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Complexes of Nickel(II) with 5-Methoxy-2-nitrosophenol (Mono-oxime of 5-Methoxy-ortho-benzoquinone)

J. CHARALAMBOUS and M. J. KENSETT
Department of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.
and J. M. JENKINS
Explosives Research and Development Establishment, Waltham Abbey, Essex EN9 1BP, U.K.
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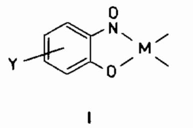
The complexes Ni(5-MeOqo)$_2$, Ni(5-MeOqo)$_2$·2py, Ni(5-MeOqo)$_2$·PhNH$_2$, K[Ni(5-MeOqo)$_3$], Ni(4-Clqo)$_2$·PhNH$_2$ and K[Ni(4-Clqo)$_3$]·(CH$_3$)$_2$CO, where 5-MeOqoH = 5-methoxy-2-nitrosophenol and 4-ClqoH = 4-chloro-2-nitrosophenol, have been prepared. The magnetic susceptibilities, and electronic, i.r. and mass spectra of the complexes have been investigated. In the solid state the pyridine and aniline adducts and the complexes K[Ni(5-MeOqo)$_3$] and K[Ni(4-Clqo)$_3$]·(CH$_3$)$_2$CO contain six coordinate nickel. The complex Ni(5-MeOqo)$_2$ is dimeric in chloroform, in the vapour and in the solid, and presumably contains five coordinate nickel. The pyridine adduct is monomeric in chloroform. The aniline adducts are monomeric at low concentration but Ni(4-Clqo)$_2$·PhNH$_2$ shows some degree of association at higher concentrations. Comparison of the i.r. spectra of the complexes with that of K[(4-Clqo)$_3$Ni]·(CH$_3$)$_2$CO suggests that the NO of the ligand is probably bonded to the metal through the nitrogen atom.

Introduction

Several studies of complexes derived from 2-nitrosophenols have been reported recently[1–6] and the crystal structures of the complexes Cu(qo)$_2$·py (qoH = 4-methyl-2-nitrosophenol),[7] K[Ni(qo)$_3$]·(CH$_3$)$_2$CO (qoH = 4-chloro-2-nitrosophenol)[8] and K[Fe(qo)$_3$] (qoH = 4-vinyl phenyl ester of 3-nitroso-4-hydroxybenzoic acid)[9] have been determined. All the crystallographic studies have indicated that in each case the ring of the ligand shows a pattern of two short and four long bonds, thus demonstrating the significance of structure II in such complexes.



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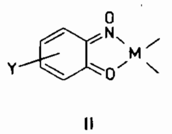


II

This paper presents studies of several types of nickel(II) complexes derived 5-methoxy-2-nitrosophenol (5-MeOqOH) and 4-chloro-2-nitrosophenol (4-ClqoH) and reports i.r. results which can be correlated with the established structure of K[Ni(4-Clqo)$_3$]·(CH$_3$)$_2$CO.[8] Complexes of nickel(II) derived from 5-methoxy-2-nitrosophenol have been reported earlier but only analytical and limited electronic and i.r. spectroscopic data were presented.[10, 11]

Experimental

Nitrosation of 3-Methoxyphenol in the Presence of Nickel Chloride using Sodium Nitrite

Sodium nitrite (17.0 g, 5 mol equiv.) in water was added to a stirred solution of nickel chloride hexahydrate (12.0 g, 1 mol equiv.) sodium acetate (30 g), glacial acetic acid (30 cm^3), and 3-methoxyphenol (12.4 g, 2 mol equiv.) in ethanol–water (2:3) (250 cm^3). The mixture was set aside at 20° C for six days and then an orange solid was filtered off, dried, and extracted (Soxhlet) successively with acetone and chloroform. After removal of the solvent from the chloroform extract and on subsequent heating at 180° C/0.1 mm a residue of orange-brown *bis (5-methoxy-o-benzoquinone-2-oximato)nickel(II)* (4.7 g, 26%; Found: C, 46.6; H, 3.3; N, 7.6; Ni, 16.4. $C_{14}H_{12}N_2NiO_6$ requires: C, 46.4; H, 3.3; N, 7.7; Ni, 16.0%) and a yellow sublimate of 3-methoxy-4-nitrosophenol (0.3 g, 2%), m.p. 175° C dec. (lit.[16] 170° C dec.; Found: C, 54.8; H, 4.6; N, 9.4. Calc. for $C_7H_7NO_3$: C, 54.9; H, 4.6; N, 9.2%; M = 153 (mass), Calc. 153) were obtained. The acetone extract on concentration gave a yellow solid which on subsequent recrystallisation from ethanol (charcoal) gave more 3-methoxy-4-nitrosophenol (20%).

