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Complexes of Cobalt(III) with 2-Nitroso-1-naphthol and 1-Nitroso-2-naphthol. (Monooximes of 1,2-Naphthoquinone)

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The complexes Co(nqo)$_3$ (nqoH = 1-nitroso-2-naphthol or 2-nitroso-1-naphthol) have been prepared by the interaction of the nitrosonaphthol with cobalt(II) chloride in air and under nitrogen. Under anaerobic conditions the formation of Co(nqo)$_3$ is accompanied by reduction of the ligand. The reduction leads to various organic products via *nitrene/quinoneimine intermediates. The complexes Co(nqo)$_3$ are also formed together with Na[Co(nqo)$_2$(NO$_2$)$_2$] by nitrosation of the respective naphthol and by the interaction of Na[Co(NO$_2$)$_6$] with nqoH. Reaction of Na$_3$[Co(NO$_2$)$_6$] with nitrosonaphthol, in the presence of sodium nitrite, gives Na[Co(nqo)$_2$(NO$_2$)$_2$]. Na[Co(nqo)$_2$(NO$_2$)$_2$] reacts with nqoH under basic conditions to give Co(nqo)$_3$ and with pyridine or benztriazole to give Co(nqo)$_2$(NO$_2$)L (L = pyridine or benztriazole).*

Introduction

Cobalt complexes derived from 1-nitroso-2-naphthol (1-nqoH) and 2-nitroso-1-naphthol (2-nqoH) (the abbreviation nqoH will be used to denote both 1-nqoH and 2-nqoH) have been known for a considerable time and the former has been used extensively as a complexing reagent for cobalt both for analytical and extraction purposes [1–3]. However, the reactions leading to the complexes and the composition and properties of the complexes have not been fully investigated. The products arising from the interaction between the nitrosonaphthols and cobalt(II) salts have been formulated as Co(nqo)$_3$. The formulation Co(1-nqo)$_2$ has been suggested for the product of the reaction between the sodium salt of 1-nitroso-2-naphthol and a cobalt(II) salt [4]. Several studies indicated that the reaction between a cobalt(II) salt and the nitrosonaphthol involves reduction of the ligand but the products arising from this process have not been investigated [5]. The i.r. spectra of Co(nqo)$_3$ have been reported [6] and recently a structural proposal has been made for Co(1-nqo)$_3$ based on studies of its ^{13}C n.m.r. spectrum [7]. Some reports have dealt with the cobalt complexes derived from sulphonated nitrosonaphthols [8] and we have studied complexes derived from 4-methyl-2-nitrosophenol and 4-chloro-2-nitrosophenol [9]. As a continuation of our studies [10] on 2-nitrosophenol complexes we now report on several cobalt(III) complexes of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol and on the reactions leading to them.

Results and Discussion

The reaction of cobalt(II) chloride with 1-nitroso-2-naphthol in methanol, in air or under nitrogen, gave a red solution and solid Co(1-nqo)$_3$ as the major product. The solution contained some Co(1-nqo)$_3$ and several other products, isolated in small or trace quantities. The soluble products, which were separated chromatographically, included 6-hydroxydibenzo[i,mn]acridine-8-one and 2-hydroxy-1,4-naphthoquinone. These were characterised by comparison with authentic samples and/or by mass spectrometry. Contrary to previous reports [4] the reaction of potassium 1-nitroso-2-naphtholate with cobalt(II) chloride also afforded the cobalt(III) complex Co(1-nqo)$_3$ as the major product together with smaller amounts of several organic products. The yield of

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TABLE I. Data for Reactions of $CoCl_2 \cdot 6H_2O$[a] with Nitrosonaphthols.

