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Complexes of Iron(III) and Iron(II) with o-Nitrosophenols (Mono-oximes of *ortho*-Benzoquinones)

J. CHARALAMBOUS[+], M. J. FRAZER,[*] and R. SIMS
Department of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.
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Complexes of the type Fe(qo)$_3$ have been prepared, where qoH = 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, phenanthrene-9,10-quinonemono-oxime, 5-methoxy-2-nitrosophenol, 5-methyl-2-nitrosophenol and 4,5-dimethyl-2-nitrosophenol. Some of the complexes react with hydrochloric acid to give FeCl(qo)$_2$ and are reduced by sodium or potassium iodide to give M[Fe(qo)$_3$]. The magnetic susceptibilities, and electronic, i.r., mass and Mössbauer spectra of the complexes Fe(qo)$_3$, FeCl(qo)$_2$ and M[Fe(qo)$_3$] have been investigated. In all complexes the metal has a low-spin electron configuration. The NO group of the ligand is probably bonded to the metal through the nitrogen atom. The complexes Fe(qo)$_3$ are monomeric in chloroform. The complexes FeCl(qo)$_2$ are dimeric in chloroform and the complexes M[Fe(qo)$_3$] are 1:1 electrolytes in acetonitrile.

Introduction

In previous papers we have described complexes of copper(II) and nickel(II) derived from 2-nitrosophenols and reported briefly on nitrosophenol complexes of other metals.[1–3] We now report on the preparation and properties of several iron complexes of types Fe(qo)$_3$, FeCl(qo)$_2$ and M[Fe(qo)$_3$] (qoH = various substituted 2-nitrosophenols, M = Na or K). Some nitrosophenol complexes of iron have been reported earlier but apart from the complexes Fe(qo)$_3$ (qoH = 1-nitroso-2-naphthol and 2-nitroso-1-naphthol) and the complex ferroverdin K[Fe(qo)$_3$] (qoH = 4-vinylphenyl ester of 3-nitroso-4-hydroxybenzoic acid) their composition and properties have not been fully investigated.[4–10] Ferroverdin is a naturally occurring compound and has been characterised by X-ray crystallography.[5] The complexes derived from the nitrosonaphthols have been prepared by the direct interaction of an iron(III) salt with the appropriate nitrosonaphthol and have been investigated mainly for analytical purposes.[6–8] Their i.r. spectra[9] have been reported and the Mössbauer spectrum[10] of the complex derived from 1-nitroso-2-naphthol has been studied.

Experimental

Preparation of Tris(quinone oximato)iron(III) Complexes

(a) By nitrosation of phenols

These were prepared by the nitrosation of a phenol in the presence of ferric chloride, by a method described earlier for the preparation of analogous copper(II) and nickel(II) complexes.[1] Analytical and other data are given in Table III.

(b) From nitrosophenols

1-Nitroso-2-naphthol (5.2 g, 3 mol equiv.) and ferric chloride hexahydrate (2.7 g, 1 mol equiv.) were stirred in methanol (100 cm^3). Tris(naphtho-2-quinone-1-oximato)iron(III) (4.7 g, 84%) was filtered off, washed with methanol, and dried at 20° C/0.5 mm.

Similarly, 2-nitroso-1-naphthol gave tris(naphtho-1-quinone-2-oximato)iron(III) (73%), phenanthrene-9,10-quinonemono-oxime gave tris(phenanthrene-9-quinone-10-oximato)iron(III) (55%), and 5-methoxy-2-nitrosophenol gave tris(5-methoxybenzo-1-quinone-2-oximato)iron(III) (55%).

The compounds obtained by methods (a) and (b) had similar analyses, identical X-ray powder diffraction patterns, and identical i.r. spectra (4000–400 cm^{-1}).

Interaction of Hydrochloric Acid with Tris(4,5-dimethylbenzo-1-quinone-2-oximato)iron(III)

Tris(4,5-dimethylbenzo-1-quinone -2 - oximato)iron (III) (1.5 g) was stirred (12 h) with aqueous hydrochloric acid (15%, 50 cm^3). Dark green *chlorobis (4,5 - dimethylbenzo - 1 - quinone - 2 - oximato)iron(III)* (1.15 g, 99%); Found: C, 48.4; H, 4.3; Cl, 9.0; Fe, 14.2; N, 6.9. $C_{16}H_{16}ClFeN_2O_4$ requires: C, 49.0; H, 4.1; Cl, 9.1; Fe, 14.3; N, 7.1%) was filtered off, washed with water and dried at 70° C/0.1 mm. Evaporation of the

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[+] Author to whom correspondence should be addressed.