Nitrosation of 4-Chlorophenol and 3-Methoxyphenol in the Presence of Nickel Chloride using Potassium Nitrite

The reactions are outlined below under the appropriate phenol.

4-Chlorophenol

Potassium nitrite (40 g, 12 mol equiv.) in water (200 cm^3) was added to a stirred solution of nickel chloride hexahydrate (10.0 g, 1 mol equiv.) potassium acetate (40 g), glacial acetic acid (40 ml), and 4-chlorophenol (10.4 g, 2 mol equiv.) in ethanol–water–acetone (3:5:1) (900 cm^3). After six days a red solid was filtered off, dried and extracted with acetone. The extract on standing gave red *potassium tris(4-chloro-o-benzoquinone-2-oximato) nickelate (II)–acetone* (2.9 g, 12%; Found: C, 39.8; H, 2.3; Cl, 16.4; N, 6.2; Ni, 8.9. $C_{21}H_{15}Cl_3KN_3NiO_7$ requires: C, 40.4; H, 2.4; Cl, 17.0; N, 6.2; Ni, 9.4%) which was filtered off and dried at 20° C/0.2 mm.

The filtrate on conventration gave bis(4-chloro-*o*-benzoquinone-2-oximato) nickel(II) dihydrate (3.7 g, 22%) (identified by i.r. spectroscopy).

3-Methoxyphenol

A similar reaction carried out with 3-methoxyphenol (2.6 g) yielded on orange solid (2.0 g) (recrystallised from acetone) which was shown to be a mixture of bis(5-methoxy-*o*-benzoquinone-2-oximato)nickel (II) and potassium tris(5-methoxy-*o*-benzoquinone-2-oximato)nickelate(II) by i.r. spectroscopy and thin layer chromatography. Attempts to separate the mixture by further recrystallisation were unsuccessful.

Preparation of Bis(5-methoxy-o-benzoquinone-2-oximato)nickel(II) from 5-Methoxy-2-nitrosophenol

5-Methoxy-2-nitrosophenol (3.2 g, 2.0 mol equiv.) in glacial acetic acid–water (1:1) (100 cm^3) was added to a solution of nickel chloride hexahydrate (1 mol equiv.) in water (150 cm^3) with stirring. After 6 h a solid of indefinite composition was filtered off and dried at 20° C/0.1 mm. The solid on heating at *ca.* 180° C/0.1 mm gave bis(5-methoxy-*o*-benzoquinone-2-oximato)nickel(II) (80%; Found: C, 46.5; H, 3.4; N, 7.7%) (confirmed by i.r. spectroscopy).

Preparation of Potassium Tris(5-methoxy-o-benzoquinone-2-oximato)nickelate(II)

Potassium 5-methoxy-*o*-benzoquinone-2-oximate (0.7 g, 1 mol equiv.) in 9:1 acetone–water (50 cm^3) was added to bis(5-methoxy-*o*-benzoquinone-2-oximato)nickel(II) (1.3 g, 1 mol equiv.) in ethanol (100 cm^3) with stirring. Orange *potassium tris(5-methoxy-o-benzoquinone-2-oximato)nickelate(II)* (1.6 g, 80%; Found: C, 45.4; H, 3.2; N, 7.6; Ni, 11.1. $C_{21}H_{18}KN_3NiO_9$ requires: C, 45.5; H, 3.3; N, 7.6; Ni, 10.6%) was filtered off and dried at 100° C/0.1 mm.

