Synthesis, spectroscopic and redox behaviour of copper(II) complexes with quinquedentate thiaaza ligands

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Abstract

Three potentially quinquedentate ligands, 1,11-diamino-6-oxa-3,9-dithiaundecane (LO), 1,6,11-triaza-3,9-dithiaundecane (LN), 1,11-diamino-3,6,9-trithiaundecane (LS) and their quadridentate analogue 1,11-diamine-3,9-dithiaundecane (LC) were prepared. Their copper(II) complexes of composition $CuL(ClO_4)_2$ have been isolated for the quinquedentate ligands, whereas for LC the dimeric complex $Cu_2(LC)_3(ClO_4)_2$ was the main product. ESR spectroscopy showed that the copper(II) complex with LO has rhombic symmetry, whereas the complexes with LN and LS are tetragonal, and the dimeric LC complex exhibits a weak Cu(II)–Cu(II) interaction. The cyclic voltammograms of the complexes with the quinquedentate ligands show a negative potential shift in comparison with the complex with the tetradentate ligand LC. Under CO, the $E_{1/2}$ value for $Cu(LS)(ClO_4)_2$ shifts anodically by 50 mV due to formation of $[Cu(LS)(CO)]^+$.

Introduction

Considerable attention continues to be paid to the study of copper(II) complexes of polydentate ligands with thiaether donors, due to their ability to mimic properties of blue copper protein active sites. Several copper(II) complexes with $CuS_2N_2^{2+}$ and CuS_4^{2+} donor set composition have been prepared and their properties investigated [1–10]. Somewhat less information is available concerning copper(II) complexes with CuS_3^{2+} or CuS_6^{2+} coordination spheres. [11–13], while in turn the coordination chemistry of copper(II) complexes with potentially quinquedentate linear thiaether-containing ligands seems even less well defined [14, 15]. Such complexes possess in their coordination core a formal vacancy which may be occupied in solution by either a solvent or substrate molecule in a biomimetic redox process. Recent work in this connection includes that on copper(II) complexes of quinquedentate pyridyl- and quinolyl-thioethers [14, 15], which exhibit quite positive redox potentials for their Cu^{2+}/Cu^+ couples. In order to help develop our understanding of the influences of pentacoordinate ligands on the properties of copper complexes, we report here the synthesis, electronic and ESR spectra and the redox behaviour of copper(II) complexes with a family of novel quinquedentate thiaaza
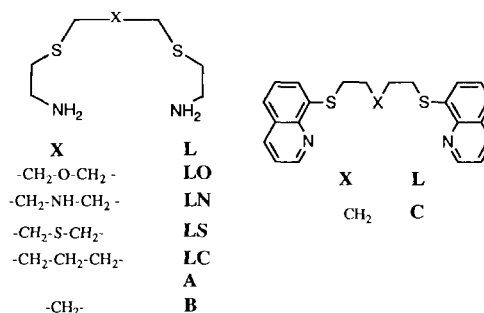
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Fig. 1. The ligands discussed herein.

X	L
-CH₂-O-CH₂-	LO
-CH₂-NH-CH₂-	LN
-CH₂-S-CH₂-	LS
-CH₂-CH₂-CH₂-	LC
	A
-CH₂-	B

X	L
CH₂	C

ligands, including the reference quadridentate N_2S_2 ligand LC (Fig. 1) which bears a non-coordinating group in its central bridge.

Experimental

Copper(II) perchlorate hexahydrate and tetraethyl-ammonium perchlorate (TEAP) were from G. F. Smith Chemical Co., the latter being recrystallized from water and dried *in vacuo* over P_4O_{10} before use. Copper(II) acetate hydrate (Fisher Scientific), 2-amino-ethanethiol hydrochloride, 1,5-dibromopentane, 2-chloroethylamine hydrochloride, bis(2-chloroethyl) ether and bis(2-chloroethyl)amine hydrochloride (all from Aldrich Chemical) were used without further purification.