[*] Present address: School of Chemical Sciences, University of East Anglia, Norwich NOR 88C.

combined filtrate and washings gave a sticky brown–black solid (*ca.* 0.3 g). Attempts to recrystallise or sublime the solid from the filtrate were unsuccessful.

Interaction of Tris(naphtho-2-quinone-1-oximato)iron (III) with Hydrochloric Acid

Tris(naphtho-2-quinone-1-oximato)iron(III) (5.7 g) was stirred (12 h) with aqueous hydrochloric acid (15%, 50 cm^3). The solvent was removed under reduced pressure at 50° C/0.1 mm and the solid remaining was heated at 100° C/0.1 mm for several days, giving a yellow sublimate which was identified by i.r. spectroscopy as 1-nitroso-2-naphthol (1.7 g, 98%) and a brown–black residue of *chlorobis(naphtho-2-quinone-1-oximato)iron(III)* (4.3 g, 99%). Found: C, 55.3; H, 2.8; Cl, 8.3; Fe, 12.8; N, 6.4. $C_{20}H_{12}ClFeN_2O_4$ requires: C, 55.1; H, 2.8; Cl, 8.2; Fe, 12.9; N, 6.4%.

Alternative Preparation of Chlorobis(naphtho-2-quinone-1-oximato)iron(III)

The sodium salt of 1-nitroso-2-naphthol (4.8 g, 2 mol equiv.) was added to a solution of ferric chloride (2.0 g, 1 mol equiv.) in acetonitrile (200 cm^3) and the mixture was stirred (3 h) then filtered, and the precipitate was extracted with chloroform. The chloroform extract was then filtered (to remove sodium chloride), and then evaporated to dryness to give brown–black *chlorobis(naphtho-2-quinone-1-oximato)iron(III)* (2.7 g, 63%). Found: C, 56.1; H, 3.0; N, 6.4; Cl, 8.2; Fe, 12.7%.

Interaction of Tris(naphtho-2-quinone-1-oximato)iron (III) with Metal Iodides

Sodium iodide (5.0 g) was added to a solution of tris(naphtho-2-quinone-1-oximato)iron(III) (3.0 g) in methanol (200 cm^3) and the mixture was stirred (12 h). The solvent was removed at 50° C/0.5 mm, and the remaining solid was washed successively with water, chloroform and diethyl ether, then dried at 100° C/0.1 mm to give *sodium tris(naphtho-2-quinone-1-oximato)ferrate(II)* (2.9 g, 93%). Found: C, 59.8; H, 2.9; Fe, 9.3; N, 7.1. $C_{30}H_{18}FeN_3NaO_6$ requires: C, 60.5; H, 3.0; Fe, 9.4; N, 7.1%. The presence of iodine was observed in the various washings, and also as a sublimate in the drying processes.

Similarly potassium iodide and tris(naphtho-2-quinone-1-oximato)iron(III) gave *potassium tris(naphtho-2-quinone-1-oximato)ferrate(II)* (95%). Found: C, 59.8; H, 2.8; Fe, 10.8; N, 7.4. $C_{30}H_{18}FeKN_3O_6$ requires: C, 58.9; H, 2.9; Fe, 10.9; N, 6.9%.

Magnetic Measurements

Magnetic moments were measured by the Gouy method. The apparatus was calibrated with HgCo (CNS)$_4$. The moments of all compounds were measured at room temperature with a permanent magnet (3600 Oe). The susceptibilities were measured over a range of temperature (90–300° K) at 6300 Oe in an atmosphere of nitrogen and over a range of field strengths (15,900–4000 Oe) at 25.0° C in air.

I.r., Electronic and Mass Spectra

These were recorded as described earlier.[2]

^{57}Fe Mössbauer Spectra

Mössbauer spectra were obtained through the Physico-Chemical Measurements Unit at Harwell, as was the computer-fitted date for the resultant spectra. The chemical shifts obtained were quoted relative to that of iron. A ^{57}Co/Pd source was used.

