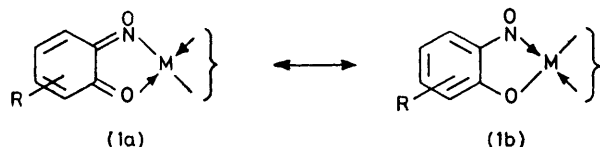


Interaction of Copper Complexes Derived from 1,2-Quinone Mono-oximes (2-Nitroso-phenols) with Amines

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The reactions of 1,2-diaminoethane with the copper(II) complexes of 4-methyl- and 5-methoxy-1,2-benzoquinone 2-oxime involve deoxygenation of the ligand and reduction of the metal, and lead to 2-amino-4-methylphenol and 2-amino-7-methoxy-3*H*-phenoxazin-3-one, respectively. Reactions of the copper(II) complex of 1,2-naphthoquinone 2-oxime with 1,2-diaminoethane and with aniline occur in an analogous fashion, and lead to dibenzo[*b,i*]phenazine-5,12-diol and 2-amino-1,4-naphthoquinone 4-*N*-phenylimine, respectively. The copper(II) complex of 1,2-naphthoquinone 1-oxime reacts with aniline to give bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)bis(aniline)copper(II) and with 1,2-diaminoethane to give a complex mixture of products. The reactions are rationalized in terms of nitrene intermediacy.

METAL complexes derived from 1,2-benzoquinone mono-oximes (2-nitroso-phenols) [(1a) \leftrightarrow (1b)] are readily obtainable, and are potentially useful for the preparation of a wide variety of compounds. Previously we reported that various nickel(II), zinc(II), copper(II), and iron(II)



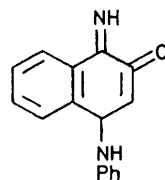
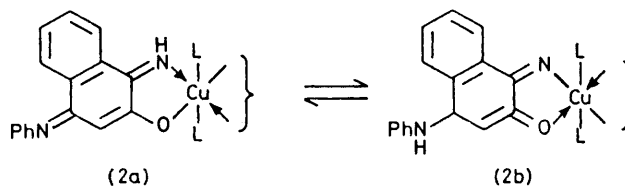
complexes derived from 1,2-benzoquinone mono-oximes are deoxygenated by triphenylphosphine to give dihydroxyphenazines or iminophosphorane complexes.¹ Other investigations have shown that the interaction of copper(II) 1,2-benzoquinone mono-oxime complexes with dimethyl acetylenedicarboxylate provides a convenient route to 1,4-benzoxazines.² As a continuation of our studies on the chemistry of complexes derived from 1,2-benzoquinone mono-oximes³ and of their synthetic potential we are at present investigating their interaction with amines under a variety of conditions. Such interaction could occur in a variety of ways. These include adduct formation and/or attack of the amine on the CO group, the NO group, or the aromatic ring. Here we report reactions of several copper(II) complexes with aniline and with 1,2-diaminoethane, carried out in conditions that encourage the azeotropic removal of water.

RESULTS

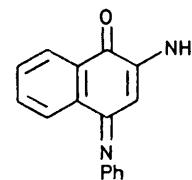
Bis(1,2-naphthoquinone 1-oximato)copper(II) reacted with aniline to give bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)bis(aniline)copper(II) (2a; L = PhNH₂) which can also be formulated as the tautomer (2b; L = PhNH₂). This compound was insoluble in common solvents but it could be crystallised from pyridine as the dipyridine adduct (2; L = pyridine). Pyrolysis of the dipyridine adduct yielded bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)copper(II) (2; delete L). Reaction of the dipyridine adduct with

hydrochloric acid gave 4-phenylamino-1,2-naphthoquinone, presumably *via* hydrolysis of the initially liberated protonated ligand (3).

