Studies on the Oxygenolysis of 9,10-Phenanthrenequinone by CuXL (X = Cl or Br; L = Pyridine, 2,2'-Bipyridine, and 1,10-Phenanthroline) Complexes

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The oxygenolysis of 9,10-phenanthrenequinone by CuXL [X = Cl or Br; L = pyridine (py), 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen)] to well defined mixed-ligand diphenato-complexes $[Cu_2X_2(C_{14}H_8O_4)L_n]$ (n = 4, L = py; n = 2, L = bipy or phen) is reported. In the reaction of the quinone with preformed copper–dioxygen complexes under argon half of the copper was converted into the diphenatocopper complexes and the other half was isolated as CuXL or $CuXL_3$ complexes. Possible modes for the oxygenolysis are discussed.

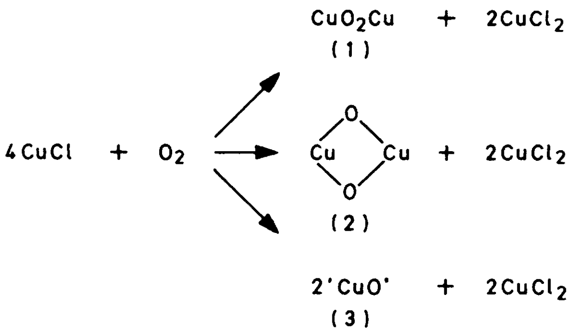
Oxidative cleavage of aromatic rings is a widespread reaction in nature. Typically, the enzyme pyrocatechase [1] catalyses the oxidative cleavage of the aromatic ring of catechol,[2] probably *via o*-benzoquinone,[3] to give *cis,cis*-muconic acid (hexa-2,4-dienedioic acid) with the incorporation of one dioxygen molecule into the substrate.[4] Pyrocatechase and other related oxygenases are known to require either copper [5] or iron ions.[6] In studies on biological oxidation, the activation of dioxygen is of great interest. Several metal-containing non-enzyme model reactions for pyrocatechase have been tested. The oxidation of 3,5-di-t-butylcatechol catalyzed by several metal salts resulted in the corresponding quinone.[7] The oxidation of catechol with oxygen in the presence of copper(I) chloride and a small amount of methanol gave the monomethyl ester of *cis,cis*-muconic acid.[8] It was subsequently shown that methoxocopper(II) chloride and probably binuclear copper(II) complexes with methoxo- and hydroxo-bridging ligands are the oxidants.[9] With the binuclear methoxocopper(II) chloride–pyridine complex, 3,5-di-t-butylcatechol was converted into the corresponding quinone and then to dimethyl *cis,cis*-muconate.[10] 3,5-Di-t-butylcatecholatocopper(II) complexes give, after oxygenation and acidic hydrolysis, 3,5-di-t-butyl-5-(carboxymethyl)-2-furanone as the ring-cleavage product.[11]

Our aim was to investigate the direct oxygenation of 9,10-phenanthrenequinone catalysed by copper(I) halide complexes with pyridine (py), 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen) in the absence of water and methanol, enabling the isolation of the primary oxidation products, and to obtain further insight into the structure of the dioxygen–copper complexes in solution and the mode of oxygenolysis.[12]

Results and Discussion

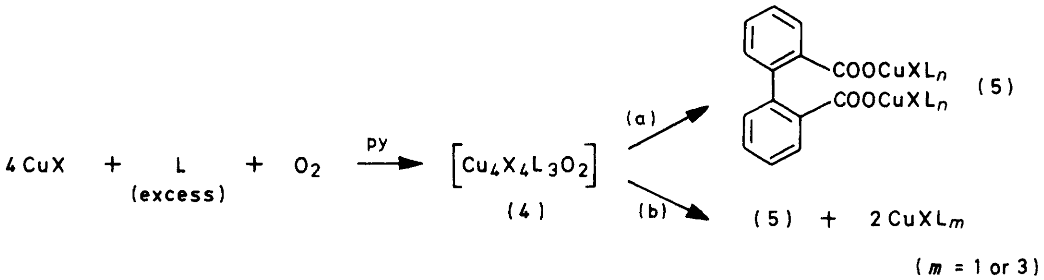
In the reaction of copper(I) chloride with dioxygen in pyridine and other solvents in the presence of pyridine the formation of $[CuCl_2(py)_2]$ and oxygen-containing products (1),[13] (2),[9] and (3) [14] (Scheme 1) has been proposed. We found previously [15] that in the reaction of $[(CuClL)_2]$ (L = pyridine, methyl- and dimethyl-pyridines) with dioxygen, analytically pure copper–dioxygen complexes of type $[Cu_4Cl_4L_3O_2]$ (4) could be isolated. Similar primary oxidation products have been assumed in solution with the ligands *N,N*-dimethylacetamide, dimethyl sulphoxide, and *N*-methyl-2-pyrrolidinone on the basis of cryoscopic measurements.[16]