Mass spectra were obtained on a Finnigan-4500 instrument; the spectral data are truncated below 8% or $m/e = 65$, and only the most intense member of an isotope multiplet is given. EPR spectra were obtained from a Varian E-12 X-band spectrometer calibrated near $g = 2$ with the diphenylpicrylhydrazyl radical, and optical spectra using Perkin-Elmer 320 and 330 spectrophotometers. Rotating disc electrode polarography and cyclic voltammetry were performed under N_2 (boil-off from Air Products liquid N_2) in a three-electrode cell utilizing a PAR-173 potentiostat and a PAR-176 i/E converter, the various platinum wire and disc working electrodes being referred to an Ag^+ (0.01 M, 0.1 M, NEt_4ClO_4, CH_3CN)/Ag electrode. The acetonitrile (MeCN) used as solvent for electrochemistry was distilled off phosphorus(V) oxide under N_2; N,N-dimethylformamide (DMF) was distilled off CaH_2 under vacuum, and carbon monoxide was Air Products grade 2.3. Voltammograms were corrected for iR drop by a modification of Parker's procedure [16]. Elemental microanalyses were performed by Robertson Microanalytical Laboratories (Madison, NJ). EPR spectra were simulated (to second order in the resonance fields) on a Prime-6450 computer using software derived from the work of Lozos et al. [17].

Syntheses

1,11-Diamino-6-oxa-3,9-dithiaundecane
dihydroperchlorate monohydrate (LO·2HClO₄·H₂O)

To sodium (2.3 g, 0.1 mol) dissolved in 250 ml of methanol was added 2-aminoethanethiol hydrochloride (11.36 g, 0.1 mol), and the resulting solution was heated under an N_2 atmosphere for 30 min. Bis(2-chloroethyl) ether (5.85 ml, 0.05 mol) in 50 ml of methanol was then added dropwise (at 40 °C) over 1 h, with stirring. After this addition, the reaction mixture was stirred for 3 h and then rotary evaporated, and the product oil was extracted with diethyl ether from the sodium chloride also formed. After addition of an equivalent volume of ethanol and cooling of the solution with an ice bath, 75% perchloric acid was added dropwise until the formation of white product was complete. The solution was refrigerated overnight and the product was filtered off, washed with diethyl ether and air-dried, to yield 30.5 g (69%) of white powdery product. *Anal.* Found: C, 21.6; H, 5.14; N, 6.01; Cl, 16.0. Calc. for $C_8H_{20}N_2OS_2·2HClO_4·H_2O$: C, 21.7; H, 5.46; N, 6.32; Cl, 16.0%.

1,6,11-Triaaza-3,9-dithiaundecane (LN)

This was prepared in a similar fashion from 2-mercaptoethylamine hydrochloride and bis(2-chloroethyl)amine hydrochloride as the oily free base in 65% yield, and used immediately for complex preparation,

because of its instability toward atmospheric moisture and/or CO_2.

1,11-Diamino-3,6,9-trithiaundecane (LS)

This was similarly isolated in a pure state as the free base from the reaction of bis(2-mercaptoethyl) sulfide with 2-chloroethylamine hydrochloride. After the reaction mixture was evaporated to dryness, the product was extracted with hot benzene, from which it precipitated upon cooling, to give an 80% yield of micaceous white crystals, after air-drying. MS: 241 (MH^+, 92%), 224 (13%), 164 (100%), 134 (18%), 120 (16%), 104 (62%), 87 (31%), 77 (31%). *Anal.* Found: C, 38.0; H, 8.43 N, 11.0. Calc. for $C_8H_{20}N_2S_3·0.5H_2O$: C, 38.5; H, 8.49; N, 11.2%.

1,11-Diamino-3,9-dithiaundecane dihydroperchlorate (LC·2HClO₄)

This was prepared in the same way as the corresponding salt of LO. This product was used for the preparation of the complex without further characterization.

Cu(LO)(ClO₄)₂

To a solution of 0.58 g of LO·2HClO₄·0.5H₂O in 50 ml of ethanol was added a solution of 0.27 g of cupric acetate monohydrate in 25 ml of the same solvent. The solution was heated for 10 min, during which period there formed a deep blue precipitate, which was filtered off and dried over P_4O_{10}. *Anal.* Found: C, 19.9; H, 4.07; N, 5.67; Cl, 14.2. Calc. for $C_8H_{20}Cl_2CuN_2O_{10}S_2$: C, 19.7; H, 4.14; N, 5.75; Cl, 14.6%. Yield 65%.

