Redox Activity in Binucleating Schiff Base Ligands Derived from 1,4-Dihydrazinophthalazine

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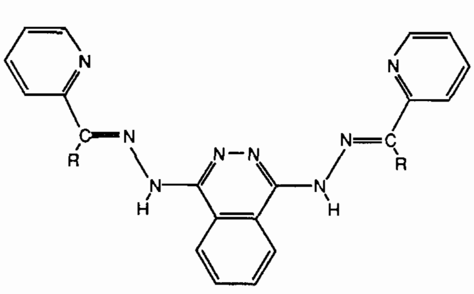
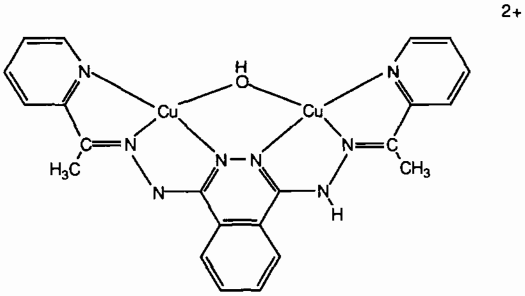
The binucleating ligands **1** and **2** are readily prepared by the condensation of two moles of pyridine-2-carboxaldehyde or 2-acetylpyridine with 1,4-dihydrazinophthalazine (dhph), respectively. The syntheses and crystal structures of the diacid salt of **1** and the corresponding chloro-bridged dinickel(II) complex were originally reported by Sullivan and Palenik [1]. More recently, the preparation, crystal structure and electrochemical characterization of the hydroxy-bridged dicopper(II) complex **3** with the mono-deprotonated ligand **2** have been described by Thompson *et al.* [2]. These authors report that complex **3** in dimethylformamide (DMF) exhibits a quasi-reversible cyclic voltammetry (CV) wave at $E_{1/2} = 0.50$ V versus SCE. In addition, controlled potential electrolysis of complex **3** at 0.65 V yields a 2*e* oxidation and produces a species with an intense visible absorption band at 470 nm ($\epsilon = 19400$ l mol^{-1} cm^{-1}). From these results they conclude that the observed process corresponds to an oxidation of the dicopper(II) complex to a stable binuclear copper(III) species. This conclusion contradicts the extensive work by Margerum *et al.* [3, 4] and others [5, 6] which indicates that hard, anionic donor groups are necessary to produce low potentials for the Cu(III)/Cu(II) couple. The relatively soft environment of the Cu(II) ions present in **3** is unlikely to allow oxidation to the Cu(III) state at the low potential observed. Furthermore, the presence of readily oxidizable functionalities in ligand **2** suggests that a ligand-based redox process may be responsible for the observed electrochemical results. We report here conclusive evidence that the redox behavior of the dicopper(II) complex **3** is indeed localized on the Schiff base ligand and does not involve oxidation to a dicopper(III) state.



1 R = H
2 R = CH$_3$



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In our laboratory, CV studies of complex **3** in dimethyl sulfoxide (DMSO) solution reveal a couple at $E_{1/2} = 0.49$ V (1×10^{-3} M; 0.1 M Et_4NClO_4; glassy carbon (GC) working electrode; SCE reference electrode) very similar to that reported [2] for DMF solutions of **3**. The quasi-reversible nature of this couple is indicated by a significantly weaker cathodic return peak and $\Delta E_p = 92$ mV (at $V = 100$ mV/s). More extensive CV studies also reveal a second, irreversible anodic process at ~1.2 V. The two anodic processes are confirmed by Osteryoung square-wave voltammetry (OSWV) with peak potentials at 0.488 and 1.19 V** (Fig. 1). Controlled potential electrolysis of **3** in DMSO at 0.80 V results in a 2*e* oxidation. The oxidation product, however, exhibits a significantly more intense absorption band ($\lambda_{max} = 473$ nm, $\epsilon = 28500$) in DMSO than that reported [2] previously. Solutions of the oxidized species are found by us to be air sensitive and must be kept under N_2 for long-term stability.

Evidence that the redox activity at 0.5 V for complex **3** occurs on the ligand and does not involve the copper ions is the observation of redox behavior for the free ligand very similar to that of the complex. CV of the free ligand **2** in DMSO (1×10^{-3} M; 0.1 M Et_4NClO_4; GC working electrode; SCE reference electrode) yields a strong anodic wave at 0.64 V which is coupled to a weaker cathodic process at −0.17 V. If the initial scan is extended further in the positive direction, an additional, irreversible anodic

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CV scans for **3 in the negative direction from +0.2 V show evidence for three quasi-reversible couples between 0 and −1.0 V (OSWV peaks at −0.12, −0.46 and −0.78 V). These negative couples presumably include the Cu(II) → Cu(I) reduction processes for complex **3**, but definitive assignments cannot be made at the present time.