X-ray Powder Pattern Photographs

These were recorded on a Philips PW 1024 Debije Scherrer Powder Camera (diameter 114.83 mm) using a PW 1008/30 X-ray generator. Exposure times were 2–3 hours. The samples were ground up and packed in 0.1 mm diameter Lindemann tubes.

Conductance Measurements

Conductance measurements were made using a Mullard E7566/3 conductivity bridge with a Mullard pipette cell type E7598/A. The cell was calibrated with a potassium chloride solution of known concentration.

Molecular Weight Measurements

Molecular weights were determined at 37° C in chloroform solution using a Mechrolab 301A osmometer.

Results and Discussion

The complexes Fe(qo)$_3$ listed in Table I have now been prepared, either by direct interaction of an iron(III) salt with the appropriate 2-nitrosophenol, or by the nitrosation, using sodium nitrite, of the appropriate phenol in the presence of an iron(III) salt. The products obtained by both methods were identical as shown by X-ray diffraction powder photographs. Nitrosation of 3-methoxyphenol in the presence of a copper(II) salt gave a complex derived from 5-methoxy-2-nitrosophenol.[1] By analogy complex *5*, which has been obtained by the nitrosation of 3-methylphenol, is formulated as a 5-methyl-2-nitrosophenol derivative rather than as a 3-methyl-2-nitrosophenol derivative. Similarly complex *6*, which has been obtained from 3,4-dimethylphenol, is formulated as a 4,5-dimethyl-nitrosophenol derivative.

Attempts to obtain and characterise the protonated ligands from complex *6* and thus confirm the formulation of this complex were unsuccessful. When the complex was treated with aqueous hydrochloric acid (5*M*) the compound FeCl(qo)$_2$ was obtained in high yield but the liberated organic species could not be isolated.

TABLE I. Physical Data of Complexes.

No.	Formula	qoH	μ_{eff}[a] (B.M.)	M		Mössbauer parameters[b]	
				Found	Calc.	δ (mm s^{-1})	Δ (mm s^{-1})
1	$Fe(qo)_3$	1-Nitroso-2-naphthol	2.21	624	572	0.096[c]	2.097
						0.149[d]	2.143
2		2-Nitroso-1-naphthol	2.46	593	572		
3		Phenanthrene-9,10-quinonemonooxime	2.38	698	722		
4		5-Methoxy-2-nitrosophenol	2.11	515	512	0.15[c]	2.30
5		5-Methyl-2-nitrosophenol	2.31	480	464		
6		4,5-Dimethyl-2-nitrosophenol	2.41	478	506	0.05[c]	0.80
7	$FeCl(qo)_2$	4,5-Dimethyl-2-nitrosophenol	2.61	800	391		
8		1-Nitroso-2-naphthol	2.45	862	435		
9	$Na[Fe(qo)_3]$	1-Nitroso-2-naphthol	Dia.			0.14[c]	0.82
						0.175[d]	2.34
10	$K[Fe(qo)_3]$	1-Nitroso-2-naphthol	Dia.				

[a] At *ca.* 295 K. [b] Relative to iron. [c] At 300 K. [d] At 77 K.

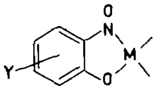
In contrast $Fe(qo)_3$ (qoH = 1-nitroso-2-naphthol) reacted smoothly with aqueous hydrochloric acid, according to equation (1).

$$Fe(qo)_3 + HCl\ aq \rightarrow FeCl(qo)_2 + qoH \qquad (1)$$

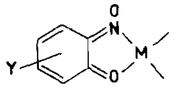
Both products of the reaction were isolated in high yield. The compound $FeCl(qo)_2$ has also been prepared by the reaction of the sodium salt of 1-nitroso-2-naphthol and ferric chloride in acetonitrile. The products, $FeCl(qo)_2$, from both reactions were shown to be identical by i.r. spectroscopy and X-ray powder photography. Reactions of iron chelates with hydrogen chloride, in water or in anhydrous media, are not well known but reactions of type (1) are shown *e.g.* by iron trisdithiocarbomates.[11] In contrast, $Fe(ox)_3$ (oxH = quinolin-8-ol) and hydrogen chloride in diethyl ether give $[oxH_2][FeCl_4]$ and $[oxH_2]Cl$.[12] The complex $Fe(qo)_3$ (qoH = 1-nitroso-2-naphthol) reacts readily with sodium or potassium iodide in acetone to give the iron(II) complex $M[Fc(qo)_3]$ (M = Na or K). Although the reduction of iron(III) compounds by iodide is well known, reduction of iron(III) neutral chelates has not been observed earlier.

