cu(II) state) optical spectra and frozen-solution ESR spectra were recorded. Previous work in dmso and dmso/EtOH glass had already shown that the solution species is clearly different from the trigonal bipyramidal form in the solid state [3]. With the related ligand BBDHp more than one solution species was clearly detected [7]. Because of the low solubility in CH$_3$CN, the frozen solution ESR spectra of the present compound were taken in CH$_3$CN/toluene/EtOH (45/45/10). This appeared to give the best glasses. As shown in Table II, two main species are present under these conditions, the ratio of which depends on the amount of added LiCl, or Bu$_4$NCl. Therefore the signals are likely to originate from [Cu(BBDH)(CH$_3$CN)$_x$]$^{2+}$ and [Cu(BBDH)Cl]$^+$. The optical spectra yield no new information, compared to that presented before [3]. To understand better the unusual electrochemical behaviour at very high concentrations of added chloride ions, ESR spectra were also recorded in the presence of a large excess of Cl$^-$.

Just as found before [7] for the related compound Cu(BBDHp)Cl$_2$, the presence of dimeric species is easily deduced from the signals below $g = 2$ and from the so-called 'half-field' signal near $g = 4.3$. The cyclic voltammetry of these systems shows irreversible behaviour and at least two redox processes. Whether these processes are stepwise reductions of the form Cu(II)$_2$ → Cu(II)Cu(I) → Cu(I)Cu(I) cannot be determined from the present results. Summarising, the following species seem to be present in CH$_3$CN solution and undergo the following reaction (see Scheme).

Finally it is to be noted that the species Cu(BBDH)Cl$^+$ has a redox potential of 0.37 ± 0.02 V (*vs.* SCE) of +0.62 V against normal hydrogen electrode. This value is quite high for Cu(II) compounds [2], and approaches the values found for the blue copper proteins [1].

Acknowledgements

M. F. C. and J. O. C. thank INIC (Lisbon) for financial support.

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