nqoH (xmol equiv.)		Conditions[b]	Products		Organic products[d]	
			$Co(nqo)_3$[c] wt (g)	Yield (%)[e]	Total wt (g)	Product number[f] (% yield)[g]
1-nqoH	(3.0)	A	5.1	88	0.65	1 (40)[h]
1-nqoH	(3.5)	A	5.6	98	0.85	1 (34)[h]
1-nqoH	(3.0)	N	4.1	71	1.20	1 (19)[h]
1-nqoH	(5.0)	N	5.6	98	2.90	1 (30)[h], 2 (13)[i]
Na(1-nqo)	(2.0)	A	3.0	51	1.77	1 (5)[h]
Na(1-nqo)	(3.0)	A	5.2	89	0.50	1 (8)[h]
2-nqoH	(3.0)	A	4.8	83	0.80	3 (2)[j], 4 (1)[k], 5 (1)[l], 6 (2)[m]
2-nqoH	(3.5)	A	5.5	95	0.88	3 (2)[j], 4 (2)[k], 5 (1)[l], 6 (3)[m]
2-nqoH	(2.5)	N	4.0	69	0.71	3 (8)[j], 4 (12)[k], 5 (2)[l], 6 (18)[m]
2-nqoH	(3.5)	N	5.6	97	1.00	3 (3)[j], 4 (7)[k], 5 (1)[l], 6 (8)[m], 7 (3)[n]
2-nqoH	(5.0)	N	5.6	97	3.07	3 (1)[j], 4 (4)[k], 5 (1)[l], 6 (6)[m], 7 (15)[n]

[a] 2.4 g, 1 mol equiv. [b] A = in air; N = under nitrogen. [c] See Table II for analytical data. [d] Each reaction afforded several products. Only those characterised are listed. [e] Based on $CoCl_2 \cdot 6H_2O$. [f] Product number: 1. 6-hydroxydibenzo[i,mn]acridine-8-one; 2. 2-hydroxy-1,4-naphthoquinone; 3. 1,2-naphthoquinone-2-imine; 4. 2-amino-N(4)-1-hydroxy-2-naphthyl-1,4-naphthoquinone monoimine; 5. 2-amino-1-naphthol; 6. dibenzo[b,i]phenazine; 7. dibenzo[b,i]phenazine-5,12-diol. [g] Based on Reaction 1 given in text. [h] m/e 297 (M^+), 269, 240; identical (t.l.c.) with authentic sample [15]. [i] m/e 174 (M^+), 146, 129, 118. [j] m/e 157 (M^+), 130, 102. [k] m/e 314 (M^+), 286, 285, 257; identical (t.l.c.) with authentic sample [11]. [l] m/e 159 (M^+), 130; identical (t.l.c.) with authentic sample [16]. [m] m/e 280 (M^+); identical (t.l.c.) with authentic sample [17]. [n] m/e 312 (M^+), 283; identical (t.l.c.) with authentic sample [11].

$Co(1\text{-}nqo)_3$ and the nature and yields of the organic products are dependent on the relative molar ratios of the reactants and conditions used (Table I). Analogous reactions involving 2-nitroso-1-naphthol gave mainly $Co(2\text{-}nqo)_3$ and several organic products isolated in small or trace amounts. The latter included 1,2-naphthoquinone-2-imine, 2-amino-N(4)-1-hydroxy-2-naphthol-1,4-naphthoquinone monoimine, 2-amino-1-naphthol, dibenzo[b,i]phenazine and dibenzo[b,i]phenazine-5,12-diol which were characterised by comparison with authentic samples and/or by mass spectrometry. The formulation of the major products of the above reactions as cobalt(III) trischelates is consistent with the analytical data and is supported by relative molecular mass measurements and their diamagnetic character.

The yields of $Co(nqo)_3$ and the nature and yields of the organic products obtained from the reactions carried out under nitrogen suggest (a) that the oxidation of Co(II) to Co(III) involves reduction/deoxygenation of the nitrosonaphthol and (b) that the stoichiometry of the reactions is as indicated by Reaction 1. Some reduction of the nitrosonaphthol also occurs when the reactions are carried out in air. These observations are in accord with earlier electrochemical studies which have indicated ligand reduction [5]. The reduction of the nitrosonaphthol gives initially a nitrene/quinoneimine species (nqH). Further reactions of this intermediate lead to the organic products via routes which we have discussed elsewhere in relation to the deoxygenation of 2-nitrosophenols or their complexes by triphenylphosphine or metal carbonyls [11–13].