Bis(1,2-naphthoquinone 2-oximato)copper(II) reacted with aniline to give a diamagnetic copper-containing solid and several soluble products. These included 2-amino-1,4-naphthoquinone 4-*N*-phenylimine (4) and a small amount of 2-phenylazo-1-naphthol.



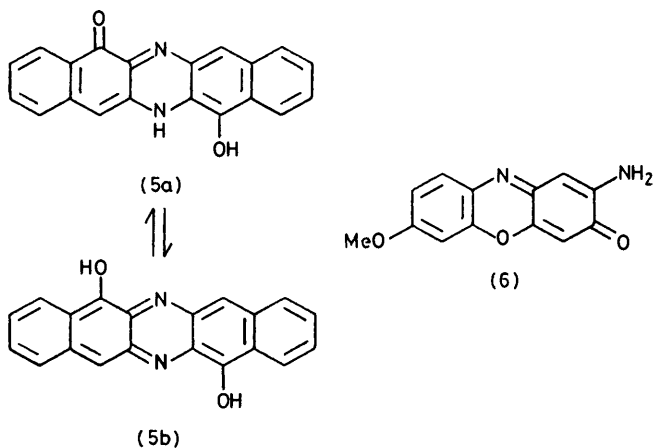
(3)



(4)

Reaction of bis(1,2-naphthoquinone 2-oximato)copper(II) with 1,2-diaminoethane also gave no copper(II) complex, but afforded in high yield a substance to which the phenazine structure (5a) rather than the diol structure (5b) was assigned. Its i.r. spectrum shows two well defined peaks in the NH/OH stretching region. The lower frequency peak at 3 310 cm⁻¹ seems too sharp to be attributed to an OH absorption lowered by hydrogen bonding. It is better explained as due to the NH group of the oxo-form (5a). The oxo-form is also indicated by the intense violet colour of both the solid and its solutions [λ_{max} (CHCl₃) 556 nm; *cf.* dibenzo[*b,i*]phenazine, λ_{max} 435 nm⁴]. Previously it has been proposed that a violet colouration is associated with hydroxyphenazines which exist in the oxo-form whereas the enolic compounds are yellow.^{5,6}

Reaction of bis(1,2-naphthoquinone 1-oximato)-copper(II) with 1,2-diaminoethane gave an ill-defined diamagnetic copper containing solid and a very complex mixture of soluble products which included 5-hydroxydibenzo[*b,i*]phenazin-12(6*H*)-one and 6-hydroxydibenz[*b,k*]acridin-8-one.

