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Copper(I) Chloride Adducts of the Monoimines of 9,10-Phenanthrenequinones and 1,2-Naphthoquinone, and their Reaction with Molecular Oxygen

ÉVA BALOGH-HERGOVICH and GÁBOR SPEIER*

Research Group for Petrochemistry, Hungarian Academy of Sciences and Department of Organic Chemistry, Veszprém University of Chemical Engineering, 8201 Veszprém, Hungary

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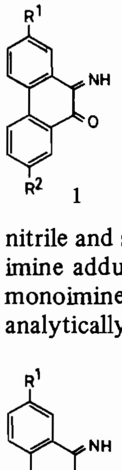
The monoimines of several 9,10-phenanthrenequinones and 1,2-naphthoquinone form 1:1 adducts with copper(I) chloride and chloro(pyridine)copper(I). The complexes [CuCl(imine)] (4,7) and [CuCl(py)imine] (3,6) are insoluble in acetonitrile and decompose in pyridine to [CuCl(py)₃] and the corresponding monoimines. In their reaction with molecular oxygen the C(9)–C(10) bond in 9,10-phenanthrenequinone monoimines and the C(1)–C(2) bond in 1,2-naphthoquinone 1-monoimine is oxidatively cleaved, giving chloro(2-cyano-2'-biphenylcarboxylato)bis(pyridine)copper(II) complexes and chloro[2-(2'-cyanophenyl)acrylato]bis(pyridine)copper(II) respectively.

Introduction

There is current interest to mimic dioxygenase-like activities of simple copper(I) complexes [1–4]. It has been shown that in the oxidation of *o*-phenylenediamine to *cis,cis*-mucononitrile [5, 6] and of catechols to *cis,cis*-muconic acids [7–12] *o*-benzoquinonediimine and *o*-benzoquinones are possible intermediates; however, only the existence of the latter has been proved [13]. It was also shown recently that *o*-quinones in the presence of ammonia can be transformed to the semi-nitriles of muconic acids [11, 14]. Apparently *o*-quinone monoimines may be assumed as intermediates in these reactions. Since only a few data on copper(I) halide complexes of *o*-quinones [15] and none on *o*-quinone monoimines are available in the literature, we decided to prepare these complexes in order to investigate their behaviour towards dioxygen. Here we report our results on some *o*-quinone monoimine copper(I) chloride complexes and their oxygenation reactions.

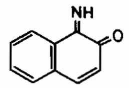
Results and Discussion

Pyridine and acetonitrile are excellent solvents for copper(I) compounds. Copper(I) chloride dissolved in pyridine yields [CuClpy$_3$] [16]. We tried to react [CuClpy$_3$] in pyridine with substituted 9,10-phenanthrenequinone monoimines (1) and *o*-naphthoquinone 1-monoimine (2) in order to isolate their monoimine complexes, but all our attempts were unsuccessful. Changing the solvent from pyridine to acetonitrile and starting from CuCl or [CuClpy], the monoimine adducts [CuCl(monoimine)] (4) and [CuCl(py)-monoimine (3) could be prepared in good yields in analytically pure form (Scheme 1 and Table I).

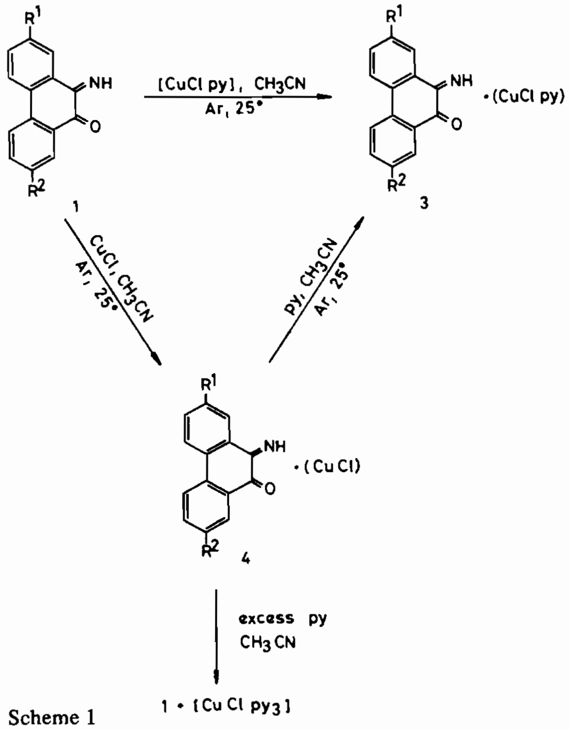


1

a) $R^1 = R^2 = H$
b) $R^1 = H; R^2 = Br$
c) $R^1 = R^2 = Br$
d) $R^1 = H; R^2 = NO_2$
e) $R^1 = R^2 = NO_2$
f) $R^1 = R^2 = t\text{-Bu}$



2



Scheme 1

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*Author to whom correspondence should be addressed.