Interaction of Bis(5-methoxy-o-benzoquinone-2-oximato)nickel(II) with Pyridine

Bis(5-methoxy-*o*-benzoquinone-2-oximato(nickel (II) (1.8 g, 1 mol equiv.) in pyridine (75 cm^3) was heated at 100° C. After 0.5 h the mixture was filtered and the filtrate added to light petroleum (40–60° C) (300 cm^3). Orange *bis(5-methoxy-o-benzoquinone-2-oximato)nickel(II)–bispyridine)* (2.0 g, 78%; Found: C, 55.5; H, 4.3; N, 10.9; Ni, 10.8. $C_{28}H_{22}N_2NiO_6$ requires: C, 55.4; H, 4.2; N, 10.8; Ni, 11.3%) was filtered off, washed with light petroleum (40–60° C) and dried at 100° C/0.1 mm.

Interaction of Bis(benzoquinone oximato)nickel(II) Complexes with Aniline

Bis(5-methoxy-*o*-benzoquinone-2-oximato)nickel(II) (3.6 g, 2 mol equiv.) and aniline (2 mol equiv.) in ethanol (200 cm^3) were heated under reflux for 4 h and then allowed to cool slowly. *Bis(5-methoxy-o-benzoquinone-2-oximato) nickel (II)–aniline* (1.9 g, 42%; Found: C, 52.9; H, 4.2; N, 9.3; Ni, 13.3. $C_{20}H_{19}N_3NiO_6$ requires: C, 52.8; H, 4.2; N, 9.2; Ni, 12.9%) was filtered off, washed with ethanol and ether and dried at 100° C/0.1 mm. A similar reaction using bis (4-chloro-*o*-benzoquinone-2-oximato)nickel(II) (3.7 g, 1 mol equiv.) gave *bis(4-chloro-o-benzoquinone-2-oximato)nickel(II)–aniline* (3.8 g, 84%; Found: C, 45.9; H, 2.7; Cl, 15.4; N, 9.4; Ni, 12.8. $C_{18}H_{13}Cl_2N_3NiO_4$ requires: C, 46.6; H, 2.8; Cl, 15.3; N, 9.1; Ni, 12.6%).

Thermogravimetric Analysis

A Stanton thermobalance (model HT-SM), programmed for a linear rise between 20 and 800° C at a rate of 4.5° C/min, was used for thermogravimetric studies. A downward flow of dry nitrogen (5 l/h) was maintained. Results arc given in Table I.

TABLE I. Thermogravimetric Analysis.

Compound	Wt. of Sample (mg)	T/° C[b]	Weight Loss (mg)		Decomposition temperature (° C) of Ni(qo)$_2$[b]
			Found	Calc[c]	
Ni(5-MeOqo)$_2$·2py	98	215	32	30	300
Ni(5-MeOqo)$_2$·PhNH$_2$	124	240	25	25	300
Ni(4-Clqo)$_2$·PhNH$_2$	210	250	41	42	310

[a] Temperature of loss of aniline or pyridine. [b] Maxima on the (rate of weight loss) against temperature curve.

[c] Calc. for 1 mol equiv. of aniline or 2 mol equiv. of pyridine.

Magnetic Measurements

Magnetic susceptibilities were determined by the Gouy method. The moments of all compounds were measured with a permanent magnet (3600 Oe).

Electronic Spectra

Diffuse reflectance spectra of the compounds diluted approximately 1 : 1 (v/v) with MgO and solution sepctra of the compounds in chloroform were recorded with a Unicam SP 700 spectrophotometer.

I.r. Spectra

These were recorded (4000–400 cm^{-1}) with Perkin–Elmer 137 and 237 spectrophotometers for Nujol and hexachlorobutadiene mulls.

Molecular Weights

Molecular weights were determined in chloroform at 37° C with a Merchrolab 301A osometer.

Mass Spectra

The mass spectra were obtained on a Hitachi RMS-4 instrument operating at 70eV and by use of a direct insertion probe at *ca.* 230° C. Exact mass measurements were carried out on AEI-MS9 at the Physicochemical Measurements Unit, Harwell.