Cu(LN)(ClO₄)₂

To a solution of copper(II) perchlorate hexahydrate (5.3 g, 14 mmol) in 20 ml of methanol a solution of 2.23 g (14 mmol) of LN in 10 ml of the same solvent was added. The solution was allowed to evaporate slowly to dryness and the resulting deep green product was washed thoroughly with diethyl ether. *Anal.* Found: C, 20.0; H, 4.23; N, 8.10. Calc. for $C_8H_{21}Cl_2CuN_3O_8S_2$: C, 19.8; H, 4.36; N, 8.65%. Yield 40%.

Cu(LS)(ClO₄)₂

This was prepared in manner similar to that for the previous complex, to give a 67% yield of dark violet product. *Anal.* Found: C, 19.7; H, 3.84; N, 5.53. Calc. for $C_8H_{20}Cl_2CuN_2O_8S_3$: C, 19.1; H, 4.01; N, 5.57%. Yield 67%.

Cu₂(LC)₃(ClO₄)₄

This was prepared similarly to Cu(LO)(ClO₄)₂, as a dark blue powder in 60% yield. *Anal.* Found: C, 27.4; H, 5.40; N, 6.72. Calc. for $C_{27}H_{66}Cl_4Cu_2N_6O_{16}S_6$: C, 27.2; H, 5.58; N, 7.05%.

Results and discussion

Syntheses

To prepare copper(II) complexes with these aliphatic ligands, we have developed the synthetic route to this group of compounds, which incorporates different 'fifth' donor atoms (O, N or S) in the linkage between the two constant S,N-termini in the ligand molecule (Scheme 1). In most cases, 2-mercaptoethylamine and the appropriate dihalo derivative were used as starting materials, though for LS, bis(2-mercaptoethyl) sulfide and 2-chloroethylamine were more conveniently utilized. The main difficulty in the preparation of aliphatic thiaaza ligands of this type is in their isolation from the reaction mixture and their further purification. Distillation under reduced pressure has customarily been used in order to separate and purify aliphatic dithiadiamine ligands. Nevertheless our experience has revealed that a significant (even major) amount of the product may be lost during this procedure on account of elimination and/or polymerization reactions which occur at high temperature. To avoid this, we have isolated ligands LO and LC as the diperchlorate salts by the addition of HClO₄ to the reaction mixtures, giving a high yield of the desired products and also permitting prolonged storage of these ligands without any evidence of their decomposition. Ligand LC had been isolated previously as an impure oil [18]. The perchlorate salt approach was not fruitful for LN, which was isolated only as the free base oil and used directly for complex synthesis thereafter. LN was obtained similarly to the method of Black and McLean [19], but by using bis(2-chloro-instead of bis(2-bromoethyl)amine. However, this rather small procedural change increased the yield of product almost threefold from the prior method [19]. The trithia-diaza ligand LS was obtained as lustrous white plates, though previous attempts to isolate this ligand in the pure form have apparently failed [7] and it has been isolated only as the hydrobromide salt [20].

Copper(II) complexes with the ligands LC, LN, LO and LS were obtained by addition of the ligands' perchlorate salts to solutions of equivalent amounts of copper(II) acetate in methanol. The importance of the
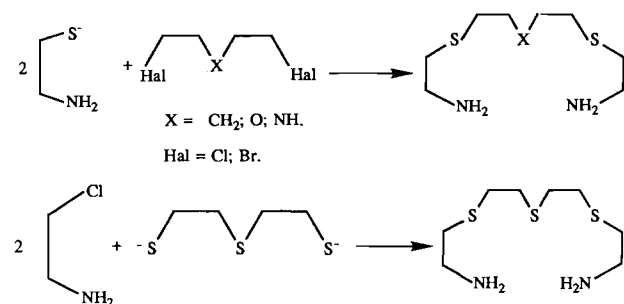
reagents' mixing sequence was established during the synthesis of cupric complexes with the ligands LN and LS in particular. After the addition of copper(II) perchlorate solution in methanol to a solution of either LN or LS in the same solvent, a brown gum precipitated, and only by adding ligand to metal were we able to obtain the desired copper(II) complex. This likely arises because in the former situation, the copper(II) complex CuL^{2+} formed has a high redox potential, and thus oxidizes the remaining ligand molecules which are in excess, to give polymeric products. We have specifically noted such a phenomenon previously, in copper(II) thiolate chelation [21, 22].