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TABLE I. Monoimine Adducts of Copper(I) Chloride Complexes.

Complex	Colour	Yield (%)	M.p./°C (decomp.)	Analyses^a (%)					
				C	H	N	Cu	Cl	Br
3a	black	88	215	59.44 (59.22)	3.88 (3.66)	7.27 (7.27)	17.71 (16.49)	9.37 (9.20)	
3b	dark-grey	73	253	48.27 (49.14)	2.60 (2.82)	6.55 (6.03)	13.07 (13.68)	7.31 (7.63)	18.09 (17.23)
3c	dark-grey	96	219	41.22 (42.01)	1.94 (2.22)	4.52 (5.15)	10.77 (11.69)	5.92 (6.52)	30.07 (29.42)
3d	olive-green	63	271	53.48 (53.02)	3.05 (3.04)	9.63 (9.76)	14.05 (14.76)	7.72 (8.23)	
3e	bottle-green	74	234	51.01 (48.01)	2.47 (2.54)	12.12 (11.78)	13.36 (13.36)	7.75 (7.45)	
3f	black	64	188	65.20 (65.20)	6.30 (6.10)	5.20 (5.60)	12.40 (12.80)	6.50 (7.10)	
4a	brown	95	217	54.26 (54.90)	3.00 (2.96)	4.50 (4.57)	19.55 (20.75)	12.03 (11.57)	
4b	dark-brown	83	255	42.81 (43.65)	2.28 (2.09)	3.49 (3.63)	16.66 (16.49)	9.46 (9.20)	21.54 (20.76)
4c	dark-brown	75	178	36.28 (36.23)	1.63 (1.52)	2.99 (3.02)	13.12 (13.69)	7.80 (7.64)	34.78 (34.44)
4d	dark-brown	92	215	46.90 (47.87)	2.45 (2.29)	8.03 (7.97)	18.26 (18.09)	9.91 (10.09)	
4e	brown	61	293	42.11 (42.43)	2.24 (1.78)	12.20 (10.60)	14.02 (16.03)	7.20 (8.94)	
4f	black	92	234	63.11 (63.10)	6.20 (6.00)	4.00 (3.30)	14.10 (15.20)	7.60 (7.50)	
6	black	73	163	53.36 (53.73)	3.80 (3.60)	8.43 (8.35)	18.12 (16.95)	9.86 (10.57)	
7	black	77	194	46.70 (46.88)	3.20 (2.75)	6.00 (5.46)	23.90 (24.80)	13.30 (13.83)	

^{a}Calculated values in parenthesis.

The 1-monoimine of 1,2-naphthoquinone (2) gave in a similar reaction the adducts [CuClpy$C_{10}H_7NO$] (6) and [CuCl$C_{10}H_7NO$] (7). The complexes 3 are very slightly soluble in acetone, nitromethane and chloroform, slightly soluble in dichloromethane and acetonitrile, and insoluble in methanol and ethanol. No molecular weight measurements could be made because of low solubility. The complexes 4 exhibit similar solubility properties; compounds 3 and 4, however, readily dissolve in pyridine and from this solution [CuClpy_3] can be isolated, formed by displacement of the monoimine ligand by pyridine.

The complexes 4 can be transformed easily to 3 in acetonitrile if only a stoichiometric amount of pyridine is used. The compounds 3, 4, 6 and 7 are diamagnetic and probably associated through bridging chloro or monoimine ligands to a rather high molecular complexity.