In the oxygenations of 9,10-phenanthrenequinone with copper(I) chloride or bromide and amine (py, bipy, or phen) in pyridine as solvent, according to Scheme 2(a) the chloro- and bromo-diphenatocopper(II) complexes (5a)—(5f) precipitated in nearly quantitative yields as blue or green microcrystalline analytically pure compounds (see Table 1). The fact that halogen-containing diphenatocopper(II) complexes were formed raised some doubts as to the correctness of the formulations in Scheme 1 since the complexes (1)—(3) do not contain halogen and are certainly the species which attack the quinone. When copper(I) halide is oxygenated in the presence of a ligand in pyridine until oxygen-uptake ceases (stoicheiometry 4 : 1) and the dioxygen is swept out by bubbling argon through the solution, or when solid $[Cu_4X_4L_3O_2]$ complexes are dissolved in pyridine under argon, we obtain a solution which reacts with 9,10-phenanthrenequinone (stoicheiometry 1 : 1 for O_2 absorbed by the quinone) under argon to give the copper(II) diphenate complexes (5a)—(5f) which precipitate from the reaction mixture as blue or green fine crystals. Their yields are nearly quantitative (calculated from the dioxygen content of the O_2-containing complexes) and they always contain exactly half the original amount of the copper employed in the reaction mixture. After removal of the copper(II) diphenate complexes from the filtrate, yellow to red copper(I) halide complexes of types CuXL (X = Cl or Br; L = py, bipy, or phen) or $CuXL_3$ (L = py, X = Cl) were obtained in relatively high yields. These results suggest that (at least formally) in the oxygenation of copper(I) halides in the presence of pyridine type ligands only 2 mol of Cu^I are oxidized to Cu^{II} and the remaining 2 mol do not donate electrons to the co-ordinated oxygen but have some as yet obscure co-ordinative stabilizing role in the complex formed. However, Scheme 2 can be regarded as representing the first metal-assisted oxygenolysis of an *o*-quinone to well defined carboxylato-complexes.



Scheme 1. Pyridine ligands are omitted

The carboxylatocopper(II) complexes (5a)—(5f) show strong $\nu_{asym}(CO_2)$ bands between 1 595 and 1 626 cm^{-1} and $\nu_{sym}(CO_2)$ frequencies in the range of 1 347—1 374 cm^{-1} suggesting unidentate co-ordination of each carboxylate group of the ligand (Table 2).



	X	L	n
(5a)	Cl	py	2
(5b)	Cl	bipy	1
(5c)	Cl	phen	1
(5d)	Br	py	2
(5e)	Br	bipy	1
(5f)	Br	phen	1

Scheme **2.** (a) 9,10-Phenanthrenequinone, O_2; (b) same quinone, argon

Table 1. Characterization of diphenatocopper(II) complexes

Complex	Colour	Yield (%)	M.p. (°C) (decomp.)	Analytical data * (%) C	H	N	Halogen	Cu
(5a) $[Cu_2Cl_2(py)_4(C_{14}H_8O_4)]$	Blue	97	235—237	53.7 (54.1)	3.7 (3.7)	7.7 (7.4)	9.3 (9.4)	16.5 (16.8)
(5b) $[Cu_2Cl_2(bipy)_2(C_{14}H_8O_4)]$	Blue	98	250—255	54.9 (54.4)	3.4 (3.2)	7.5 (7.5)	9.2 (9.5)	16.4 (16.9)
(5c) $[Cu_2Cl_2(phen)_2(C_{14}H_8O_4)]$	Blue	95	165—170	58.6 (57.2)	4.2 (3.0)	7.0 (7.0)	8.5 (8.9)	15.5 (15.9)
(5d) $[Cu_2Br_2(py)_4(C_{14}H_8O_4)]$	Green	97	175—180	49.8 (48.4)	3.4 (3.4)	6.7 (6.6)	18.6 (18.9)	15.4 (15.1)
(5e) $[Cu_2Br_2(bipy)_2(C_{14}H_8O_4)]$	Green	94	182—185	47.7 (48.6)	2.8 (2.9)	6.8 (6.7)	19.2 (19.0)	15.5 (15.1)
(5f) $[Cu_2Br_2(phen)_2(C_{14}H_8O_4)]$	Green	96	187—190	52.1 (51.4)	3.0 (2.7)	6.4 (6.3)	18.3 (18.0)	14.0 (14.3)

* Theoretical values in parentheses.

