

Electrochemical studies on CuN_2O_2 chromophore

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Electrochemistry of $\text{Cu}(\text{nqo})_2$ and $\text{Cu}(\text{nqo})_2\text{.im}$ ($\text{nqo} \equiv$ 1-nitroso-2-naphtholate anion, $\text{im} \equiv$ imidazole) has been studied in acetonitrile by cyclic voltammetry and coulometry at platinum electrodes under N_2 atmosphere. The square planar complex $\text{Cu}(\text{nqo})_2$ shows a quasireversible Cu(I/II) couple at -0.30 V and a quasireversible Cu(II/III) couple at 0.78 V vs saturated calomel electrode. This is the first report of the observation of a Cu(II/III) couple in a CuN_2O_2 chromophore. The potentials of both the couples are lowered in the pentacoordinated species $\text{Cu}(\text{nqo})_2\text{.im}$.

Electrochemistry of copper(II) complexes having a CuN_2O_2 chromophore has not been studied properly. So far, to our knowledge, there are only a few isolated reports on such studies¹⁻³ where only a Cu(I/II) couple has been observed below -0.65 V vs SCE (saturated calomel electrode). However, there is no report of the observation of a Cu(II/III) couple in such complexes. Recently we have undertaken studies on the same. Results of our preliminary investigations are briefly reported here.

Experimental

The complex $\text{Cu}(\text{nqo})_2\text{.H}_2\text{O}$ ($\text{nqo} \equiv$ 1-nitroso-2-naphtholate anion) was prepared by two methods. One of them was a procedure reported earlier by Charalambous *et al.*⁴ and the other method is described below. Copper(II) acetate monohydrate (0.5 g, 2.5 mmol) was dissolved in 100 cm^3 of methanol. To this solution was added a methanol solution (75 cm^3) of 1-nitroso-2-naphthol (0.85 g, 5 mmol) with constant stirring. The resulting deep brown mixture was boiled for 5 min within which a silky precipitate started appearing. Then it was allowed to stand in the air for 1 h. A dark silky compound so obtained was filtered off and washed with methanol (5 cm^3). It was recrystallised from chloroform; yield, 0.70 g (~ 70%). By the procedure developed by us, one can avoid stirring for 8 h as described by Charalambous *et al.*⁴ Instead of heating under reduced pressure⁴, we have

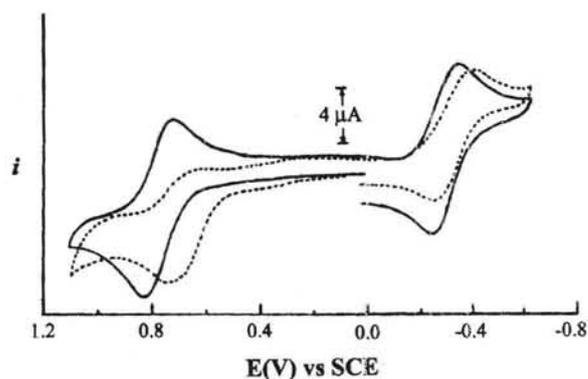


Fig. 1—Cyclic voltammograms of $\text{Cu}(\text{nqo})_2$ [—, $1.11 \text{ mmol dm}^{-3}$] and $\text{Cu}(\text{nqo})_2\text{.im}$ [---, $0.83 \text{ mmol dm}^{-3}$] in acetonitrile (0.1 mol dm^{-3} in tetraethylammonium perchlorate) at 298 K; scan rate in both the cases is 50 mV s^{-1} .

prepared the dehydrated complex $\text{Cu}(\text{nqo})_2$ by heating the mono aquo adduct $\text{Cu}(\text{nqo})_2\text{.H}_2\text{O}$ (2.00 g) at 150°C under atmospheric pressure (for 3 h). The dark brown imidazole adduct $\text{Cu}(\text{nqo})_2\text{.im}$ was obtained by reacting imidazole with the dehydrated compound $\text{Cu}(\text{nqo})_2$ in 1:1 molar proportion following a procedure given by Charalambous *et al.*⁴ and was recrystallised from chloroform; yield, ~ 65%. $\text{Cu}(\text{nqo})_2\text{.im}$ [$\mu_{\text{eff}} = 1.82 \mu_{\text{B}}$ at 296 K; measured by a PAR vibrating sample magnetometer (model 155)], which is new, analysed well (using a Perkin-Elmer 2400II analyzer). The electrochemical measurements were performed using EG&G PARC electrochemical analysis system (model 250/5/0). The potentials reported here are uncorrected for liquid junction potentials.