We were not successful in isolating a monomeric copper(II) complex with the ligand LC; in all cases a dimeric copper(II) complex (vide infra) of composition $Cu_2(LC)_3(ClO_4)_4$ was isolated as the dominant product. A reasonable possibility for the connection between two monomeric moieties is via axial coordination of the amino donors of the third ligand molecule (Fig. 2, V), because of these N-donors' preferential binding to copper(II) in comparison with the thioether sulfurs. A similar type of copper(II) product was observed [7] with 1,8-diamino-3,6-dithiaoctane (A, Fig. 1), and was assumed to be polymeric. Although its N-methylimi-dazole adduct $CuA(NMeim)^{2+}$ is monomeric and pentacoordinate [23], our attempts to prepare the corresponding $Cu(LC)(NMeim)(ClO_4)_2$ have been unsuccessful. It is also of interest that the copper(II) complex with 1,9-diamino-3,7-dithiaoctane (B, Fig. 1), closely related to LC and A, does exist in the monomeric form [7]. In the case of B as a ligand, dimeric complexes were not produced and this was attributed [7] to the different geometry of the coordination core in com-
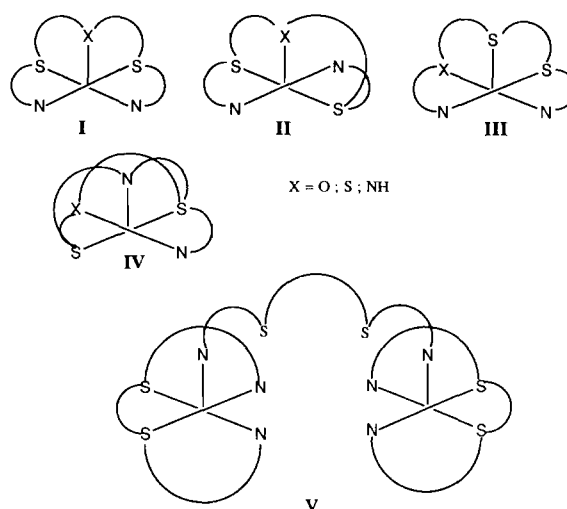

Fig. 2. Various modes for wrapping the NSXSN linear quin-quedentate ligands about a tetragonal-pyramidal copper(II) centre.

X = CH₂; O; NH.

Hal = Cl; Br.

Scheme 1.

parison with $CuA(ClO_4)_2$. It was proposed that in the last complex, the ligand is inadequately flexible to adopt a square-planar arrangement around copper(II), whereas such an environment is accessible in the case of ligand B. Although LC should possess more flexible chelate rings, we attribute its reluctance to form a mononuclear complex to the entropic consequences of the pentamethylene bridge between the two sulfurs; this would lead to an unusual [24] eight-membered chelate ring in a mononuclear compound.

Electronic and ESR spectra

Three absorption bands were observed in the electronic spectra of the copper(II) complexes in acetonitrile solutions. They all possess a transition of high intensity in the near-UV, while a moderately intense band is observed in the red region, and the weakest band is observed in the near-IR. The visible spectra (Table 1) of the copper(II) complexes are generally similar to those of known complexes with amino-thioether ligands. While the absorption band in the higher energy (30 kK) region is attributed to $(\sigma)S \rightarrow Cu(II)$ charge transfer, the assignment for the red band is moot [7, 25–28]. The comparatively low intensity of this transition (~ 160–300 M^{-1} cm^{-1}) would seem to militate against its being mainly $(\pi)S \rightarrow Cu(II)$ charge transfer in nature, whereas on the other hand, its intensity seems rather excessive for a purely d–d transition (despite the appropriate energy), although these often exhibit enhanced intensity with strong donors (such as macrocyclic amines).