Table 2. Infrared and diffuse reflectance spectral data for diphenatocopper(II) complexes

Complex	I.r.[a] ν_{asym} (CO_2)	I.r.[a] ν_{sym} (CO_2)	Reflectance[b]		
(5a)	1 626	1 352	32.33	27.25w	14.00
(5b)	1 604	1 358	32.10	17.20w	13.80
(5c)	1 620	1 347	31.70	17.20w	13.73
(5d)	1 620	1 347	32.30	—	15.00
(5e)	1 595	1 348	32.10	16.60 (sh)	13.00
(5f)	1 622	1 374	31.75	17.50 (sh)	13.50

[a] In cm^{-1}, Nujol mulls. [b] In 10^3 cm^{-1}; MgO as the reference. w = Weak, sh = shoulder.

The solid-state e.s.r. spectra of the carboxylatocopper(II) complexes (5), at room temperature and 120 K, were found to be identical and isotropic, except for (5a) and (5e), giving one broad signal at g *ca.* 2.10—2.13 (Table 3). Similar spectral properties have been found for some binuclear carboxylatocopper(II) complexes,[17] and were believed to arise from magnetic interactions between the copper(II) entities.[18] The shape and the g values of the spectra of solutions of complexes (5) in methanol and pyridine were identical to those found for the solid state suggesting intramolecular interactions. The e.s.r. spectra of complexes (5a) and (5e) indicate a rhombic type geometry; however, despite the fact that three g values were obtained, interaction cannot be excluded because $G < 4$ [19] (see Table 3).

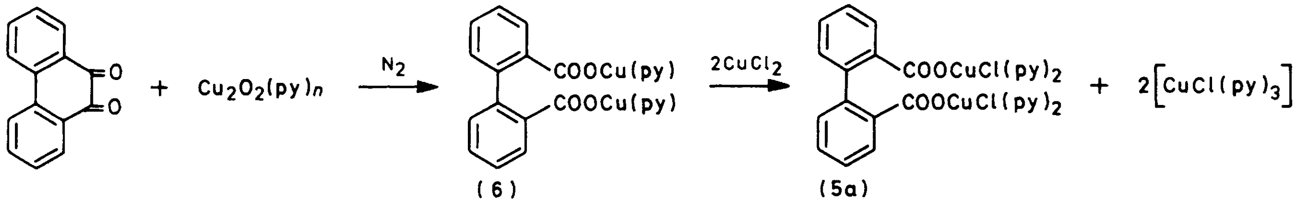
Comparing the reflectance spectra of complexes (5) (Table 2) with those of known structures,[18] it is reasonable to assume that the copper in the present complexes has a distorted rhombic octahedral symmetry [(5a) is elongated rhombic octahedral since the lowest $g > 2.04$; (5e) is compressed rhombic octahedral since the lowest $g < 2.03$]. A more definite structural assignment cannot be made at this stage. Recently, it was pointed out [20] that the connection between the stereochemistry of copper(II) and its solid-state electronic spectrum is not always straightforward. In this case the assumption can be made that the binuclear units are highly associated *via* halogen bridges (which explains also the insolubility of the complexes) giving rise to six-co-ordination.

In the reflectance spectra of complexes (5a)—(5f) below 20 000 cm^{-1} there are two absorptions at 13 000—14 000 cm^{-1} and of lesser intensity at 16 600—17 500 cm^{-1} [(5e) and (5f) showed only shoulders]. Similar spectra have been obtained by Hathaway and co-workers [19] for some diethylenetriamine-copper(II) complexes, which were considered to be consistent

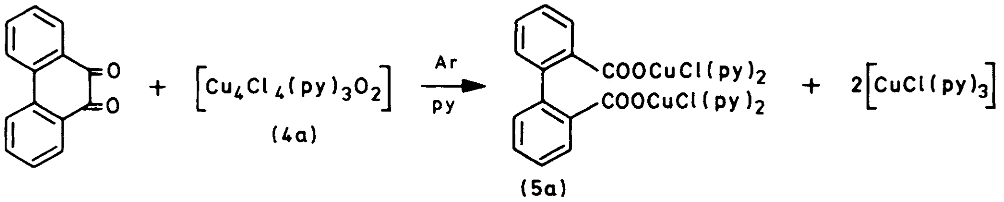
Table 3. E.s.r. parameters at room temperature and magnetic moments at different temperatures

