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The Formation of Dinuclear Catecholato Copper(II) Complexes from Strongly Oxidizing *o*-Quinones and Copper(I) Halides

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Abstract

Strongly oxidizing *o*-quinones, such as tetrachloro-1,2-benzoquinone and tetrabromo-1,2-benzoquinone with copper(I) chloride and bromide in pyridine give a new type of dinuclear catecholato copper(II) complexes of the formulae [(catecholate)$Cu_2X_2(py)_4$] (2) (X = Cl, Br). 3,5-Di-t-butyl-6-nitro-1,2-benzoquinone with copper(I) chloride results in a similar dinuclear copper(II) complex, but that with copper(I) bromide gives a mixture of (2) and [(catecholate)-$Cu(py)_2$] (3).

Introduction

Interactions of *o*-quinones with a number of low-valent transition metal complexes have been described. These reactions lead to quinone, semiquinone, and catecholato complexes depending on the nature of the metal complexes and the oxidizing potential of the quinones [1]. Surprisingly, very little data on such reactions with copper complexes are available from the literature. It has been only stated that d^{10} complexes, such as [$AuClPPh_3$] and [$AgClPPh_3$], do not give adducts with terachloro-1,2-benzoquinone [2]. We have shown that some *o*-quinones form $[CuXpy]_2 \cdot o$-quinone complexes with copper(I) chloride and bromide in good yields [3]. Using ligand exchange reactions $[Cu(C_6H_4O_2)_2]^{2-}$ and $[Cu(C_6Cl_4O_2)_2]^{2-}$ complexes with bulky tetraalkylammonium ions [4] and [(cat)CuL] (L = ethylenediamine, 2,2′-bipyridine, and 1,10-phenanthroline) type compounds have been prepared and characterized [5]. A fair number of semiquinone (sq) complexes [L_n-Cu(sq)] with various phosphorus ligands were investigated by ESR methods [6]. Semiquinone complexes such as [$Cu(sq)_2$], [$Cu_2(sq)_2(MeO)_2$], and [Cu(sq)(t-$BuNC)_2$] were isolated and those of [Cu(sq)L] with ligands such as phosphines, phosphites, arsines, isocyanide and carbon monoxide investigated in solution by ESR [7]. Herein, we report on the facile, thermal addition of strongly oxidizing *o*-quinones to [CuX-$(py)_3$] (X = Cl, Br) complexes in pyridine.

Experimental

Copper(I) chloride (Reanal), copper(I) bromide (EGA-Chemie), tetrachloro-1,2-benzoquinone (Fluka AG), tetrabromo-1,2-benzoquinone (EGA-Chemie) were used as supplied. 3,5-Di-t-butyl-6-nitro-1,2-benzoquinone was prepared according to the literature [8]. Pyridine was dried over KOH and then distilled over CaH_2 under argon before use. All reactions were carried out under argon. ESR spectra were run from solid samples at room temperature. The following instruments were used: Specord 75 IR and Specord M40 (Carl Zeiss) spectrophotometers, JEOL JES-FE3X ESR spectrometer and a Bruker-B-E 10B8 magnetic balance.

Preparation of Catecholato Dicopper(II) Complexes (General Procedure)

To a solution of copper(I) chloride or bromide (5 mmol) in dry pyridine (10 ml) the quinone, tetrachloro-1,2-benzoquinone or tetrabromo-1,2-benzoquinone (2.5 mmol) in acetonitrile (5 ml) was added and stirred. The products deposited immediately, were filtered off, washed with a small amount of acetonitrile and dried in vacuum to give the catecholato dicopper(II) complexes (2). Yields and analytical data are collected in Table I.

Reaction of 3,5-Di-t-butyl-6-nitro-1,2-benzoquinone with Copper(I) Chloride and Bromide

Using 3,5-di-t-butyl-6-nitro-1,2-benzoquinone and copper(I) chloride, under identical conditions as before, blue crystals of dichlorobis(pyridine)copper(II) were isolated; yield 0.40 g (1.36 mmol). (Found C, 39.14; H, 3.29; N, 8.90. $C_{10}H_{10}N_2CuCl_2$ requires C, 40.98; H, 3.68; N, 9.55%). From the brown filtrate, after evaporation of half the amount of the

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TABLE I. Characterisation of Catecholato Dicopper(II) Complexes.