It is interesting that the complexes may be ranked identically according to the energies of either the red or the near-UV bands: $CuN_2S_3^{2+} > CuN_2OS_2^{2+} > N_2S_2^{2+} > CuN_3S_2^{2+}$. This may be evidence in favour of a CT contribution for both these bands, because according to Jørgensen's theory of CT bands [29], the LMCT and d–d band should not *both* follow the same energy sequence. One of the more straightforward approaches in this regard is a tetragonal model by Nikles *et al.* [25], which predicts LMCT in the visible region, with the $3b_1$ MO of sulfur as its origin. The reduction of CT intensity for this red band is then attributed to poor overlap between the donor S orbital and the copper(II) ground state $3d_{x^2-y^2}$ orbital [26]. In the series of compounds described here, such a transition can hardly avoid being coincident with a d–d transition, so that an assignment describing the bands as of mixed origin, i.e. $d\pi(Cu)/3b_1(S) \rightarrow d_{x^2-y^2}(Cu)$ seems most appropriate.

Somewhat less predictable behaviour of these compounds was exhibited in their cryogenic ESR spectra in DMF glasses. The copper(II) complex with the reference ligand LC exhibits a spectrum lacking the hyperfine pattern usual for monomeric copper(II) species. Instead, the presence of a strong, broad resonance with weak hyperfine lines closely spaced on its low-field side (Fig. 3) clearly indicates the existence of a dimeric copper(II) species under these conditions [21, 22]. The hyperfine splitting on the low-field side allowed a rough estimate of the Cu(II)–Cu(II) distance (5.2 Å) to be made by using the procedure described by Yokoi and co-workers [30, 31]. The Cu(II)–Cu(II) interaction

TABLE 1. Spectroscopic characteristics of the compounds

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	g_0^a	$10^4 \times |A_0|$ (cm^{-1})	$g_\parallel$	$10^4 \times |A_\parallel|$ (cm^{-1})	$g_\perp$	$10^4 \times |A_\perp|$ (cm^{-1})
$Cu(LO)(ClO_4)_2$	850	66	2.096	59	2.195[b]	108[b]	2.025[c]	93[c]
	575	280					2.125[d]	16[d]
	350	2000			2.159[e]		2.071[e]	
							2.017[e]	
$Cu(LN)(ClO_4)_2$	876	113	2.089	86	2.244	159	~ 2.05	~ 50
	620	232			2.205[f]	182[f]		
	390	3300			2.154[e]		2.04[e]	
$Cu(LS)(ClO_4)_2$	850	91	2.089	75	2.171	188	2.05	19
	560	167						
	342	5300						
$Cu_2(LC)_3(ClO_4)_4$	850	98	2.093	91	2.281[h]	112[h]	2.00	80
	606	307						
	380	2100						

[a]Solution ESR data are from DMF; g_0, A_0 from ambient T spectra; $g_\parallel$, $A_\parallel$, $g_\perp$ at 77 K; $A_\perp$ via $3A_0 = A_\parallel + 2A_\perp$. g_0, $g_\parallel \pm 0.003$; $10^4 A \pm 3$; $g_\perp \pm 0.01$. [b,c,d]g_3 (A_3), g_1 (A_1) and g_2 (A_2) of rhombic system, from simulation using linewidths of 75, 75 and 85 Gauss, respectively. [e]Neat powder at 77 K; the LO complex is rhombic. [f]The minor of two components. [h]$g_\parallel$ and $A_\parallel$ were estimated from the putative 7-line hyperfine pattern using the position of the fourth line and the hyperfine splitting as representing $H_\parallel$ and $a_\parallel/2$, respectively.
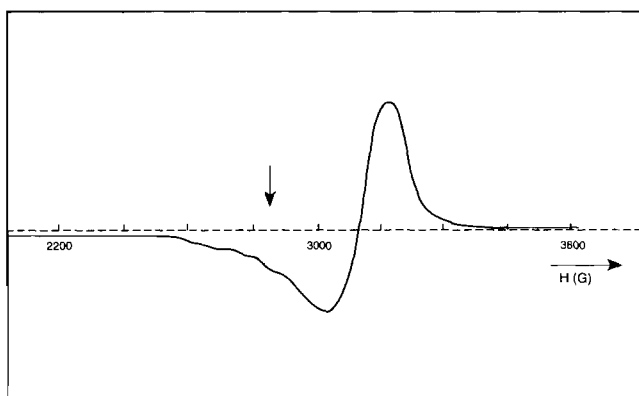
Fig. 3. ESR spectrum of $Cu_2(LC)_3(ClO_4)_2$ in DMF at 77 K. The arrow marks the field about which the estimates of $g_{\parallel}$ and $A_{\parallel}$ are centred.