Complex	$g_\perp$	$g_\parallel$	$g_{av.}$	G [a]	$\mu_{eff.}$/B.M. [b]	θ/K
(5a)	$g_y = 2.084$ $g_x = 2.061$	2.217	2.128	2.97	1.65	4
(5b)			2.136		1.78	18
(5c)			2.100		1.60	23
(5d)			2.106		1.71	9
(5e)	$g_x = 2.025$ $g_y = 2.145$	2.221	2.132	1.71	1.69	9
(5f)			2.096		1.68	15

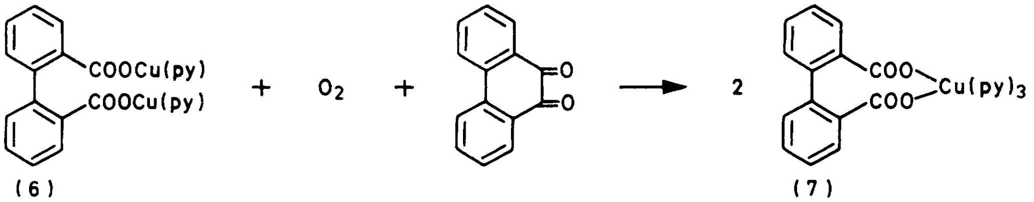
[a] $G = (g_\parallel - 2)/(g_\perp - 2)$, $g_\perp = \frac{1}{2}(g_x + g_y)$, $g_\parallel = g_z$. [b] 1 B.M. = 9.274×10^{-24} A m^2; $\mu_{eff.}$ per Cu atom in the range of 90—290 K.



Scheme 3.



Scheme 4.



Scheme 5.

with a rhombic octahedral or square-pyramidal stereochemistry.

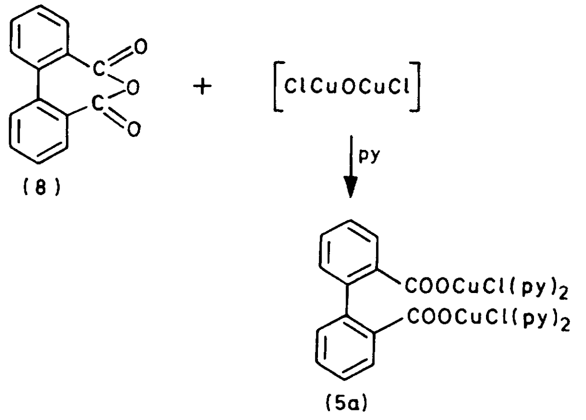
The magnetic susceptibilities obey the Curie–Weiss law in the temperature range of 90—300 K, with positive Weiss constants indicating very weak ferromagnetic interaction of the copper centres (Table 3). The magnetic moments do show little temperature dependence. This seems to be somewhat contradictory to the low $\mu_{eff.}$ values measured for complexes (5a)—(5f), suggesting rather an antiferromagnetic interaction.

In order to clarify a few details of the oxidative ring cleavage of *o*-quinones with the copper(I) halide–amine–O_2 system we investigated some reactions which could be assumed to proceed during oxygenolysis. Since in Scheme 2 the diphenatocopper complexes (5a)—(5f) formed contain halogen, two paths can be postulated.

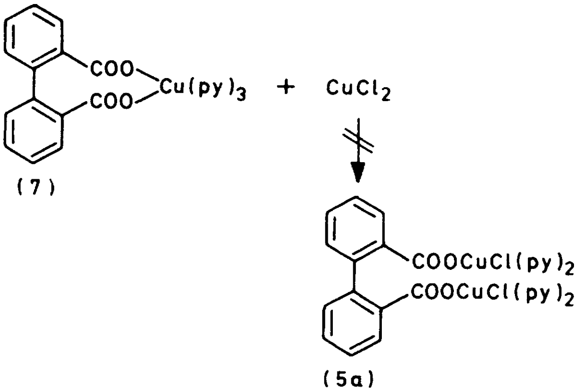
(*i*) The assumptions of Scheme 1 are correct and one of the copper–oxygen complexes of types (1)—(3) attacks the *o*-quinone giving the copper(I) diphenate complex (6), which is oxidized by the $CuCl_2$ to complex (5a) and CuCl according to Scheme 3. Since we were not able to prepare complexes (1)—(3) free of [$CuCl_2(py)_2$], the first step of Scheme 3 cannot be experimentally proved. However, complex (6) can easily be prepared [21] and it reacts rapidly with $CuCl_2$ in pyridine to give (5a) and [$CuCl(py)_3$] or [{$CuCl(py)$}$_2$].