Complex	Colour	Yield[a] (%)	M.p. (°C) (decomp.)	Analytical data[b] (%)					
				C	H	N	Cu	Chloride	Bromide
2a	greenish yellow	73	205–7	41.91	2.84	7.98	16.93	26.03	–
				(41.07)	(2.65)	(7.37)	(16.71)	(28.00)	–
2b	brown	69	184–5	35.87	2.79	7.02	14.19	14.82	16.92
				(36.77)	(2.37)	(6.60)	(14.96)	(16.69)	(18.81)
2c	greenish yellow	64	120–2	34.01	2.20	5.94	14.41	8.60	30.84
				(33.29)	(2.14)	(5.97)	(13.54)	(7.56)	(34.08)
2d	ochre	96	174–5	28.72	2.05	5.51	12.60	–	44.13
				(30.40)	(1.96)	(5.46)	(12.37)	–	(46.70)
2e	brown	64	110–13	51.05	5.00	9.21	17.90	8.18	–
				(52.37)	(5.04)	(8.98)	(16.29)	(9.09)	–

[a] Not optimized. [b] Theoretical values in parentheses.

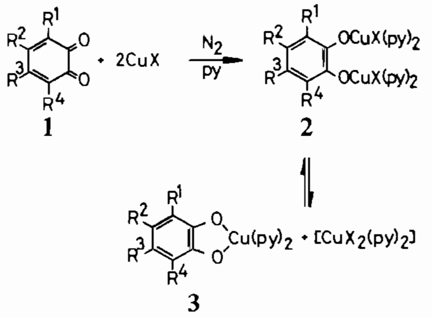
solvent and adding ether to the solution, only mixtures of (2e) and (3e) were obtained.

A solution of copper(I) chloride (0.40 g, 4.0 4.0 mmol) and 3,5-di-t-butyl-6-nitro-1,2-benzoquinone (0.53 g, 2.0 mmol) in pyridine (10 ml) were then heated up rapidly. On cooling green needles of $[CuCl_2(py)_2]$ deposited, which were filtered off, washed with ether and dried in vacuum. Yield 0.22 g (0.75 mmol). Found: C, 40.70; H, 3.61; N, 9.61. $C_{10}H_{10}N_2CuCl_2$ requires C, 40.98; H, 3.68; N, 9.55%). The filtrate was concentrated to half its volume by evaporation of the solvent and ether was added. After standing, brown needles were separated, which were filtered, washed with ether and dried in vacuum to give dichloro(3,5-di-t-butyl-6-nitrocatecholate)tetrakis(pyridine) dicopper(II) (2e). For yield and analytical data see Table I.

In an analogous manner, with copper(I) bromide (0.57 g, 4.0 mmol) and 3,5-di-t-butyl-6-nitro-1,2-benzoquinone (0.53 g, 2.0 mmol) in pyridine (10 ml) after cooling, only green crystals of $[CuBr_2(py)_2]$ deposited. Yield 1.10 g (72%). (Found: C, 28.34; H, 2.55; N, 6.70. $C_{10}H_5N_2CuBr_2$ requires C, 31.48; H, 2.64; H, 7.34%).

Results and Discussion

Silver and gold d^{10} complexes did not react with tetrachloro or tetraboromo-1,2-benzoquinone despite the high oxidation potential of the quinones [2]. The plausible explanation may arise from the stabilizing effect of the phosphine ligands for the lower oxidation state of the metals. No similar reactions with copper(I) complexes have been attempted. A different situation can be anticipated by changing the from phosphorus ligands to nitrogen ones. In fact, we found that copper(I) chloride and bromide in pyridine solution under an atmosphere of argon are easily accessible to oxidation by tetrachloro and tetrabromo-1,2-benzoquinones. In their reactions, new dinuclear copper(II) catecholate complexes (2a–d) were formed in good yields according to Scheme 1. The electron transfer reaction is very fast and exothermic. We assume that the quinones are reduced in two successive one-electron reduction by the copper(I) pyridine complexes $[CuX(py)_3]$ (X = Cl, Br). However, the assumed mononuclear copper(II) semiquinone complex could not be detected by ESR in solution. During the reaction highly coloured complexes(2) were formed, which are relatively stable with air in the solid form but easily decompose in solution in the presence of dioxygen or moisture.



a; $R^1 = R^2 = R^3 = R^4 = Cl$; X = Cl
b; $R^1 = R^2 = R^3 = R^4 = Cl$; X = Br
c; $R^1 = R^2 = R^3 = R^4 = Br$; X = Cl
d; $R^1 = R^2 = R^3 = R^4 = Br$; X = Br
e; $R^1 = R^2 =$ t-Bu; $R^3 = H$; $R^4 = NO_2$; X = Cl
f; $R^1 = R^2 =$ t-Bu; $R^3 = H$; $R^4 = NO_2$; X = Br

In the case of 3,5-di-t-butyl-6-nitro-1,2-benzoquinone by mixing with copper(I) halides after standing only a short time, blue or green needles of $[CuX_2(py)_2]$ (X = Cl, Br) separated in varying yields depending on the reaction conditions and the solvent, and on addition of ether, brown compounds were separated. Using only pyridine as the solvent, com-

TABLE II. Infrared and Electronic Spectra of Catecholato Dicopper(II) Complexes.