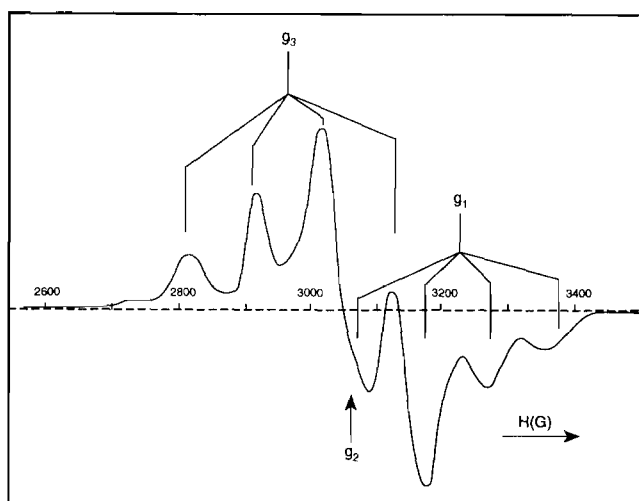Fig. 4. ESR spectrum of $Cu(LO)(ClO_4)_2$ in DMF at 77 K. The resonance near 2720 G (272 mT) is due to a minor Cu(II) component.

is correspondingly weak, and its nature is such that there is an absence of any of the complex superhyperfine triplet structure that is often observed in such dimers [30, 31]. We have no direct structural diagnostics for this dimer, but the possibilities include linkage of a pair of CuN_2S_2 cores by an N,N'-donor LC bridge.

The $g_{\parallel}$ tensor is the ESR characteristic most sensitive to changes in the geometry of the coordination unit, so it is not surprising that substitution of the central methylene unit in LC by the donor heteroatom (S, NH, O) somewhat reduces this parameter for the copper(II) quinquedentate complexes. For $Cu(LO)^{2+}$, the cryogenic DMF solution ESR spectrum (Fig. 4) contains seven lines, analysis of which necessitated simulation, and this revealed marked g anisotropy (Table 1). This rhombic distortion ($R = 0.70$ [32]) signals a low symmetry of the coordination polyhedron, and we favour a distorted structure derived from II (Fig. 2), as it (i) places

the weakest (ether-O) donor axially, and (ii) avoids meridianal spanning of $> 180°$ over the distorted polyhedron by adjacent chelate rings. The rhombicity is present to at least the same extent in the crystalline state ($R \approx 0.6$).

An akin problem of choice among possible isomers exists in the case of the $Cu(LN)^{2+}$ complex, which displays signals from two different copper(II) species in its ESR spectrum, neither of which is due to "free" copper(II) in DMF [14]. Two arrangements of donor atoms are presumed to be present in solution (Fig. 2, I–IV) though for reasons similar to those above, we should expect structure III to be dominant in this case.

Electrochemistry

The redox properties of the copper(II) complexes were examined by cyclic voltammetry in acetonitrile solutions at a platinum wire electrode at scan rates varying from 10 to 200 mV s^{-1}. All the complexes (including $Cu_2(LC)_3(ClO_4)_4$) showed one cathodic peak, associated with the reduction of the CuL^{2+} species to its CuL^+ counterpart, and on scan reversal, one anodic peak attributed to the reoxidation. The peak potential separations (ΔE_p) varied from 80 to 200 mV (Table 2). Formal electrode potentials ($E_{1/2}$) were estimated as the mean of the cathodic and anodic peak potentials. It was interesting to note that the redox behaviour became more Nernstian after saturation of the solutions with carbon monoxide (Table 2), which also in some cases caused a shift of the $E_{1/2}$ value.