(*ii*) It is, however, also possible, that complexes (1)—(3) and [$CuCl_2(py)_2$] equilibrate with the copper–dioxygen complex [$Cu_4Cl_4(py)_3O_2$] (4a) in pyridine solution and the latter attacks the 9,10-phenanthrenequinone yielding (5a) and [$CuCl(py)_3$] as shown in Scheme 4.

The reason, we believe, that pathway (*ii*) is the true course of the oxygenolysis of the *o*-quinone is based on the following evidence. According to Scheme 3 the intermediacy of (6) is apparent. However, this complex reacts very rapidly with dioxygen in the presence of 9,10-phenanthrenequinone to give the copper(II) complex (7) [21] as shown in Scheme 5. Since complex (7) in pyridine does not show scrambling of the ligands with $CuCl_2$ according to Scheme 6 and therefore no (5a) is formed in this way, one should observe (7) as a reaction



Scheme 6.



Scheme 7.

product, if (6) is the intermediate of oxygenolysis. In the oxygenation of 9,10-phenanthrenequinone with CuXL (X = Cl or Br; L = py, bipy, or phen) in pyridine the yields of complex (5) are, however, nearly quantitative and no formation of (7) could be observed. On the other hand, complex (6) reacts with dioxygen in the presence of $CuCl_2$ and 9,10-phenanthrenequinone in pyridine to give a mixture of (5a) and (7) (ratio 2 : 3), which seems to us to be evidence for the absence of (6) as an intermediate in the oxygenation reaction (Scheme 2).

From these experiments we conclude that the *o*-quinone reacts with a copper–dioxygen complex of type (4). The Cu–X bond seems to remain intact during the reaction and the $[CuX_2(py)_2]$ complexes formed in solution by the equilibria proposed earlier do not play the role of oxidant towards the diphenatocopper(I) complexes.

Very little information could be obtained about the mechanism of the ring-cleavage reaction of 9,10-phenanthrenequinone (Scheme 4). We know, that copper(I) chloride and bromide form stable, solid $[\{CuX(py)\}_2]$·quinone adducts with 9,10-phenanthrenequinone.[22] However, the initial rate of dioxygen uptake of copper(I) chloride in pyridine is not influenced by the presence of 9,10-phenanthrenequinone, which suggests that the quinone is not co-ordinated to the copper in pyridine solution and primarily the copper–dioxygen complex (4) is formed, attacking the quinone in a subsequent step. It was shown recently that in the reaction of 3,5-di-t-butyl-*o*-benzoquinone with H_2O_2, 2,4-di-t-butylmuconic acid anhydride is the key intermediate, which could be detected even in 50% methanol solution, and gave after solvolysis the corresponding substituted muconic acid and lactones.[23] All efforts to detect the expected diphenic acid anhydride (8) as the primary ring-cleavage product in the reaction of 9,10-phenanthrenequinone with $[Cu_4Cl_4(py)_3O_2]$ in pyridine have failed, however. On the other hand, diphenic acid anhydride reacts very rapidly with [ClCuOCuCl] {prepared *in situ* in nearly 100% yield from $[Cu_4Cl_6(py)_4O]$ by adding pyridine and filtering off $[CuCl_2(py)_2]$} to the diphenatocopper(II) complex (5a) as shown in Scheme 7.