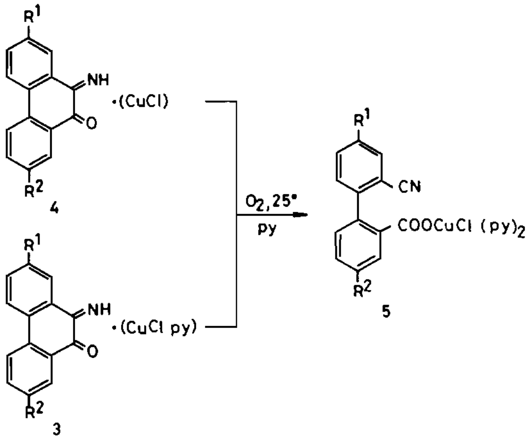
The IR spectra of the monoimine complexes show sharp ν(NH) and ν(CO) absorptions. The latter are (insignificantly) shifted compared to those of the free ligands (Table II). This suggests that no electron transfer to the monoimines has taken place upon complexation, and that the C–O groups are only very weakly involved in the co-ordination to copper [17]. The appearance of the N–H stretching vibrations, however, suggests that the imine group is co-ordinated to the copper, since in the free ligands the ν(NH) vibrations are either absent or give a broad band as a result of N–H...O hydrogen bonding.

The monoimine complexes 3, 4, 6 and 7 are sensitive toward air and dioxygen and take up dioxygen in solution according to Scheme 2, resulting in the carboxylato copper(II) complexes 5 and 8. Relevant data are collected in Table III.

TABLE II. Infrared Spectra of Copper(I) Chloride Monoimine Adducts[a] (cm^{-1}).

Complex	ν(CO)	ν(NH)
3a	1662	3202
3b	1667	3192
3c	1669	3192
3d	1684	3196
3e	1693	3196
3f	1667	3190
4a	1659	3194
4b	1655	3187
4c	1672	3188
4d	1670	3167
4e	1669	3185
4f	1668	3194
6	1655	3184
7	1654	3186

[a] In Nujol.



Scheme 2

TABLE IV. Infrared Spectra of Carboxylato Copper(II) Complexes (cm^{-1}).

Complex[a]	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν(CN)	$\Delta\nu$(CN)
5a	1627	1399	2222	6
5b	1605	1343	2217	1
5c	1631	1343	2219	3
5d	1632	1352	2216	6
5e	1611	1351	2222	2
5f	1603	1364	2222	4
8	1612	1385	2215	3

[a] In Nujol.

From the infrared spectra of these carboxylato copper(II) complexes (Table IV) the conclusion may be drawn that since the $\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$ values are rather high, monodentate co-ordination of the carboxylato ligands is probable [18]. The insignificant change in the ν(CN) vibrations compared to that in the free ligands shows that the C–N groups are not co-ordinated to the copper. The room temperature magnetic measurements (Table V) of 5 and 8 fall between 1.78–2.20 B.M. and only 5b, 5c, 5e and 8 show relatively small dependences on temperature in the range 85–290 K, indicating slight antiferromagnetic interactions. The ESR measurements of the solid samples taken at room temperature (Table V) give axial spectra of 5b, 5c, 5e and 8 with the lowest $g > 2.04$. They indicate a rhombic type geometry with $G < 4$ [19], suggesting magnetic inter-

TABLE III. Carboxylato Copper(II) Complexes.

Complex	Colour	Yield (%)	M.p./°C (decomp.)	Analyses[a] (%)					
				C	H	N	Cu	Cl	Br
5a	blue	75	227	59.61 (60.12)	3.68 (3.78)	8.20 (8.77)	14.04 (13.26)	7.89 (7.39)	
5b	blue	89	186	50.73 (51.62)	2.90 (3.06)	6.58 (7.52)	11.83 (11.38)	6.60 (6.34)	15.37 (14.31)
5c	turquoise	97	220	44.55 (45.23)	2.77 (2.53)	6.45 (6.59)	10.11 (9.97)	5.97 (5.56)	24.39 (25.07)
5d	blue	97	156	55.65 (54.96)	3.44 (3.26)	10.99 (10.68)	12.14 (12.11)	6.21 (6.76)	
5e	greenish-blue	80	205	50.49 (50.62)	2.99 (2.83)	12.24 (12.29)	11.11 (11.15)	6.70 (6.22)	
5f	blue	81	240	64.80 (64.94)	5.20 (5.79)	7.50 (7.13)	10.10 (10.73)	6.20 (5.99)	
8	blue	74	201	55.40 (55.94)	3.40 (3.75)	9.90 (9.78)	14.50 (14.79)	8.20 (8.25)	

[a] Theoretical values in parentheses.

TABLE V. Magnetic Susceptibility and ESR Parameters of Carboxylato Copper(II) Complexes.