The $E_{1/2}$ values obtained for the complexes with the ligands under investigation are rather positive, as is shown by the majority of copper–thioether complexes [1, 4–6, 9, 21, 33, 34]. The redox potentials of the CuL^{2+}/CuL^+ couples (LC, LO) are considerably lower in comparison with those reported for similar complexes with quinolyl- or pyridyl-thioether ligands such as C (Fig. 1) [15]. This observation is consistent with previous observations that the replacement of aliphatic moieties in the ligand structure by aromatic ones induces a

TABLE 2. Redox properties of the complexes[a]

Complex	N$_2$ atmosphere		CO atmosphere	
	$E_{1/2}$ (mV)	ΔE_p[b] (mV)	$E_{1/2}$ (mV)	ΔE_p[b] (mV)
$Cu(LO)(ClO_4)_2$	+451	83	+400	70
$Cu(LN)(ClO_4)_2$	+216	85	+221	80
$Cu(LS)(ClO_4)_2$	+321	83	+376	85
$Cu_2(LC)_3(ClO_4)_4$	+500	140	+505	200

[a]Referred to the non-aqueous Ag^+/Ag electrode (see text), which is at c. +545 mV vs. the SHE. [b]ΔE_p values are from extrapolation to zero scan rate.

positive shift in the redox potentials of the Cu^{2+}/Cu^+ couples [1, 14, 15].

In a crystal field model, coordination of an axial fifth donor atom tends to raise the energy of the Cu $d_{x^2-y^2}$ orbital, and therefore increasing axial donor strength toward Cu(II) should lower the redox potential of the $Cu^{2+/+}$ couple. In extreme cases, the axial donor may cause the d_{z^2} orbital to become the ground state [25], but this situation cannot be said to pertain even in $Cu(LO)^{2+}$, although its structure is on the appropriate distortion pathway [35]. Stability constants [36, 37] indicate aliphatic donor strengths toward copper(II) to be in the order $N > S > O$. With a complementary ordering ($N \approx S > O$) [38] with respect to copper(I) overlaid, the order of the redox potentials of the quinquedentate complexes: $CuN_2OS_2 > CuN_2SS_2 > CuN_2NS_2$ may ultimately be rationalized.

The least electrochemical reversibility was observed in the case of the dimeric complex $Cu_2(LC)_3(ClO_4)_4$, which agrees with the dramatic structural rearrangements expected for its coordination core. The observation of only a single (non-Nernstian) voltammetric process suggests that the two coppers(II) are reduced at essentially the same $E_{1/2}$. The peak width is such, that even if the two $E_{1/2}$s were separated by considerably more than the theoretical 18 mV minimum [39], they would not be resolvable.

Impregnation of the CuL^{2+} complexes' acetonitrile solutions with carbon monoxide increased the reversibility of the electrochemical processes. The most noteworthy change was observed for the complex $Cu(LS)^{2+}$ for which the $E_{1/2}$ value shifted anodically by 55 mV. Conversely, saturation of the $Cu(LO)^{2+}$ solution with CO caused a shift in the opposite (cathodic) direction. We attribute the anodic shift in the first case to formation of the adduct $[Cu(LS)(CO)]^+$ ($K = 9$ atm^{-1}), by analogy with $[(CO)Cu(14\text{-ane-}S_4)]^+$ [1], while the cathodic CO shift in the case of $Cu(LO)^{2+}$ may arise through involvement of the CO in a more complex reaction sequence coupled to the electron-transfer which generates the copper(I).