Furthermore diphenic acid anhydride also reacts with $[Cu_4Cl_4(py)_3O_2]$ to give (5a) in 90% yield, but no formation of anhydride (8) could be detected in the reaction of 9,10-phenanthrenequinone with [ClCuOCuCl] in pyridine. These results suggest that the copper species responsible for the oxidation of the *o*-quinone are not of the type proposed for the oxygenated product of tetrakis[(*N*,*N*-diethylnicotinamide)-halogenocopper(I)] having two equivalent Cu–O–Cu structural components.[24] The mechanism of these oxygenation reactions, we believe, is different from those radical pathways found for protic substrates such as phenols, thiols, amines, *etc.*[25] It does not seem reasonable to assume hydroxo-bridged copper(II) as proposed by Rogič and Demmin [9] and Schouten *et al.*[26]

The results do suggest the possibility of an analogy between the mechanisms of ring-cleavage of 3,5-di-t-butyl-*o*-benzoquinone by H_2O_2 and that of 9,10-phenanthrenequinone by the copper–dioxygen complex (4), but no direct evidence has been found for the formation of diphenic acid anhydride as an intermediate until now. Further work is in progress to obtain suitable single crystals of complexes (5)—(7) for *X*-ray crystallography and to elucidate the possible mechanism of the oxygenation.

Experimental

All reactions were carried out under an atmosphere of pure, dry argon with reagent grade solvents. Infrared spectra were recorded on a Specord 75 IR (Carl Zeiss, Jena) spectrometer, e.s.r. spectra on a JEOL JES-FE3X spectrometer, and reflectance spectra on a PMQ II (Carl Zeiss) spectrophotometer. The magnetic susceptibilities were determined on a Bruker B-E 10B8 magnetic susceptibility system. M.p.s were measured on an Electrothermal Apparatus.

Oxygenolysis of 9,10-*Phenanthrenequinone by* CuX (X = Cl *or* Br) *and* O_2 (*General Procedure*).—A solution of copper(I) chloride or bromide (10 mmol) in absolute pyridine in the absence or presence of 2,2′-bipyridine or 1,10-phenanthroline was saturated with dioxygen (O_2 uptake *ca.* 60 cm^3) and 9,10-phenanthrenequinone (1.04 g, 5 mmol) was added and stirred under dioxygen. After *ca.* 5 h, 60 cm^3 more of dioxygen had been consumed with concomitant precipitation of a blue or green microcrystalline material. The latter was filtered off, washed with pyridine and then with diethyl ether, and dried *in vacuo* to give the diphenatocopper(II) complex (5). Yields and analytical data are collected in Table 1.

Oxygenation of 9,10-*Phenanthrenequinone with Copper–Dioxygen Complexes formed* in situ *under Argon*.— (*a*) *With copper*(I) *chloride and pyridine*. Copper(I) chloride (1.98 g, 20 mmol) was dissolved in purified pyridine (40 cm^3) and saturated with dioxygen. After O_2 uptake had ceased (*ca.* 120 cm^3) the solution was purged with argon and under argon 9,10-phenanthrenequinone (1.04 g, 5 mmol) was added. After standing overnight, blue dichloro(diphenato)tetrakis-(pyridine)dicopper(II) (5a) deposited. It was filtered off, washed with pyridine and ether, and dried *in vacuo*. Yield 3.8 g, 5.0 mmol. Adding ether (100 cm^3) to the filtrate gave bright yellow crystals, which were filtered off, washed with ether, and dried *in vacuo* to give chlorotris(pyridine)copper(I), yield 3.4 g (10.1 mmol) (Found: C, 52.9; H, 4.3; Cl, 10.9; Cu, 17.5; N, 11.5. $C_{15}H_{15}ClCuN_3$ requires C, 53.6; H, 4.5; Cl, 10.5; Cu, 18.9; N, 12.5%).

(*b*) *With copper*(I) *bromide and pyridine*. In an analogous manner, copper(I) bromide (2.87 g, 20 mmol), 9,10-phenanthrenequinone (1.04 g, 5 mmol), and pyridine (30 cm^3) gave dibromo(diphenato)tetrakis(pyridine)dicopper(II) (5d), yield 5.6 g (4.9 mmol). From the filtrate bromo(pyridine)copper(I) was obtained, yield 2.3 g (10.3 mmol) (Found: C, 27.2; H, 2.1; Br, 35.6; Cu, 27.2; N, 6.0. C_5H_5BrCuN requires C, 27.0; H, 2.3; Br, 35.9; Cu, 28.6; N, 6.3%).