$$2CoCl_2 + 7nqoH \rightarrow$$

$$2Co(nqo)_3 + H_2O + 4HCl + \underset{\substack{\downarrow \\ \text{organic products}}}{[nqH]} \qquad (1)$$

The complex $Co(2\text{-}nqo)_3$ was also obtained, together with the complex $Na[Co(2\text{-}nqo)_2(NO_2)_2]$, by the nitrosation of 1-naphthol using sodium nitrite and acetic acid in the presence of cobalt(II) chloride hexahydrate. Similarly nitrosation of 2-naphthol afforded $Co(1\text{-}nqo)_3$ and $Na[Co(1\text{-}nqo)_2(NO_2)_2]$. The dinitro complexes also resulted from the reaction of sodium hexanitrocobaltate(III) with the respective nitrosonaphthol in the presence of sodium nitrite. Their formulation is indicated by analytical data, their diamagnetism and their conductivity in acetone (Λ_M = ca. 150 Ω^{-1} cm^2 mol^{-1}) which is typical of a 1:1 electrolyte [14]. Further support for the formulation is provided by their reaction with pyridine or benztriazole to give diamagnetic, non-conducting complexes of type $Co(nqo)_2(NO_2)L$

TABLE II. Analytical Data for Nitrosonaphtholcobalt(III) Complexes.

Complex	Elemental Analysis										Relative Molecular Mass		Molar Conductance Ω^{-1} cm^2 mol^{-1}
	Found(%)					Required(%)					Found	Required	
	C	H	N	Co	Na	C	H	N	Co	Na			
Co(1-nqo)$_3$	62.4	3.1	7.0	10.3	–	62.5	3.1	6.1	10.3	–	530 ± 40	575	–
Co(2-nqo)$_3$	62.5	3.7	6.6	10.7	–	62.6	3.1	6.1	10.3		545 ± 45	575	–
Na[Co(1-nqo)$_2$(NO$_2$)$_2$]	45.3	2.7	11.0	10.9	4.6	46.3	2.4	11.4	11.2	4.4	–	–	142
Na[Co(2-nqo)$_2$(NO$_2$)$_2$]	45.4	2.8	10.3	10.6	4.0	46.3	2.4	11.4	11.2	4.4	–	–	156
Co(1-nqo)$_2$(NO$_2$)py[a]	56.6	3.7	9.5	10.7	–	56.8	3.2	10.6	11.2	–	–	–	0.5
Co(2-nqo)$_2$(NO$_2$)py[b]	57.0	3.7	9.4	10.5	–	56.8	3.2	10.6	11.2	–	–	–	2.8
Co(1-nqo)$_2$(NO$_2$)bzt	54.5	3.3	13.8	9.5		55.0	3.1	14.8	9.5	–	–	–	1.2
Co(2-nqo)$_2$(NO$_2$)bzt	54.6	3.2	14.1	9.4		55.0	3.1	14.8	9.5	–	–	–	1.6

[a] py = pyridine. [b] bzt = benztriazole.

(L = pyridine or benztriazole) and sodium nitrite. Each of the complexes Na[Co(nqo)$_2$(NO$_2$)$_2$] reacted readily with the respective nitrosonaphthol under neutral or basic conditions to give Co(nqo)$_3$. Under acidic conditions no reaction occurred thus accounting for the isolation of two types of complexes in the nitrosation reactions.

The i.r. spectra of all complexes are consistent with the NO group of the ligand bound through the nitrogen atom and their diamagnetic character is in accord with the strong ligand field of the 1-nqo$^-$ and2-nqo$^-$ ligands [10]. Attempts to obtain structural information on the complexes of type Co(nqo)$_3$ by mass spectrometry were unsuccessful. No metal-containing ions were observed in the spectra indicating decomposition of the complexes in the mass spectrometer. Thin layer chromatographic examination of all products formulated as Co(nqo)$_3$ showed the presence of two components. This suggests that each product is a mixture of two isomers. The formation of isomers is not unexpected. The ambidentate and asymmetric nature of the ligand can give rise to linkage and/or geometrical isomers. Attempts to separate the two isomers by column chromatography failed. However, upon heating the mixture of these isomers in toluene under reflux almost complete conversion of one isomer into the other was achieved.