Complex	ν_{max} (nm) (lg ϵ)[a]	$\nu_{(catecholate)}$ (cm^{-1})[b]
2a	225(4.29); 252(4.05); 258(4.05); 263(3.93); 748(2.31)	795; 970; 981; 1256; 1528; 1628
2b	224(4.34); 252(4.42); 258(4.44); 265(4.32)	795; 970; 976; 1258; 1528; 1628
2b[c]	254(4.51); 258(4.53); 776(2.39)	
2c	229(4.49); 252(4.34); 258(4.35); 264(4.28)	796; 932; 948; 1283; 1631
2c[c]	260(4.57); 266(4.51); 774(2.36)	
2d	227(4.44); 252(4.25); 258(4.26); 263(4.18)	792; 927; 948; 1284; 1623
2d[c]	254(4.61); 259(4.62); 769(2.70)	
2e	214(4.39); 252(4.33); 258(4.34); 263(4.25); 760(2.47)	815; 994; 1255

[a]In MeOH. [b]Nujol mulls. [c]In CH_2Cl_2.

pound (2e) could be obtained in low yield with variable reproducibility. When pyridine-acetonitrile mixtures were used, only mixtures of (2e) and (3e) could be isolated or, occasionally, one or the other of both in pure form but with very poor reproducibility. With [CuBr(py)$_3$] only mixtures of (2f) and (3f) were obtained. In these cases the dinuclear catecholato copper(II) complexes (2) equilibrate with the mononuclear catecholato copper(II) complexes (3) and [CuX$_2$(py)$_2$] (X = Cl, Br) as a result of ligand transfer reactions. The reason for this equilibrium seems to be the somewhat lower oxidation capability of 3,5-di-t-butyl-6-nitro-1,2-benzoquinone resulting in a less stable catecholato dicopper(II) complex, which decomposes partly to (3) possessing a chelating catecholate ligand with increased stability. Complexes of type (3) have been only isolated having bidentate ligands e.g. N,N'-tetramethylethylenediamine, 2,2'-bipyridine and 1,10-phenanthroline [5].

In the IR spectra of the complexes no absorption due to ν(C=O) vibration can be observed. Characteristic absorptions are listed in Table II for compounds (2) indicating catechol coordination. These occur at 1220–1260 cm^{-1} and at about 1270 cm^{-1} with substantial intensity in all thc complexes reported here.

Table II also summarizes the electronic absorption maxima for complexes (2). Intense absorptions in the region 214–266 nm are due to $\pi \rightarrow \pi^*$ transitions in the catecholato ligand and ligand to metal charge transfer from pyridine ligand to copper(II). Bands with weaker absorptivities at 748–776 nm can be assigned to d–d transitions in the copper(II) centers.

The dinuclear catecholato copper(II) complexes (2) were found to be paramagnetic, with magnetic moments in the range of 1.66–1.93 BM per copper atom in the temperature interval 290–85 K, indicating slight antiferromagnetic interaction between the two copper(II) nucleus (Table III). This means further, that (i) the distance between the two copper(II) atoms is too great to have direct interaction and/or (ii) magnetic exchange through the bridging catecholato ligand is poor in these complexes. The failure of exchange through the bridging catecholato ligand may have also geometrical reasons of nonsuitable orbital interactions.

TABLE III. ESR Parameter at Room Temperature and Magnetic Moments at Different Temperatures.

Complex	g_x	g_y	g_z	G[a]	μ_{eff} (BM)[b] (290 K)	(85 K)
2a	2.060	2.084	2.219	3.04	1.78	1.75
2b	2.064		2.214	3.35	1.81	1.71
2c	2.062		2.215	3.48	1.93	1.73
2d	2.046	2.077	2.251	4.09	1.81	1.80
2e	2.062	2.085	2.220	3.00	1.80	1.66

[a]$G = g_{\parallel} - 2/g_{\perp} - 2$. [b]1 BM = 9.274×10^{-24} Am^2, μ_{eff} per Cu atom in the range of 85–290 K.

The ESR data of the complexes (2) are listed in Table III. The compounds (2b) and (2c) show axial spectra with lowest g > 2.04. The *g* values, related by the expression $G = g_{\parallel} - 2/g_{\perp} - 2$, are somewhat lower than 4, in agreement with some exchange coupling [11]. The other compounds exhibit rhombic spectra with lowest $g < 2.04$, which would be consistent with elongated rhombic octahedral or rhombic square-planar stereochemistries.

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