(*c*) *With copper*(I) *chloride and* 2,2′-*bipyridine*. Copper(I) chloride (0.99 g, 10 mmol) and 2,2′-bipyridine (1.56 g, 10 mmol) dissolved in acetonitrile (40 cm^3) were treated with dioxygen until O_2 uptake ceased (*ca.* 60 cm^3). Then the solution was swept with an argon stream, under argon 9,10-phenanthrenequinone (0.50 g, 2.5 mmol) was added, and the mixture left overnight. The blue compound which deposited was filtered off, washed with ether (20 cm^3), and dried *in vacuo* to give bis(2,2′-bipyridine)dichloro(diphenato)dicopper(II) (5b), yield 1.5 g (2.0 mmol). The solvent of the filtrate was pumped off and the dry residue treated with ether (15 cm^3). After filtration the dark brown solid was dried *in vacuo* to give (2,2′-bipyridine)chlorocopper(I), yield 0.40 g (1.6 mmol) (Found: C, 47.5; H, 3.5; Cl, 13.8; Cu, 24.6; N, 11.1. $C_{10}H_8ClCuN$ requires C, 47.1; H, 3.2; Cl, 13.9; Cu, 24.9; N, 11.0%).

(*d*) *With copper*(I) *bromide and* 2,2′-*bipyridine*. In an analogous manner starting from copper(I) bromide (1.44 g, 10 mmol) and 9,10-phenanthrenequinone (0.50 g, 2.5 mmol) the products were bis(2,2′-bipyridine)dibromo(diphenato)dicopper(II) (5e), yield 2.0 g (2.4 mmol), and (2,2′-bipyridine)bromocopper(I), yield 0.40 g (1.33 mmol) (Found: C, 40.0; H, 2.5; Br, 26.1; Cu, 20.8; N, 9.2. $C_{10}H_8BrCuN_2$ requires C, 40.1; H, 2.7; Br, 26.7; Cu, 21.2; N, 9.4%).

(*e*) *With* [CuCl(phen)]. Chloro(1,10-phenanthroline)copper(I) (2.8 g, 10 mmol) dissolved in acetonitrile (40 cm^3) was treated with dioxygen until uptake ceased (*ca.* 60 cm^3). Then argon was bubbled through the solution, 9,10-phenanthrenequinone (0.50 g, 2.5 mmol) added, and the mixture left overnight under argon. The blue compound which precipitated was filtered off, washed with acetonitrile (20 cm^3), and dried *in vacuo* to give dichloro(diphenato)bis(1,10-phenanthroline)dicopper(II) (5c), yield 2.0 g (2.6 mmol). To the filtrate, ether (100 cm^3) was added precipitating a further small amount of the diphenato-complex, which was filtered off and the filtrate evaporated *in vacuo*. The greenish yellow residue was taken up in dichloromethane (30 cm^3) and by adding ether (100 cm^3) to the clear solution a grey solid separated, which was filtered off, washed with ether (10 cm^3), and dried *in vacuo* to give chloro(1,10-phenanthroline)copper(I), yield 0.30 g (1.1 mmol) (Found: C, 51.2; H, 3.3; Cl, 12.9; Cu, 22.4; N, 9.3. $C_{12}H_8ClCuN_2$ requires C, 51.6; H, 2.9; Cl, 12.7; Cu, 22.8; N, 10.0%).

(*f*) *With* [CuBr(phen)]. In an analogous manner, bromo(1,10-phenanthroline)copper(I) (2.24 g, 10 mmol) and 9,10-phenanthrenequinone (0.50 g, 2.5 mmol) in acetonitrile (70 cm^3) gave dibromo(diphenato)bis(1,10-phenanthroline)dicopper(II) (5f), yield 2.3 g (2.6 mmol), and bromo(1,10-phenanthroline)copper(I), yield 0.3 g (0.93 mmol) (Found: C, 44.6; H, 2.8; Br, 24.8; Cu, 19.0; N, 8.6. $C_{12}H_8BrCuN_2$ requires C, 44.5; H, 2.5; Br, 24.7; Cu, 19.6; N, 8.7%).

Preparation of Diphenatotris(*pyridine*)*copper*(II) (7).—Diphenic acid (2.42 g, 10 mmol) was dissolved in ethanol (25 cm^3) and copper(II) acetate monohydrate (2.0 g, 10 mmol) dissolved in ethanol (75 cm^3) was added with stirring. The blue compound which precipitated was filtered off and dried *in vacuo*. This was then treated with pyridine (50 cm^3) for 3 h, and the product was filtered off, washed with ether, and dried *in vacuo*. Yield 4.6 g (85%) (Found: C, 64.6; H, 4.3; Cu, 11.4; N, 7.9. $C_{29}H_{23}CuN_3O_4$ requires C, 64.4; H, 4.3; Cu, 11.8; N, 7.8%).