Experimental

See Tables I and II for analytical and other data.

Reaction of Cobalt(II) Chloride Hexahydrate with 1-Nitroso-2-naphthol or 2-Nitroso-1-naphthol

A solution of cobalt(II) chloride hexahydrate (2.4 g, 1 mol equiv.) in methanol (50 cm^3) was added to a solution of the nitrosonaphthol (x mol equiv.) in methanol (100 cm^3) and the mixture was stirred (3 h). The resulting mixture of isomers of tris(naphthoquinoneoximato)cobalt(III) was filtered off, washed with methanol and dried at 100 °C/0.1 mm. The combined filtrate and washings on drying at 40 °C/0.1 mm gave a multicomponent residue which was chromatographed on silica gel using toluene followed by gradual change to chloroform and then to methanol.

Nitrosation of 1- or 2-Naphthol in the Presence of Cobalt(II) Chloride Hexahydrate

A solution of sodium nitrite (10.2 g, 5 mol equiv.) in water (50 cm^3) was added to a stirred solution of 1-naphthol (12.8 g, 2 mol equiv.), cobalt(II) chloride hexahydrate (7.0 g, 1 mol equiv.), acetic acid (15 cm^3) and sodium acetate (15 g) in ethanol–water (2:1) (300 cm^3). After 3 h the mixture was filtered to give a dark purple solid which was dried at 100 °C/1 mm and then successively extracted (Soxhlet) with chloroform and acetone. Removal of the solvent from the chloroform and acetone extracts gave residues of tris(1,2-naphthoquinone-2-oximato)-cobalt(III) (10.8 g, 45%) and *sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobaltate(III)* (2.1 g, 10%) respectively.

Similarly, nitrosation of 2-naphthol gave tris(1,2-naphthoquinone-1-oximato)cobalt(III) (41%) and *sodium dinitrobis(1,2-naphthoquinone-1-oximato)-cobaltate(III)* (26%).

Interaction of Sodium Hexanitrocobaltate(III) with 1-Nitroso-2-naphthol or 2-Nitroso-1-naphthol

A solution of 1-nitroso-2-naphthol (0.5 g, 3 mol equiv.) in methanol (50 cm^3) was added dropwise to a solution of sodium hexanitrocobaltate(III) (0.4 g, 1 mol equiv.) in water (50 cm^3). After stirring for 2 h the mixture was filtered to give tris(1,2-naphthoquinone-1-oximato)cobalt(III) (98%).

Similarly tris(1,2-naphthoquinone-2-oximato)cobalt(III) (98%) was obtained when 2-nitroso-1-naphthol was used.

Interaction of Sodium Hexanitrocobaltate(III) with 1-Nitroso-2-naphthol or 2-Nitroso-1-naphthol in the Presence of Sodium Nitrite

A solution of 1-nitroso-2-naphthol (0.35 g, 2 mol equiv) in methanol (50 cm^3) was added dropwise to a stirred solution of sodium hexanitrocobalt(III) (0.4 g, 1 mol equiv.) and sodium nitrite (0.7 g, 10 mol equiv.) in water (50 cm^3). After stirring for 2 the mixture was dried at 50 °C/0.1 mm and the residue was extracted with acetone. Removal of the solvent from the acetone extract gave sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (0.5 g, 96%).

Similarly, 2-nitroso-1-naphthol gave sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobaltate(III) (95%).

Interaction of Sodium Dinitrobis(naphthoquinoneoximato)cobaltate(III) with Pyridine

Sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (0.7 g, 1 mol equiv.) and pyridine (0.3 g, 3 mol equiv.) in acetone (200 cm^3) were heated under reflux (10 h). The mixture was dried and the residue was extracted with chloroform (200 cm^3). The extract, on drying at 50 °C/0.1 mm gave a residue of *nitrobis(1,2-naphthoquinone-1-oximato)pyridinecobalt(III)* (84%).