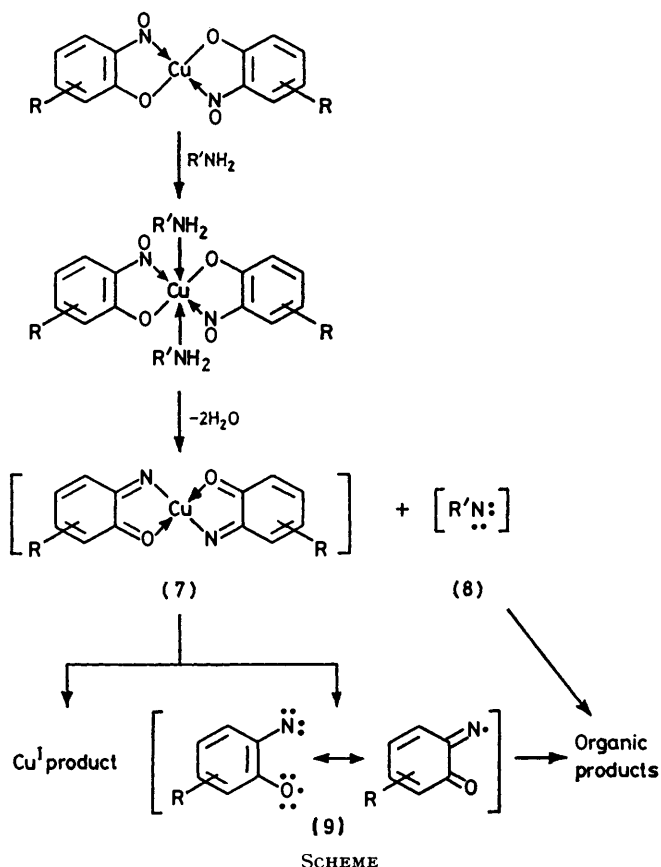


The interaction of 1,2-diaminoethane with bis(4-methyl-1,2-benzoquinone 2-oximato)- and bis(5-methoxy-1,2-benzoquinone 2-oximato)-copper(II) was studied to see whether phenazine formation would occur. Each reaction gave a near quantitative yield of copper in the form of insoluble diamagnetic products, indicative of redox reactions leading to copper(I) species. No indication of phenazine formation was observed, however. From the reaction involving bis(4-methyl-1,2-benzoquinone 2-oximato)copper(II) the main product was 2-amino-4-methylphenol. The reaction involving bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) gave 2-amino-7-methoxy-3*H*-phenoxazin-3-one (6). As several possible structures were in accord with the spectroscopic properties of this latter substance its characterisation was confirmed by an X-ray crystallographic study.⁷ It reacted with acetic anhydride to yield a monoacetyl derivative.

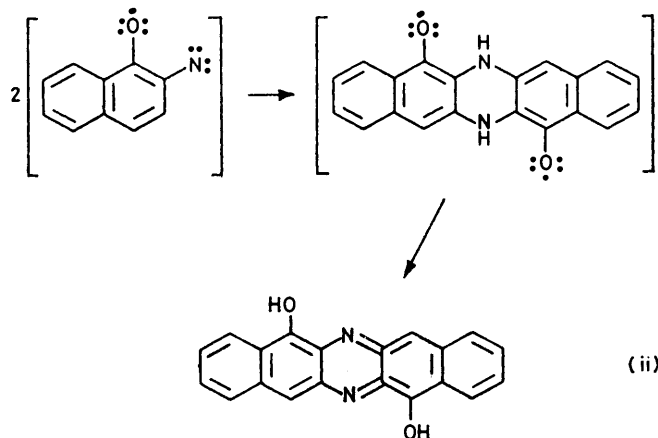
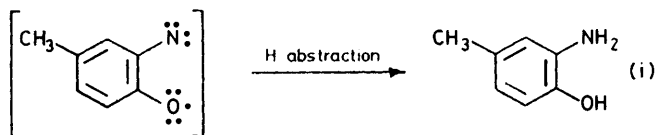
DISCUSSION

Although the products from the above reactions vary considerably in character, their formation can be rationalised in a similar manner in terms of deoxygenation of the NO group of the ligand and the intermediacy of nitrene species.

The reactions involving 1,2-diaminoethane can be rationalised as indicated in the Scheme. It is assumed that the reaction of the copper(II) 1,2-quinone mono-oxime complex with the amine leads to a quinone imine complex (7) and the nitrene (8). The former undergoes an internal redox reaction to give a copper(I) product and the deoxygenated ligand radical (9). Subsequent dimerisation of this radical, or most probably interaction with its precursors and/or hydrogen abstraction by the radical, leads to the organic products isolated, *e.g.* reactions (i) and (ii).



The suggested formation of the copper(I) product is in accord with the diamagnetic character of the ill-defined solids obtained from the reactions. The proposed redox reaction parallels the behaviour of other copper(II) ^{1,8}



and manganese(III) complexes.⁹ The formation in the reactions studied of amines and the phenazone (5a) is in keeping with the intermediacy of nitrenes. Thus nitrene intermediates were invoked to account for amine and phenazine formation in the pyrolyses of 4-methoxyphenyl azide¹⁰ and both 1- and 2-naphthyl azide.¹¹

The reactions involving aniline and the copper(II) naphthoquinone oxime complexes can be rationalised in a similar fashion. In these cases, however, the deoxygenation is accompanied by attack on the 4-position of the naphthoquinone oxime ligand. The attack involves the amine or most probably the nitrene. The formation of a copper(II) naphthoquinone imine complex as the main product of the reaction of the 1-oxime complex with aniline provides direct evidence for deoxygenation. Its isolation most probably reflects its insolubility, which suppresses its subsequent reaction.