Complex	Temp. (K)	$g_\perp$	$g_\parallel$	μ_{eff}/B.M.[a]		G[b]
				(290 K)	(85 K)	
5a	293	$g_x = 2.0622$ $g_y = 2.0840$	2.2192	1.83	1.80	2.99
5b	293	2.0830	2.2186	2.02	1.86	2.63
5c	293	2.0813	2.2198	2.13	1.94	2.70
5d	293	$g_x = 2.0028$ $g_y = 2.0807$	2.2088	1.97	1.97	5.00
5e	293	2.0806	2.2204	2.06	1.89	2.73
5f	293	$g_x = 2.0622$ $g_y = 2.0831$	2.2203	2.09	2.05	3.03
8	293	2.0838	2.2299	2.00	1.85	2.74

[a] 1 B.M. = 9.274×10^{-24} A m^2. [b] $G = g_\parallel - 2/g_\perp - 2$.

TABLE VI. Electronic Spectra of Carboxylato Copper(II) Complexes[a].

Complex	ν_{max}/cm^{-1} (ϵ/dm^3 mol^{-1} cm^{-1})
5a	45454(9 323); 39841(4 718); 38911(4 268); 37879(3 145); 34843(1 997); 13123(88)
5b	44444(16 653); 39841(11 895); 38911(11 475); 37879(8 816); 33784(2 798); 13210(85)
5c	46083(25 691); 39841(21 080); 39063(18 884); 38023(14 053); 34014(4 391); 12887(144)
5d	45455(7 359); 39683(13 353); 38760(13 878); 37879(10 619); 32895(2 733); 12987(91)
5e	45662(21 209); 39841(15 215); 38911(15 676); 37879(14 293); 35587(11 527)
5e[b]	39683(10 209); 38610(10 776); 37594(11 181); 35971(10 938); 13210(132)
5f	46083(7 125); 39841(10 984); 38911(11 430); 37879(8 461); 34014(2 375)
5f[b]	39841(10 939); 38760(11 605); 37879(10 368); 34014(4 756); 12987(354)
8	45249(19 615); 39683(17 831); 38760(18 188); 37879(14 978); 33898(6 062); 13228(111)

[a] In MeOH. [b] In MeCN.

actions of the copper(II) entities, also supported by the temperature dependent magnetic measurements. The compounds 5a, 5f, and 5d gave three g-value spectra. The first two have the lowest g-values (higher than 2.04) and the latter one lower than 2.03, giving rise to the assumption that they have elongated rhombic and compressed rhombic symmetries.

Considering the UV–VIS spectra (Table VI) of the carboxylato copper(II) complexes compared with those of known structures discussed in the literature [20], one sees that they do not contradict the stereochemical assumptions concluded from the ESR data. The d–d transitions were found around 13,000 cm^{-1}.

The carboxylato copper complexes may form high associates *via* halogen or carboxylato bridges (this is also in accord with the low solubility of the complexes) making possible 6-coordinated stereochemistry.

It would be premature at this time to discuss the mechanism of the oxygenation reaction. The following two facts, however, should be mentioned: i) the imine ligands can be replaced easily by pyridine giving [CuClpy$_3$] and the free monoimines (1); ii) the initial rates of the dioxygen uptake of copper(I) chloride in pyridine in the presence of 9,10-phenanthrenequinone monoimine (1a) (with molar ratios of imine: CuCl = 0.5–2:1) are identical with those found earlier in the absence of any added substrates [21]. From these two observations the conclusion can be drawn that the primary step in these reactions is probably the formation of the copper dioxygen complexes, formulated as active 'CuO' [22], hydroxo-bridged complexes [10], or even having formulae [Cu$_4$X$_4$py$_3$O$_2$], as proposed recently [23]. Furthermore, since protons are available from the imines, the formation of hydroxo copper complexes cannot be excluded. It seems reasonable however to disregard the possibility of the existence of amido copper compounds, as proposed by Rogič *et al.* [11, 14] in their similar reactions of substituted *o*-benzoquinones in the presence of ammonia with the CuCl–O$_2$–pyridine system yielding *cis,cis*-muconic acid mononitriles.

The carboxylato copper(II) complexes (5) could also be obtained when 9,10-phenanthrenequinones (1) were pre-treated with ammonia and then oxygenated in the presence of copper(I) chloride in pyridine. We consider that in these reactions monoimines are formed prior to the oxygenation by the copper system. These reactions provide an alternative mechanism for the transformation of *o*-quinones to muconic acid mononitriles with the CuCl–O$_2$–pyridine system in the presence of ammonia.