Preparation of Diphenatobis(*pyridine*)*dicopper*(I) (6).—Diphenatotris(pyridine)copper(II) (5.42 g, 10 mmol) and copper powder (0.76 g, 12 mmol) were suspended in pyridine (40 cm^3) and refluxed under argon for 1 h. The colour of the solution became orange. The copper metal was filtered off and the clear filtrate concentrated *in vacuo* to an almost dry residue, which was treated with ether (50 cm^3) for 2 h. The orange compound formed was filtered off, washed with ether, and dried *in vacuo* to an orange, very air-sensitive powder, yield 5.7 g (100%) (Found: C, 54.0; H, 3.8; Cu, 23.9; N, 5.4. $C_{34}H_{18}Cu_2N_2O_4$ requires C, 54.9; H, 3.5; Cu, 24.2; N, 5.3%); $\nu(CO_2)$ at 1 620 and 1 343 cm^{-1}.

Preparation of Complex (7) *from* (6) *and* 9,10-*Phenanthrenequinone with Dioxygen*.—To a solution of complex (6) (0.53 g, 1 mmol) in pyridine (20 mol) was added 9,10-phenanthrenequinone (0.25 g, 1.2 mmol). The mixture was stirred under dioxygen (O_2 uptake *ca.* 25 cm^3) for 2 h. Blue microcrystals deposited, which were filtered off, washed with ether, and dried *in vacuo* to give complex (7), yield 1.0 g (95%), $\nu(CO_2)$ at 1 621 and 1 348 cm^{-1}.

Preparation of Complex (5a) *from* (6) *with Copper*(II) *Chloride*.—To a solution of complex (6) (1.05 g, 2 mmol) in pyridine (30 cm^3) was added anhydrous copper(II) chloride (0.54 g, 4 mmol). The mixture was stirred under argon for 2 h. The blue, microcrystalline material which formed was filtered off, washed with pyridine and ether, and dried *in vacuo* and was found to be complex (5a), yield 1.5 g (*ca.* 100%). Ether (100 cm^3) was added to the filtrate. The yellow crystals which formed were filtered off, washed with ether, and dried *in vacuo* to give chlorotris(pyridine)copper(I), yield 1.3 g (97%).

Oxygenation of 9,10-*Phenanthrenequinone in the Presence of Complex* (6) *and Copper*(II) *Chloride*.—To a solution of $CuCl_2$ (0.08 g, 0.6 mmol) in pyridine (50 cm^3) saturated with dioxygen, 9,10-phenanthrenequinone (0.06 g, 0.3 mmol) and complex (6) 0.16 g, 0.2 mmol) were added. The mixture was stirred under dioxygen for 5 h. Blue, microcrystalline material separated which was filtered off, washed with ether, and dried *in vacuo* to give a mixture of complexes (7) (59%) and (5a) (41%) calculated from the elemental analysis (Found: C, 60.2; H, 4.3; Cl, 3.9; Cu, 12.3; N, 7.4%); $\nu(CO_2)$ at 1 620 br and 1 350 br cm^{-1}.

Reaction of Diphenic Acid Anhydride (8) *with* [ClCuOCuCl].—To a solution of hexachloro-μ_4-oxotetrakis(pyridine)tetracopper(II) [27] (0.70 g, 0.88 mmol) in dichloromethane (10 cm^3) was added pyridine (20 cm^3) with stirring. One third of the solvent was pumped off and the precipitate dichlorobis(pyridine)copper(II) filtered off. Yield 0.52 g (*ca.* 100%) (Found: C, 40.3; H, 3.5; Cl, 24.1; Cu, 21.2; N, 9.8. $C_{10}H_{10}Cl_2CuN_2$ requires C, 41.0; H, 3.4; Cl, 24.2; Cu, 21.7; N, 9.6%). To the filtrate, diphenic acid anhydride (0.20 g, 0.90 mmol) was added and stirred for 3 h. The blue compound which deposited was filtered off, washed with ether, and dried *in vacuo* to give complex (5a), yield 0.64 g (97%).

Reaction of Diphenic Acid Anhydride (8) *with* [$Cu_4Cl_4(py)_3O_2$] (4a).—Diphenic acid anhydride (1.12 g, 5 mmol) and [$Cu_4Cl_4(py)_3O_2$] (1.66 g, 2.5 mmol) were dissolved in pyridine

(30 cm^3) and left overnight under argon. Blue crystals deposited, which were filtered off, washed with pyridine and ether, and dried *in vacuo* to give complex (5a), yield 3.35 g (90%).

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