Some physical properties of the complexes *1–10* are given in Table I. As may be expected, the complexes $Fe(qo)_3$ are monomeric in chloroform solution and non-electrolytes in acetonitrile. The monomeric nature of $Fe(qo)_3$ (qoH = 5-methoxy-2-nitrosophenol) is also indicated by mass spectrometry. The complexes $FeCl(qo)_2$ are dimeric in chloroform and the complexes $M[Fe(qo)_3]$ (M = Na or K) are 1:1 electrolytes in acetonitrile (M = Na; Λ_∞ = 140 $ohm^{-1}cm^2 mol^{-1}$; M = K; Λ_∞ = 143 $ohm^{-1}cm^2mol^{-1}$). Accepted values for 1:1 electrolytes in acetonitrile = 120–160 ohm^{-1} cm^2 mol^{-1}.[13] Magnetic susceptibility measurements show that the complexes $FeCl_n(qo)_{3-n}$ (n = 1 or 0) have magnetic moments in the range 2.1–2.5 B.M., consistent with low spin iron(III), and that the complexes $M[Fe(qo)_3]$ are diamagnetic indicating that they are low-spin iron(II) compounds. Mössbauer parameters obtained for some of these complexes are in accord with this suggestion.The low-spin configuration of all the complexes suggests that the qo^- ligand exerts a strong ligand field. The electronic spectra of all the complexes were recorded but it was not possible to assign all the *d–d* bands and thus obtain ligand field parameters. In all cases a feature of the electronic spectra is that they include very intense charge transfer or ligand bands which tail into the *d–d* band region. Consequently *d–d* bands, where detectable, appear as shoulders on these intense bands and have very high extinction coefficients.

X-ray crystallographic studies of $Cu(qo)_2 \cdot py$ (qoH = 4-methyl-2-nitrosophenol),[14] $K[Ni(qo)_3] \cdot (CH_3)_2CO$ (qoH = 4-chloro-2-nitrosophenol),[3] and of ferroverdin $K[Fe(qo)_3]$ (qoH = 4-vinylphenyl ester of 3-nitroso-4-hydroxy-benzoic acid)[5] indicate that the NO group is bonded to the metal through the nitrogen atom and that the contribution of the quinone oxime structure (Ib) is significant.



Ia



Ib

X-ray crystallographic studies also indicate that the α-form of 5-methoxy-2-nitrosophenol has the quinone oxime structure.[15] The same structure has been suggested, on the basis of i.r. spectroscopic studies, for 1-nitroso-2-naphthol and 2-nitroso-1-naphthol.[16] The spectrum of each of these protonated ligands and of phenanthrene-9,10-quinone monooxime has a strong band in the region 1620–1680 cm^{-1} which has been

TABLE II. The Mass Spectrum of Compound *4*.

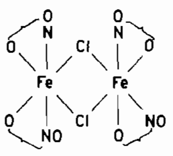
m/e	Abundance[a] (%)	Assignment
512	5	$Fe(qo)_3$
496	0.3	$Fe(qo)_3–O$
480	0.6	$Fe(qo)_3–O_2$
464	0.1	$Fe(qo)_3–O$
374	2	$Fe(qo)_3–C_3H_6O_6$
360	100	$Fe(qo)_2$
347	5	$Fe(qo)_3–C_6H_9N_3O_6$
344	1	$Fe(qo)_2–O$
330	1	$Fe(qo)_2–CH_2O$
329	2	$Fe(qo)_2–CH_3O$
328	0.2	$Fe(qo)_2–O_2$
315	3	$Fe(qo)_2–C_2H_5O$
225	7	$Fe(qo)_2–C_4H_5N_2O_4$
208	3	$Fe(qo)$
192	2	$Fe(qo)–O$
180	5	$Fe(qo)–CO$
150	7	$Fe(qo)–C_2H_3NO_2$

[a] Metal-containing species only; all species are corrected for isotopic abundance and the m/e values are given for the ions containing ^{56}Fe.