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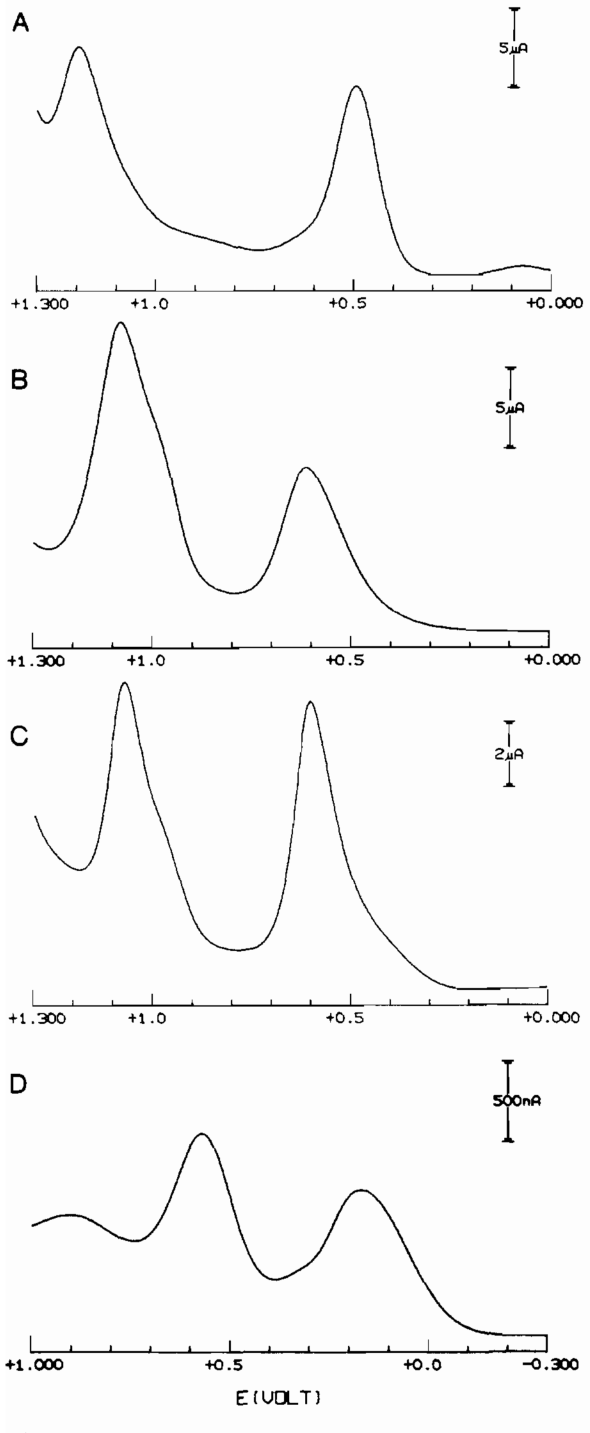

Fig. 1. Osteryoung square-wave voltammograms for (A) [Cu$_2$(L–H)(OH)(H$_2$O)$_2$](ClO$_4$)$_2$·H$_2$O; (B) L; (C) [Zn(L)(H$_2$O)](ClO$_4$)$_2$; (D) 1,4-dihydrazinophthalazine in DMSO (1 × 10^{-3} M), 0.1 M Et$_4$NClO$_4$, under N$_2$. (A)–(C), where L = 2, were taken at a glassy carbon electrode, (D), at a gold electrode.

wave is observed at 1.14 V. OSWV confirms the observed oxidations of the Schiff base ligand with peaks at 0.61 and 1.07 V (Fig. 1). The latter peak exhibits an additional shoulder at 0.98 V which suggests a more complex electrochemical process than is indicated by cyclic voltammetry. OSWV scans for the free ligand in the potential range +0.2 to −1.7 V exhibit no further redox behavior.

Electrolysis (platinum gauze electrode) of ligand **2** in DMSO at 0.83 V shows that the anodic wave at 0.64 V corresponds to a 2*e* oxidation. The absorption spectrum of oxidized **2** in DMSO exhibits peaks at 353 nm (ϵ = 11 200) and 293 nm (ϵ = 15 500) and a pronounced shoulder at *c*. 430 nm. Upon addition of base (KOH in DMSO) to the solution of oxidized **2**, an intense absorption band at 485 nm grows in and achieves a maximum intensity (ϵ = 20 600) at *c*. 5 equiv. of OH$^-$. Presumably the base neutralizes the protons released in the electrolysis and produces a neutral form of the oxidized ligand. The appearance of the 485 nm band in the oxidized free ligand suggests that the corresponding absorption band for the oxidized complex at 473 nm arises from a ligand chromophore and not from a Cu(III) species.

