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The Formation and Characterization of Copper(II) 1,4-Benzenediolate and *p*-Semiquinonate Complexes

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Abstract

Strongly oxidizing *p*-quinones such as tetrachloro-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone undergo stepwise oxidative addition reactions with copper(I) chloride and bromide in pyridine resulting in copper(II) *p*-semiquinone and dinuclear copper(II) 1,4-benzenediolate pyridine complexes.

Introduction

Quinones can potentially bond to metal ions in three different oxidation states: quinone, semiquinone, or hydroquinone. *p*-Benzoquinone and substituted *p*-benzoquinones form diene [1–3] or donor-acceptor complexes with transition metals [4–6]. The reactions of metallocenes with electron acceptors in one-electron oxidative addition give *p*-semiquinone radical complexes [7]. *p*-Quinones were found to add oxidatively to the typical metal-centered radical, $[Co(II)(CN)_5]^{3-}$ producing in aprotic media radical adducts of Co(III) with *p*-semiquinone radical ligands [8]. A series of *p*-benzoquinones were reacted with Co(II)- and Fe(II)-salen compounds to yield binuclear complexes with the composition $[M(salen)]_2Q$, where Q is the quinone moiety [9]. It was shown with IR, variable-temperature magnetic susceptibility, EPR and ^{57}Fe Mössbauer measurements, that the iron compounds consist of high-spin ferric ions bridged by the dianion of a hydroquinone [10]. The X-ray structure of $[Fe(salen)]_2HQ$ has been determined [11]. Dimeric Ni(II) and Cu(II) complexes bridged by the dianions of two 2,5-dihydroxy-1,4-benzoquinones have been characterized [12]. We have shown that some *p*-quinones form $[CuXpy]_2 \cdot p$-quinone complexes with copper(I) chloride and bromide [13]. Data are presented in this paper for the binuclear complexes resulting from the reaction of copper(I) chloride and bromide with strongly oxidizing *p*-quinones.

Experimental

Copper(I) chloride (Reanal), copper(I) bromide (EGA-Chemie), tetrachloro-1,4-benzoquinone (Fluka AG), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (EGA-Chemie) were used as supplied. Pyridine was dried over KOH and then distilled over CaH_2 under argon before use. All reactions were carried out under argon. The following instruments were used: Specord 75 IR, Specord M40 (Carl Zeiss) spectrophotometers, JEOL JES-FE3X ESR spectrometer and Bruker-B-E 10B8 magnetic balance.

Reaction of Tetrachloro-1,4-benzoquinone with Copper(I) Chloride and Bromide

To a solution of copper(I) chloride or bromide (20 mmol) in dry pyridine (20 ml) the quinone (10 mmol) in pyridine (15 ml) was added and stirred. The products, deposited immediately, were filtered off, washed with small amount of ether and dried under vacuum. Yields and analytical data are collected in Table I.

Reaction of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone with Copper(I) Chloride and Bromide

To a solution of copper(I) chloride or bromide (20 mmol) in dry pyridine (20 ml) the quinone (10 mmol) in acetonitrile (6 ml) was added slowly. Products were formed in exothermic reaction, then the solution was heated up. On cooling needles of **2c** and **2d** deposited, which were filtered off, washed with ether and dried in vacuum.

Preparation of the 2,3-Dichloro-5,6-dicyano-1,4-benzosemiquinonato Copper(II) Complex

To a solution of copper(I) chloride (20 mmol), pyridine (20 mmol) in dichloromethane (20 ml) 20 mmol quinone in acetonitrile (10 ml) was added and stirred for 2 h. The solution was concentrated to half of its volume. After standing brown needles were separated, which were filtered, washed with ether and dried. For yield and analytical data see Table I.