Experimental

Air-sensitive materials were handled by standard dinitrogen flow or vacuum techniques. Solvents were dried by standard methods and distilled before use. 1,2-Naphthoquinone 1-monoimine [24] and 9,10-phenanthrenequinone monoimine [25], 2-bromo-9,10-phenanthrenequinone monoimine [26], 2,7-dibromo-9,10-phenanthrenequinone monoimine [26] and 2,7-dinitro-9,10-phenanthrenequinone monoimine [27] were prepared by published methods. 2-Nitro-9,10-phenanthrenequinone monoimine and 2,7-di-tert-butyl-9,10-phenanthrenequinone monoimine were prepared in a similar manner and their structures confirmed by elemental analysis and IR spectra. IR spectra were recorded on a SPECORD 75 IR (Carl Zeiss, Jena) spectrophotometer. The magnetic susceptibilities were determined on a Bruker B-E 10B8 magnetic susceptibility system. The ESR spectra were run on a JEOL JES FE3X spectrometer and the electronic absorption spectra on a SPECORD M 40 (Carl Zeiss, Jena) spectrophotometer in MeOH or MeCN.

Preparation of the Adducts of Chloro(pyridine)copper(I) with 1,2-Naphthoquinone and 9,10-Phenanthrenequinone Monoimines. General Procedure

To a solution of chloro(pyridine)copper(I) (356 mg, 2 mmol) in 10 ml acetonitrile the *o*-quinone monoimines (2 mmol) dissolved in 10 ml acetonitrile were added and stirred for 4 h. Dark-coloured products formed, which were filtered off, washed with a small amount of acetonitrile, and dried under vacuum to give the monoimine adducts listed in Table I.

Preparation of the 1,2-Naphthoquinone and 9,10-Phenanthrenequinone Monoimine Adducts of Copper(I) Chloride. General procedure

To a solution of copper(I) chloride (200 mg, 2 mmol) in 10 ml acetonitrile the *o*-quinone monoimines (2 mmol) dissolved in 10 ml acetonitrile were added and stirred for 4 h. Dark-coloured products soon precipitated, which were filtered off, washed with a small amount of acetonitrile, and dried under vacuum to give the monoimine adducts listed in Table I.

The Reaction of 9,10-Phenanthrenequinone Monoimine Copper(I) Chloride Adduct with a Stoichiometric Amount of Pyridine

Chloro (9,10-phenanthrenequinone monoimine)-copper(I) (0.30 g, 1 mmol) was suspended in 5 ml acetonitrile and 0.08 ml (1 mmol) pyridine was added. The brown colour turned immediately to black. After stirring for 1 h the black product was filtered off, washed with acetonitrile and dried under vacuum to give (chloro)-9,10-phenanthrenequinone monoimine(pyridine)copper(I) (0.30 g, 78%). *Anal.* Calcd. for $C_{19}H_{14}N_2OCuCl$ (385.32) C, 59.22; H, 3.66; N, 7.27. Found: C, 59.43; H, 3.52; N, 7.30.

The Reaction of 9,10-Phenanthrenequinone Monoimine Copper(I) Chloride Adduct with Excess Pyridine

Chloro (9,10-phenanthrenequinone monoimine)-copper(I) (0.30 g, 1 mmol) was dissolved in pyridine (5 ml), the solvent pumped off and the residue treated with chloroform. Yellow crystals formed which were filtered, washed with ether and dried under vacuum to give chlorotris(pyridine)copper(I) (0.20 g, 60%). *Anal.* Calcd. for $C_{15}H_{15}N_3CuCl$ (336.28): C, 53.57; H, 4.49; N, 12.49. Found: C, 53.12; H, 4.38; N, 12.23.

The Reaction of 9,10-Phenanthrenequinone Monoimine Copper(I) Chloride Adducts with Dioxygen. General Procedure

9,10-Phenanthrenequinone monoimine adducts (2 mmol) or a mixture of the phenanthrenequinone monoimine (2 mmol) and copper(I) chloride (2 mmol) were dissolved in pyridine (10 ml) and stirred under dioxygen until gas uptake ceased (~24 ml O_2). The solvent was pumped off and the dry residue treated with ether several times; the blue solids were filtered off, washed with ether, and dried under vacuum to give the carboxylato copper(II) chloride complexes listed in Table III.

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