EXPERIMENTAL

¹H N.m.r. spectra were measured using Perkin-Elmer R12B and Bruker HFX 90 FT spectrometers. I.r. spectra were recorded with a Pye-Unicam SP 2000 spectrophotometer. The mass spectra were obtained using A.E.I. MS9 and MS50 spectrometers. Magnetic moments were determined at room temperature using a Gouy balance equipped with a permanent magnet of field strength 3 600 Oe. The adsorbent used in the chromatography columns was Merck Kieselgel 60 (70–230 mesh), and t.l.c. was carried out using precoated Merck Kieselgel 60 F₂₅₄ plates.

General Procedure for the Reactions of the Metal Complexes with Amines.—The amine was slowly added to a stirred mixture of the complex in toluene, which was then heated under reflux in nitrogen, using a Dean–Stark water separator, for the time given. After stirring at room temperature for a further 2 h the mixture was worked up.

Bis(1,2-naphthoquinone 1-oximato)copper(II) with aniline. The copper(II) complex (4.10 g, 10.1 mmol) and aniline (5.60 g, 60.2 mmol) in toluene (100 cm³) were heated for 48 h. The mixture was filtered and the residue washed with toluene and light petroleum (b.p. 40–60 °C) to give brown *bis(1,4-hydro-1-imino-4-phenylimino-2-naphtholato)bis(aniline)copper(II)* (5.10 g, 68%) (Found: C, 70.6; H, 4.8; Cu, 8.4; N, 10.9. C₄₄H₃₆CuN₆O₂ requires C, 71.0; H, 4.9; Cu, 8.5; N, 11.3%).

Bis(1,2-naphthoquinone 2-oximato)copper(II) with aniline. The copper(II) complex (4.10 g, 10.1 mmol) and aniline (5.60 g, 60.2 mmol) in toluene (130 cm³) were heated for 20 h. Filtration gave an intractable black solid (1.50 g) (Found: Cu, 22.1%; 52% recovery) (diamagnetic) with an ill-defined i.r. spectrum. Evaporation of the filtrate under reduced pressure gave a black oil (7.40 g), which was chromatographed on silica gel (toluene). This gave a solid which crystallised from light petroleum (b.p. 80–100 °C) as dark orange-red needles of 2-phenylazo-1-naphthol (0.054 g, 2%), m.p. 136.5–137 °C (lit.¹² 137 °C); *m/z* 248 (*M*⁺). Also obtained from the chromatography column was a solid, which crystallised from light petroleum (b.p. 100–120 °C) as orange-red needles of 2-amino-1,4-naphthoquinone 4-*N*-phenylimine (0.68 g, 27%), m.p. 120–120.5 °C (lit.¹³ 123 °C) (Found: C, 77.3; H, 4.8; N, 11.2. Calc. for C₁₆H₁₂N₂O: C, 77.4; H, 4.9; N, 11.3%); *v*_{max.} (KBr) 1 663 (C=O), 3 390, and 3 500 cm⁻¹ (NH₂);

δ (CD₂Cl₂) 4.70 (2 H, br, s, NH₂, exchanged with D₂O), 6.10 (1 H, s, naphthoquinonoid H-3), and 6.77–8.55 (9 H, m, aromatic); *m/z* 248 (*M*⁺).