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TABLE I. Characterization of Diphenolato Dicopper(II) Complexes

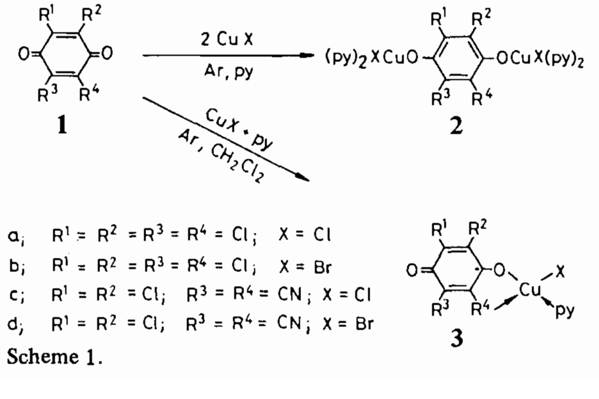
Complex	Colour	Yield[a] (%)	Melting point (°C) (decomp.)	Analytical data[b] (%)					
				C	H	N	Cu	Chloride	Bromide
2a	brown	92	180–182	41.68	2.74	7.61	16.79	27.52	
				(41.07)	(2.65)	(7.37)	(16.71)	(28.00)	
2b	reddish brown	96	180–184	36.80	2.34	6.57	14.60	16.66	18.41
				(36.77)	(2.37)	(6.59)	(14.96)	(16.69)	(18.81)
2c	green	64	220–222	45.60	2.91	11.02	16.90	19.45	
				(45.36)	(2.72)	(11.33)	(17.14)	(19.13)	
2d	dark green	87	195–196	40.54	2.72	9.95	14.89	8.67	19.15
				(40.50)	(2.42)	(10.12)	(15.30)	(8.53)	(19.24)
3c	brown	57	74–76	38.85	1.46	9.18	15.23	25.24	
				(38.54)	(1.24)	(10.38)	(15.68)	(26.25)	

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

Results and Discussion

Only a few dimeric transition metal complexes have been reported with *p*-quinone derivatives as bridging units. However, no oxidative addition of *p*-quinones to Cu(I) complexes have been attempted. We found that copper(I) chloride and copper(I) bromide in pyridine solution under an argon atmosphere are easily oxidized by tetrachloro-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. In these reactions new dinuclear copper(II) 1,4-benzenediolate complexes (**2a**–**2d**) were formed in good yields according to Scheme 1. The electron transfer is very fast and exothermic, the products are formed immediately. We assume that the quinones are reduced in two successive one-electron reductions by the $[CuX(py)_3]$ complexes formed in the pyridine solution. ESR spectra of the complexes **2** show the presence of traces of copper(II) semiquinone moieties.

From the reaction mixture of an equimolar amount of copper(I) chloride, pyridine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in dichloromethane we could isolate the mononuclear copper(II) semiquinone complex (**3**). Scheme 1 represents the one-electron oxidative addition of the quinone to copper(I). The unpaired electron is completely transferred to the quinone, and the resulting semiquinone radical is linked to the copper(II) via one oxygen atom.



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; $R^1 = R^2 = Cl$; $R^3 = R^4 = CN$; $X = Cl$
d; $R^1 = R^2 = Cl$; $R^3 = R^4 = CN$; $X = Br$

Scheme 1.

Infrared spectra were recorded for the compounds prepared as Nujol mulls. In the IR spectra no C=O stretching bonds are observed above 1640 cm^{-1} for all complexes, indicating that the quinones have been reduced. Characteristic absorptions are listed in Table II for compounds 2. The bands at 1200–1220 cm^{-1} are the CO stretchings of the dianions of the hydroquinones. The **2c** and **2d** complexes show a splitted, medium-intensity band at about 2200 cm^{-1}, which is assignable to the CN stretching band of the coordinated 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The corresponding IR band for uncoordinated quinone is barely seen at 2232 and 2243 cm^{-1}. In the IR spectra of compound **3c** the C=O stretching band is seen at 1690 cm^{-1}, the C–O band of the anion at 1213 cm^{-1}. The semiquinone ligand shows a sharp splitted CN band at 2207 and 2223 cm^{-1}. The 20–25 cm^{-1} shift to the lower energies is indicative of an intramolecular interaction between the nitrogen and copper(II) ion.