Titration of a solution of electrochemically oxidized ligand **2** with Cu(II) (as Cu(ClO$_4$)$_2$·6H$_2$O in DMSO) produces a species with an absorption band at 474 nm which is similar in band shape and position to the characteristic band exhibited by oxidized **3**. The oxidized ligand, however, only takes up approximately 1 mole of Cu(II) and the 474 nm band only achieves an intensity corresponding to ϵ = 12 200. The addition of base or excess Cu(II) to this solution produces no change in this characteristic band. The electrolysis of **2** and subsequent spectral titrations were carried out under N$_2$ since oxidized **2** decomposes slowly in the presence of air. DMSO solutions of oxidized **2** kept under N$_2$ showed no spectral change over several days.

The electrochemical behavior of a monozinc(II) complex* of **2** provides additional support that the oxidation process in **3** is ligand centered. CV of the monozinc(II) complex in DMSO at a glassy carbon electrode yields irreversible anodic waves at 0.63 V and 1.08 V (OSWV, 0.60 V and 1.06 V (Fig. 1)), very similar to those observed for the free ligand **2**. Controlled potential oxidation of the monozinc(II) complex at a platinum gauze electrode at +900 mV yields an *n* value of 2.27. The oxidized monozinc(II) complex exhibits absorption bands at 349 nm (ϵ = 11 600) and 297 nm (ϵ = 16 900), similar to that of the oxidized free ligand.

The pattern of two oxidation processes observed for the dicopper(II) complex **3**, the free ligand **2** and the monozinc(II) complex of **2** parallels the two oxidations we have observed [7] previously for 1,4-

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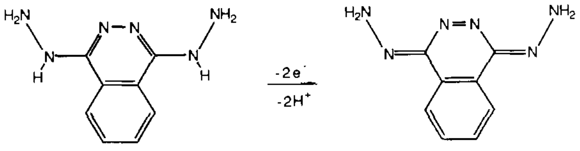
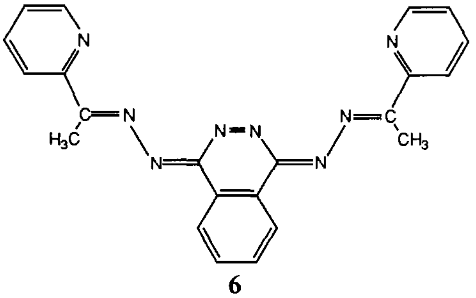
*Addition of 2 moles zinc perchlorate hexahydrate to a 5% aqueous methanol solution of ligand **2** (1 mole) yielded only crystalline Zn(**2**)(H$_2$O)(ClO$_4$)$_2$. *Anal.* Calc. for C$_{22}$H$_{22}$N$_8$O$_9$Cl$_2$Zn: C, 38.93; H, 3.27; N, 16.51; Cl, 10.45. Found: C, 38.80; H, 3.15; N, 16.59; Cl, 10.16%.

dihydrazinophthalazine, the precursor to ligand 2. The first oxidation of dhph in DMSO (Au electrode) occurs at 0.17 V by OSWV (Fig. 1) and controlled potential electrolysis yields $n = 2$. A second oxidation peak occurs at 0.56 V. We attribute the first 2*e* oxidation of dhph to the process **4** → **5** involving the



4 **5**

phthalazine ring and the two proximal nitrogens from the hydrazine substituents, a process analogous to the oxidation of *p*-phenylenediamine to *p*-phenylenediimine. By analogy, the first 2*e* oxidation of the Schiff base ligand 2 and its corresponding complexes is proposed to involve the same redox process and to result in the highly conjugated ligand species **6**. The second anodic process seen in the CV and OSWV at 1.1 V for 2 probably corresponds to a further oxidation of the azine moieties.



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Our studies clearly reveal that the 2*e* oxidation of the dicopper(II) complex of 2 is centered on the binucleating ligand and does not produce a dicopper(III) species. Unfortunately, it is not possible to generate a species identical to the oxidized dicopper(II) complex by the addition of Cu(II) to the oxidized ligand. The addition of Cu(II) to a solution of electrochemically oxidized ligand 2 produces a species with a spectral band at 474 nm with less than half the intensity of the band from the directly oxidized dicopper(II) complex 3. This observation suggests that a significant portion of the oxidized free ligand is not in a form suitable for binuclear coordination of copper(II). Since the two side-arm groups of the proposed oxidation product (**6**) are based on azine functionalities, one possible explanation is that the oxidation of 2 produces a mixture of *syn–anti* isomers, some of which are unfavorable for binuclear coordination. The *syn–anti* interconversion of azines is well known [8, 9] to be quite slow and isomerization to a favorable binucleating form would not occur readily. Further studies are in progress to elucidate the details of the ligand-based redox behavior and the nature of the oxidized ligand.

Acknowledgement

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