Bis(1,2-naphthoquinone 1-oximato)copper(II) and diaminoethane. The copper(II) complex (4.10 g, 10 mmol) and 1,2-diaminoethane (3.60 g, 60 mmol) in toluene (100 cm³) were heated for 16 h. The mixture was filtered and the residue washed with hot toluene to give an intractable solid (2.0 g) (Found: Cu, 25%; 79% recovery) (diamagnetic) with an ill-defined i.r. spectrum. The combined filtrate and washings on concentration afforded a tarry residue (3.7 g), which was chromatographed (elution with toluene followed by gradual change to ethyl acetate). All fractions were multi-component. Selected fractions were rechromatographed (preparative plate) to give 5-hydroxydibenzo[*b,i*]phenazin-12(6*H*)-one [*m/z* 313 (*M*⁺); identical (t.l.c.) with an authentic sample¹⁴] and 6-hydroxydibenzo[*b,h*]acridin-8-one [*m/z* 297 (*M*⁺); identical (t.l.c.) with an authentic sample¹⁵].

Bis(1,2-naphthoquinone 2-oximato)copper(II) with diaminoethane. The copper(II) complex (2.00 g, 4.9 mmol) and 1,2-diaminoethane (1.80 g, 30 mmol) in toluene (75 cm³) were heated for 24 h. Filtration afforded a dark violet residue, which was extracted (Soxhlet) with toluene. The extract was filtered and the residue crystallised from toluene as fine dark violet needles of *dibenzo[b,i]phenazine-5,12-diol* (0.70 g, 91%), m.p. 280–284 °C (decomp.) (Found: C, 77.2; H, 4.0; N, 9.1. C₂₀H₁₂N₂O₂ requires C, 76.9; H, 3.9; N, 9.0%); $\lambda_{max.}$ (CHCl₃) 560 nm (ϵ 805 m² mol⁻¹); *v*_{max.} (hexachlorobutadiene) 1 643, 3 310, and 3 400 cm⁻¹; δ [(CD₃)SO] 6.07 (2 H, br, s, exchanged with D₂O) and 7.56–8.96 (10 H, m); *m/z* 312 (*M*⁺). The residue in the Soxhlet thimble was an intractable black solid (0.89 g) (Found: Cu, 33.7%; 97% recovery) (diamagnetic) with an ill-defined i.r. spectrum.

Bis(4-methyl-1,2-benzoquinone 2-oximato)copper(II) with diaminoethane. The copper(II) complex (1.70 g, 5.1 mmol) and 1,2-diaminoethane (1.80 g, 30 mmol) in toluene (60 cm³) were heated for 20 h. Filtration gave an intractable black solid (1.60 g) (Found: Cu, 17.5%; 96% recovery) (diamagnetic) with an ill-defined i.r. spectrum. Evaporation under reduced pressure gave a tarry brown solid which was chromatographed on silica gel (elution with toluene). This gave pale yellow plates of 2-amino-4-methylphenol (0.44 g, 71%), m.p. 133–134 °C (lit.¹⁶ 135 °C) (Found: C, 68.1; H, 7.6; N, 11.6. Calc. for C₇H₉NO: C, 68.2; H, 7.4; N, 11.4%); *m/z* 123 (*M*⁺).

Bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) with diaminoethane. The copper(II) complex (1.84 g, 5 mmol) and 1,2-diaminoethane (1.80 g, 30 mmol) in toluene (60 cm³) were heated for 24 h. Filtration afforded a black residue which was extracted (Soxhlet) with toluene. The extract was filtered and the residue crystallised from pyridine as dark red needles of 2-amino-7-methoxy-3*H*-phenoxazin-3-one (0.29 g, 48%), m.p. 269–270 °C (decomp.) (Found: C, 64.1; H, 4.0; N, 11.5. C₁₃H₁₀N₂O₃ requires C, 64.4; H, 4.2; N, 11.6%); *v*_{max.} (Nujol) 1 645, 3 300 (OH), and 3 450 cm⁻¹ (NH₂); δ [(CD₃)₂SO] 4.13 (3 H, s, CH₃O) and 6.30–7.70 (7 H, m, the broad signal at δ 6.35 disappeared in D₂O); *m/z* 242 (*M*⁺). The residue in the Soxhlet thimble was an intractable black solid (1.82 g) (Found: Cu, 18.1%; 99% recovery) (diamagnetic) with an ill-defined i.r. spectrum.