Similarly *nitrobis(1,2-napthoquinone-2-oximato)pyridinecobalt(III)* (80%) was obtained when sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) was used.

Interaction of Sodium Dinitrobis(naphthoquinoneoximato)cobaltate(III) with Benztriazole

Sodium dinitrobis(1,2-naphthoquinone-1-oximato) cobaltate(III) (1.29, 1 mol equiv.) and benztriazole (0.8 g, 3 mol equiv.) in acetone (200 cm^3) was heated under reflux (10 h). The mixture was dried and the residue was extracted with chloroform. The extract was dried and washed with methanol to give *nitrobis(1,2-naphthoquinone-1-oximato)benztriazolecobalt(III)* (38%).

Similarly *nitrobis(1,2-naphthoquinone-2-oximato) benztriazolecobalt(II)* (42%) was obtained when sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobalt(III) was used.

Interaction of Sodium Dinitrobis(naphthoquinoneoximato)cobaltate(III) with Nitrosonaphthol under Neutral Conditions

A solution of 1-nitroso-2-naphthol (0.04 g, 1 mol equiv.) in methanol (10 cm^3) was added to a solution of sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (0.19 g, 1 mol equiv.) in acetone (50 cm^3). The mixture was stirred (3 h) and was then dried. The residue was extracted with chloroform and the extract was dried to give tris(1,2-naphthoquinone-1-oximato)cobalt(III) (88%).

Similarly bis(1-naphthoquinone-2-oximato)cobalt(III) (89%) was obtained when 2-nitroso-1-naphthol and sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobalt(III) were used.

Interaction of Sodium Dinitrobis(naphthoquinoneoximato)cobaltate(III) with Nitrosonaphthol under Basic Conditions

A solution of 1-nitroso-2-naphthol (0.04 g, 1 mol equiv.) in methanol (10 cm^3) was added to a solution of sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (0.19 g, 1 mol equiv.) in acetone (50 cm^3). Sodium hydroxide (2 *M*, 8 drops) was added. The mixture was stirred (1 h) and dried. The residue was extracted with chloroform. The chloroform extract was dried to give tris(1,2-naphthoquinone-1-oximato)cobalt(III) (90%).

Similarly tris(1,2-naphthoquinone-2-oximato)cobalt(III) (90%) was obtained when 2-nitroso-1-naphthol and sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobaltate(III) were used.

Interaction of Sodium Dinitrobis(naphthoquinoneoximato)cobaltate(III) with Nitrosonaphthol under Acidic Conditions

Sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (0.102 g, 1 mol equiv.) and 1-nitroso-2-naphthol (0.040 g, 1 mol equiv.), were stirred in acetic acid (10 cm^3) for 1 h. After removal of the solvent the resultant solid was extracted with chloroform to give sodium dinitrobis(1,2-naphthoquinone-1-oximato)cobaltate(III) (98% recovery). The chloroform extract on drying gave a residue of 1-nitroso-2-naphthol (96% recovery).

Similarly, 2-nitroso-1-naphthol and sodium dinitrobis(1,2-naphthoquinone-2-oximato)cobaltate(III) were recovered in 97 and 96% yield respectively.

Action of Heat on Tris(naphthoquinoneoximato)cobaltate(III)

A mixture of isomers of tris(1,2-naphthoquinone-1-oximato)cobalt(III) (R_f 0.35 and 0.42 in chlorofom) (0.5 g) was heated in toluene (50 cm^3) under reflux 168 h. Removal of the solvent gave tris(1,2-naphthoquinone-1-oximato)cobalt(III) (mainly R_f 0.35).

Similarly, a mixture of isomers of tris(1,2-naphthoquinone-2-oximato)cobalt(III) (R_f 0.40 and 0.47 in chloroform) gave tris(1,2-naphthoquinone-2-oximato)cobalt(III) (mainly R_f 0.40).

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