The electronic absorption spectra of the complexes are also summarized in Table II. Intense absorptions in the region 205–266 nm are due to $\pi-\pi^*$ transitions in the ligands and from the ligands to copper(II). The weak bands at 744–772 nm can be assigned to d–d transitions in the copper(II) centers.

Magnetic susceptibility data for the dinuclear diphenolato copper(II) complexes (**2**) are collected in Table III, where it can be seen that the magnetic moments are in the range of 1.61–1.85 (BM) per copper atom at 270 K. The μ_{eff} data show little temperature dependence in the interval 290–85 K,

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

Complex	ν_{max} (nm) (log ϵ)[a]	ν(phenolato)[b] (cm^{-1})	ν(CN)[b] (cm^{-1})
2a	214(4.34); 252(4.24); 257(4.23); 264(4.15); 760(2.85)	1080; 1218; 1603; 1623	
2b	214(4.41); 252(4.23); 257(4.22); 265(4.14)	1070; 1216; 1598; 1620	
2b[c]	253(4.48); 259(4.50); 266(4.42); 767(2.02)		
2c	205(4.34); 252(4.48); 258(4.50); 264(4.41)	1081; 1215; 1604; 1638	2198; 2207
2c[c]	254(4.31); 260(4.34); 265(4.28); 744(2.42)		
2d	205(4.38); 252(4.53); 257(4.56); 264(4.43); 772(2.28)	1062; 1206; 1595	2198
3c	251(4.03); 257(4.02); 263(3.93); 813(2.80)	1075; 1217; 1612	2207; 2223

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

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

Complex	g_x	g_y	g_z	g^*	g^{*a}	G^b	μ_{eff}(BM)[c]	
							290 K	85 K
2a	2.063	2.084	2.219	2.0039	2.0053	2.98	1.68	1.60
2b		2.084	2.213	2.0045	2.0053	2.52	1.66	1.49
2c	2.063	2.084	2.220	2.0037	2.0053[d]	2.99	1.85	1.80
2d		2.067	2.200	2.0038	2.0054	2.98	1.61	1.57
3c		2.089	2.214	2.0048	2.0049[e]	2.40	1.29	

[a] In CH_3CN, g^* semiquinone radical. [b] $G = g_{\parallel} - 2/g_{\perp} - 2$. [c] 1 BM = 9.274×10^{-24} Am^2, μ_{eff} per Cu atom. [d] Hyperfine structure can be seen with $A_N(2) = 0.61$ G. [e] In CH_2Cl_2.

indicating slight antiferromagnetic interaction between the two copper(II) nuclei. This means that the magnetic exchange through the bridging diphenolato ligand is poor in the complexes. The compound $[Cu_2(Me_5dien)_2(DHBQ)](BPh_4)_2$ (Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine, $DHBQ^{2-}$ = dianion from 2,5-dihydroxy-1,4-benzoquinone) shows no signs of an exchange interaction with susceptibility data [12]. The semiquinone complex **3c** was also found to be paramagnetic, the μ_{eff} value was 1.29 (BM) at 270 K.

The EPR data of the complexes **2** and **3** are collected in Table III. The compounds **2b** and **2d** show axial spectra with the lowest $g > 2.04$. The g values, related by the expression $G = g_{\parallel} - 2/g_{\perp} - 2$, are somewhat lower than 4, showing little exchange coupling [14]. For the **2a** and **2c** compounds rhombic spectra were observed with the lowest $g > 2.04$, which would be consistent with elongated rhombic octahedral or rhombic square-planar stereochemistries. An additional narrow signal with the g = 2.004–2.005 can also be seen for all of the complexes. The presence of this signal could indicate that there is a small amount of semiquinone complex in the samples.

The EPR spectrum of complex **3c**, may be attributed to a [CuClpy(*p*-DDSQ)](*p*-DDSQ = 2,3-dichloro-5,6-dicyano-1,4-benzosemiquinone) species containing a *p*-semiquinone radical bonded to the Cu^{II} central metal atom via the oxygen donor atom.

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