Reaction between Bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)bis(aniline)copper(II) and Pyridine.—The copper

complex (5.10 g) was added with stirring to pyridine (150 cm³), and the mixture was heated under reflux for 1 h. On cooling the solution afforded red-brown fibrous needles of *bis*(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)*bis*-(pyridine)copper(II) (4.10 g, 84%) (Found: C, 70.0; H, 4.5; Cu, 8.7; N, 11.3. C₄₂H₃₂CuN₆O₂ requires C, 70.4; H, 4.5; Cu, 8.9; N, 11.7%).

Pyrolysis of Bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)*bis*(pyridine)copper(II).—The *bis*(pyridine)copper(II) complex (0.8444 g) was heated at 160 °C and 0.3 mmHg for 1 h. The residue was brown *bis*(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)copper(II) (0.6764 g) (Found: C, 68.7; H, 4.2; Cu, 11.5; N, 10.0. C₃₂H₂₂CuN₄O₂ requires C, 68.9; H, 4.0; Cu, 11.4; N, 10.0%). The distillate, collected in a trap cooled in a solid carbon dioxide-ethanol bath, was shown to be pyridine (i.r.).

Reaction between Bis(1,4-dihydro-1-imino-4-phenylimino-2-naphtholato)*bis*(pyridine)copper(II) and Hydrochloric Acid.—The *bis*(pyridine)copper(II) complex (0.15 g) was shaken with a mixture of aqueous hydrochloric acid (15%; 50 cm³) and chloroform (50 cm³) for 10 min. After neutralisation (NaHCO₃), the chloroform and aqueous layers were separated. The aqueous layer was then further extracted with chloroform. The combined chloroform extracts were dried (MgSO₄), filtered, and evaporated to 10 cm³ volume under reduced pressure. The residue obtained after filtration was washed with light petroleum (b.p. 40–60 °C) to give red 4-phenylamino-1,2-naphthoquinone (0.08 g, 76%), m.p. 258–261 °C (decomp.) (lit.,¹⁷ 254–256 °C) (Found: C, 76.9; H, 4.6; N, 5.4. Calc. for C₁₆H₁₁NO₂: C, 77.1; H, 4.5; N, 5.6%); *m/z* 249 (*M*⁺).

Reaction between Dibenzo[b,i]*phenazine-5,12-diol and Acetic Anhydride*.—Acetic anhydride (1.5 cm³) and dibenzo[b,i]-phenazine-5,12-diol (0.20 g) in pyridine (15 cm³) were heated under reflux for 5 h. After cooling, the mixture was filtered and the residue crystallised from pyridine as red fibrous needles of 5-acetoxydibenzo[b,i]phenazin-12-ol (0.04 g,

17%), m.p. 329–332 °C (decomp.) (Found: C, 74.8; H, 4.2; N, 7.6. C₂₂H₁₄N₂O₃ requires C, 74.6; H, 4.0; N, 7.9%); λ_{max} (CHCl₃) 514 nm (ε 1 389 m² mol⁻¹); *m/z* 354 (*M*⁺). Water (30 cm³) was slowly added to the stirred filtrate and the mixture was filtered. The residue crystallised from light petroleum (b.p. 100–120 °C) as glittering red-green crystals of 5,12-diacetoxydibenzo[b,i]phenazine (0.08 g, 32%), m.p. 255–256 °C (Found: C, 72.5; H, 4.1; N, 7.0. C₂₄H₁₆N₂O₄ requires C, 72.7; H, 4.1; N, 7.1%); λ_{max} (CHCl₃) 489 nm (ε 1 614 m² mol⁻¹).

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