Acknowledgements

References

1 U. Sakaguchi and A. W. Addison, J. Chem. Soc., Dalton Trans., (1979) 600.

2 T. Yamabe, K. Hori, T. Minato, K. Fukui and Y. Sugiura, Inorg. Chem., 21 (1982) 2040.

3 H. Toftlund, J. Becher, P. H. Olsen and J. Z. Pedersen, Israel J. Chem., 25 (1985) 56.

4 L. Siegfried and T. A. Kaden, Helv. Chim. Acta, 67 (1984) 29.

5 M. J. Martin, J. F. Endicott, L. A. Ochrymowycz and D. B. Rorabacher, Inorg. Chem., 26 (1987) 3012.

6 K. D. Karlin and J. K. Yandell, Inorg. Chem., 23 (1984) 1847.

7 A. R. Amundsen, J. Whelan and B. Bosnich, J. Am. Chem. Soc., 98 (1977) 6730.

8 E. Bouwman, W. L. Driessen and J. Reedijk, Coord. Chem. Rev., 104 (1990) 143.

9 D. E. Nikles, M. J. Powers and F. L. Urbach, Inorg. Chem., 22 (1983) 3210.

10 V. V. Pavlishchuk, K. B. Yatsimirskii, P. E. Strizhak and J. Labuda, Inorg. Chim. Acta, 164 (1989) 65.

11 S. R. Cooper and S. C. Rawle, Struct. Bonding (Berlin), 72 (1990) 2.

12 S. R. Hartman and S. R. Cooper, J. Am. Chem. Soc., 108 (1986) 1202.

13 K. Wieghardt, H.-S. Kuppers and J. Weiss, Inorg. Chem., 24 (1985) 3067.

14 R. P. F. Kanters, R. Yu and A. W. Addison, Inorg. Chim. Acta, 196 (1992) 97.

15 V. V. Pavlishchuk, P. E. Strizhak, K. B. Yatsimirskii and J. Labuda, Inorg. Chim. Acta, 151 (1988) 133.

16 V. D. Parker, in A. J. Bard (ed.), Electroanalytical Chemistry, Vol. 14, Marcel Dekker, New York, 1986, p. 28.

17 G. P. Lozos, B. M. Hoffman and C. G. Fronz, QCPE, 11 (1974) 265.

18 Y. Agnus, R. Louis, J. P. Gisselbrecht and R. Weiss, J. Am. Chem. Soc., 106 (1984) 93.

19 D. St. C. Black and I. A. McLean, Aust. J. Chem., 24 (1971) 1391.

20 M. G. B. Drew, D. A. Rice and K. M. Richards, J. Chem. Soc., Dalton Trans., (1980) 2503.

21 A. W. Addison, T. N. Rao and E. Sinn, Inorg. Chem., 23 (1984) 1957.

22 A. W. Addison, P. J. Burke, K. Henrick, T. N. Rao and E. Sinn, Inorg. Chem., 22 (1983) 3645.

23 J. F. Richardson and N. C. Payne, Inorg. Chem., 17 (1978) 2111.

24 Y. Qu and N. Farrell, Inorg. Chem., 31 (1992) 930.

25 D. E. Nikles, A. B. Anderson and F. L. Urbach, in K. D. Karlin and J. Zubieta (eds.), Copper Coordination Chemistry; Biochemical and Inorganic Perspectives, Adenine, New York, 1983, p. 203.

26 E. I. Solomon, K. W. Penfield and D. E. Wilkox, Struct. Bonding (Berlin), 53 (1983) 2.

27 D. E. Nikles, M. J. Powers and F. L. Urbach, Inorg. Chim. Acta, 55 (1985) LS5.

28 T. E. Jones, D. B. Rorabacher and L. A. Ochrymowycz, J. Am. Chem. Soc., 97 (1975) 7485.

29 C. K. Jørgensen, Prog. Inorg. Chem., 12 (1970) 101.

30 H. Yokoi and M. Chikira, J. Chem. Soc., Dalton Trans., (1975) 2101.

31 H. Yokoi and T. Isobe, Bull. Chem. Soc. Jpn., 46 (1973) 447.

32 A. W. Addison, Inorg. Chim. Acta, 162 (1989) 217.

33 N. J. Ray, L. Hulett, R. Sheahan and B. J. Hathaway, J. Chem. Soc., Dalton Trans., (1981) 1463.

34 M. M. Bernardo, R. R. Schroeder and D. B. Rorabacher, Inorg. Chem., 30 (1991) 1241.

35 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, J. Chem. Soc., Dalton Trans., (1984) 1349.

36 L. G. Sillén and A. E. Martell (eds.), *Stability Constants of Metal–Ion Complexes,* Chemical Society Special Publication No. 17, The Chemical Society, London, 1964.

37 M. A. Augustin, J. K. Yandell, A. W. Addison and K. D. Karlin, *Inorg. Chim. Acta, 55* (1981) L35.

38 M. M. Bernardo, M. J. Heeg, R. R. Schroeder, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem., 31* (1992) 191.

39 J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc., 100* (1978) 4248.