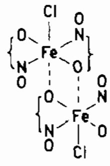
assigned to the ν(C = O) stretching vibration. In the spectra of the iron complexes derived from these ligands this band shifts to *ca.* 1600 cm^{-1} indicating a significant contribution from the quinone oxime structure (Ib) in the complexes. For the complexes derived from the other 2-nitrosophenols the protonated ligands have not been isolated. However, in common with the complexes mentioned above, their i.r. spectra show strong bands at *ca.* 1600 cm^{-1} indicating that structure (Ib) is probably significant in these complexes also.

We have earlier used mass spectrometry to indicate the mode of bonding of the NO group in complexes of 2-nitrosophenols.[2] The spectra of all the $Fe(qo)_3$ and $FeCl(qo)_2$ complexes were recorded. In all cases, except $Fe(qo)_3$ (qoH = 5-methoxy-2-nitrosophenol), the spectra show no metal-containing ions indicating decomposition of the complexes in the mass spectrometer. The spectrum of the complex derived from 5-methoxy-2-nitrosophenol contains several metal-containing ions. These ions, which carry *ca.* 20% of the total ion current, are listed in Table II. The spectrum shows a large number of peaks corresponding to ions resulting from loss of oxygen atoms *e.g.* $[Fe(qo)_3–16]^+$ and $[Fe(qo)_3–32]^+$. Peaks corresponding to ions arising from the loss of oxygen atoms and methoxy side groups or ligand groups are also present *e.g.* $[Fe(qo)_3–(qo + 16)]^+$ and $[Fe(qo)_3–(CH_3O + 48)]^+$. These peaks indicate that the NO group is bonded to the metal through the nitrogen atom. On the basis of i.r. spectroscopic studies it has been suggested that in the complexes $Fe(qo)_3$ (qoH = 1-nitroso-2-naphthol and 2-nitroso-1-naphthol) and other related complexes the bonding involves the oxygen atom of the NO group.[9] However, this interpretion was subsequently questioned.[17] In view of the structure of ferroverdin and the mass spectrometric behaviour of the complex derived from 5-methoxy-2-nitrosophenol bonding through the nitrogen is considered as the most probable for the complexes reported in this paper.

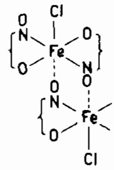
For the complexes $FeCl(qo)_2$ possible structures in solution may involve either bridging chlorines (II) or bridging qo$^-$ ligands (IIIa and IIIb).



II



IIIa



IIIb

In the solid state polymeric structures are also possible. Variable temperature and variable field-strength magnetic susceptibilities of the complexes $FeCl(qo)_2$ show that their magnetic properties are independent of the temperature and field strength. The graphs of χ_A^{-1} against T are linear and give a very small Weiss constant (< 3°) in both cases. These observations suggest that the complexes $FeCl(qo)_2$ are magnetically dilute. For structure type IIIa some systems, such as the dimeric nickel complex $Ni_2(qo)_4$,[1] show strong antiferromagnetic coupling between the metal atoms. The absence of such interaction in the complexes $FeCl(qo)_2$ would exclude structures of type IIIa.

TABLE III. Analytical and Other Data.

Phenol	Product[a]	Colour	Yield (%)	Decomp. Temp.[b] (°C)	Found (%)				Requires (%)			
					C	H	N	Fe	C	H	N	Fe
$2\text{-}C_{10}H_7OH$	*1*	Dark Brown	80	247	63.9	3.3	7.3	9.5	63.2	3.2	7.3	9.8
$1\text{-}C_{10}H_7OH$	*2*	Dark Brown	92	228	63.4	3.3	7.1	10.1	63.2	3.2	9.8	7.3
$3\text{-}MeOC_6H_4OH$	*3*	Green	60	225	48.9	3.7	8.0	11.0	49.2	3.5	8.2	11.0
$3\text{-}MeC_6H_4OH$	*5*	Green	5	272	54.6	4.2	9.2	11.9	54.5	3.9	9.1	12.1
$3,4(Me)_2C_6H_3OH$	*6*	Green	46	312	55.8	4.7	8.3	11.2	56.9	4.7	8.3	11.2

[a] Nos. from Table I. [b] Determined by thermogravimetric analysis.

Further support for this is provided by comparison of the i.r. spectra of pairs of compounds $Fe(qo)_3$ and $FeCl(qo)_2$. Bridging via the ring oxygen would lead to lowering of the $\nu(C = O)$; this is not found. The far i.r. spectra of these pairs of compounds were compared but bands due to Fe–Cl could not be assigned and distinction between structure types (II) and (III) could not be made.

Acknowledgments

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