Results and discussion

The complexes chosen for our purpose are $\text{Cu}(\text{nqo})_2$ and $\text{Cu}(\text{nqo})_2\text{.im}$ where nqo is 1-nitroso-2-naphtholate anion and im imidazole. While $\text{Cu}(\text{nqo})_2$ has been reported earlier by Charalambous *et al.*⁴, the imidazole adduct is new. The electrochemical behaviour of the two complexes has been examined by cyclic voltammetry in acetonitrile under dry N_2 atmosphere at a planar EG&G PARC G0228 platinum milli electrode.

On the negative side of SCE, $\text{Cu}(\text{nqo})_2$ shows a quasireversible reduction at -0.30 V (Fig. 1) and an irreversible one near -1.30 V. The couple at -0.30 V is

a Cu(I/II) couple [Eq. (1)], since the corresponding nickel(II) complex, Ni(nqo)₂, does not show any



electrochemical activity up to -1.0 V vs SCE.⁵ Coulometry performed at -0.55 V vs SCE in acetonitrile at a platinum wire gauge electrode confirmed the one electron stoichiometry [4.80 mg of Cu(nqo)₂ was electrolysed. Experimental coulomb, 1.103; theoretical, 1.140]. The reduced species gives a blue-green colour in acetonitrile which quickly reverts back to the reddish-brown colour of Cu(nqo)₂ upon exposing to air. Among all the copper(II) complexes with a CuN₂O₂ chromophore examined electrochemically,¹⁻³ the potential of the Cu(I/II) couple is raised significantly in Cu(nqo)₂. For a brief discussion on the factors responsible for the value of the potential of a Cu(I/II) couple in a CuN₂O₂ chromophore, the reader is referred to ref 6. In our case, the significant rise in the Cu(I/II) potential seems to be due to the possible π-acidity of the ligated organic moiety. That ligand π-acidity can raise the potential of a Cu(I/II) couple to a great extent is now very well established in the case of CuN₄ chromophore^{7,8}. The E_{1/2} of the Cu(I/II) couple is lowered slightly (by ~ 40 mV; Fig. 1) in Cu(nqo)₂.im presumably because the reduction is attended by the dissociation of imidazole. Such effects are known⁹.

On the positive side of the SCE, Cu(nqo)₂ displays a quasireversible oxidation at 0.78 V (Fig. 1). We believe that this oxidation is metal based[†] and does not originate from the coordinated ligand (Eq. 2). The reasons for this are as follows. (a) The corresponding Ni(II)



complex Ni(nqo)₂ shows a metal based one-electron oxidation (confirmed by EPR)⁵ around 0.5 V vs SCE and examples are known where it has been found¹⁰ that in a similar ligand environment; Ni(II/III) couple appears at a slightly lower potential than the Cu(II/III) couple; (b) The potential of couple (2) is lowered

considerably (by ~ 100 mV; Fig. 1) in the imidazole adduct; (c) There is a marked change in the cyclic voltammetric reversibility of the couple (2) in going from Cu(nqo)₂ to Cu(nqo)₂.im (Fig. 1); the reversibility of a ligand based oxidation should be independent of the pentacoordination. Most possibly, the pentacoordination in Cu(nqo)₂.im renders the generated Cu(III) species unstable leading to a considerable decrease in the cathodic peak current on reversal of the potential scan (Fig. 1). While examples of pentacoordinate species for d⁸ systems are not rare,^{11,12} surprisingly for Cu(III), to date, there is only one example.¹³ Incidentally, both the complexes Ni(nqo)₂ and Cu(nqo)₂ and the free ligand nqoH (H: the dissociable proton) show irreversible oxidations beyond 1.2 V vs SCE. To our knowledge, a II/III couple for copper with the N₂O₂ coordination sphere has not been demonstrated earlier. It is mentioned here that at present in oxidations by copper enzymes, Cu(III) species are increasingly being proposed as intermediates.¹⁴ Hence, the relevance and importance of our present work are apparent.

From our results, it seems that an o-quinone oxime (a function present in our ligand nqoH) has the ability to stabilise the higher oxidation states as well as lower ones of a transition metal. This property of an o-quinone oxime has not been explored fully.¹⁵ We believe the results obtained here will be very helpful in understanding the various interesting redox reactions undergone by the copper(II) complexes of o-quinone oximes¹⁶⁻¹⁸. Further studies encompassing the isolation and characterisations of the various copper(III) species are ongoing.

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†Attempts to do coulometry at 1.0 V vs SCE gave rise to continuous slow accumulation of coulombs. But comparison of current heights and peak-to-peak separations of the cyclic voltammograms with those of the Cu(I/II) couple at the same scan rates (Fig. 1) leads to the fact that couple (2) involves only one electron.

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