Results and Discussion

Nitrosation of 3-methoxyphenol using sodium nitrite yields the neutral complex Ni(5-MeOqo)$_2$ and 3-methoxy-4-nitrosophenol. If potassium nitrite is used instead of sodium nitrite the complex K[Ni(5-MeOqo)$_3$] is also formed in low yield. Nitrosation of 4-chlorophenol using potassium nitrite leads to the hydrated complex Ni(4-Clqo)$_2$ · 2H$_2$O and K[Ni(4-Clqo)$_3$]·(CH$_3$)$_2$CO which yield the complexes Ni(4-Clqo)$_2$ and K[Ni(4-Clqo)$_3$] respectively on heating at 140° C and 220° C. The complex Ni(5-MeOqo)$_2$ has also been obtained directly by the reaction of nickel(II) chloride with 5-methoxy-2-nitrosophenol. In contrast to earlier reports[10, 11] the product obtained initially had indefinite composition but yielded the complex Ni(5-MeOqo)$_2$ on heating. The complex K[Ni(5-MeOqo)$_3$] has also been prepared by the interaction of the potassium salt of 5-methoxy-2-nitrosophenol with Ni(5-MeOqo)$_2$. Complexes prepared by two or more methods were shown to be identical by i.r. spectroscopy.

The complex Ni(5-MeOqo)$_2$ reacts readily with pyridine to give the 1:2 adduct Ni(5-MeOqo)$_2$ · 2py which loses pyridine quantitatively at *ca.* 215° C. Similar behaviour has been observed earlier with the complexes Ni(4-Xqo)$_2$ (X = Cl, Br, CH$_3$, t-C$_4$H$_9$).[2] In contrast the complexes Ni(5-MeOqo)$_2$ and Ni(4-Clqo)$_2$ react with aniline to give 1:1 adducts, which lose aniline quantitatively between 200 and 250° C.

The X-ray structure analysis of the complex K[Ni(4-Clqo)$_3$] · (CH)$_3$)$_2$CO indicates a distorted octahedral arrangement around the nickel(II) atom.[8] The diffuse reflectance spectra (Table II) of the pyridine and aniline adducts of Ni(5-MeOqo)$_2$ and of K[Ni(5-MeOqo)$_3$] are similar to the spectrum of K[Ni(4-Clqo)$_3$] · (CH$_3$)$_2$CO suggesting that in these complexes also the nickel atom is in a distorted octahedral environment. This implies that the aniline adducts are dimeric in the solid state. The spectra show two main bands at 9.0–11.0 and 15.5–18.0 kK which are compatible with the lowest-energy triple–triplet transitions expected for nickel(II) in an approximately octahedral field.[12] Shoulders are observed at *ca.* 7 and 20 kK the latter being on the tail of a very intense absorption at higher energy. The spectrum of the complex Ni(5-MeOqo)$_2$ shows an additional band at 12.5 kK, suggesting that this complex has a different geometry. The spectrum is compatible with five-coordination,[13] compares favourably with the reflectance spectra of the dimeric complexes Ni(4-Xqo)$_2$ (X = Cl, Br, CH$_3$, t-

TABLE II. Some Properties of Ni(II) Complexes Derived from 5-MeOqoH and 4-ClqoH.

Compound	M		μ_{eff}/B.M. (295K)	Reflectance Spectra ν_{max}/kK
	Found	Calc.		
Ni(5-MeOqo)$_2$	875	362	2.57	21.0[b], 17.1, 12.5, 9.8, 7.2[b]
K[Ni(5-MeOqo)$_3$]	–	–	3.17	20.4[b], 16.4, 10.0,7.1[b]
Ni(5-MeOqo)$_2$ · 2py	535	520	2.91	21.5[b], 17.1, 9.3, 7.1[b]
Ni(5-MeOqo)$_2$ · PhNH$_2$	462	455	2.87	20.4[b], 15.0, 10.4, 7.1[b]
Ni(4-Clqo)$_2$ · PhNH$_2$	394(0.13)[a] 499(0.42) 647(0.84)	464	2.76	18.7, 8.8, 7.2[b]
K[Ni(4-Clqo)$_3$] · (CH$_3$)$_2$CO	–	–	2.88	18.7, 8.9, 7.1[b]

[a] Wt. (g) of sample/100 cm^3 solvent. [b] Shoulder.

$C_4H_9)^2$ and suggests that the complex Ni(5-MeOqo)$_2$ is also dimeric.

Molecular weight measurements (Table II) indicate that the complex Ni(5-MeOqo)$_2$ is dimeric and its pyridine adduct monomeric in chloroform. The complexes Ni(5-MeOqo)$_2$ · PhNH$_2$ and Ni(4-Clqo)$_2$ · PhNH$_2$ are monomeric at low concentrations but the latter, which is sufficiently soluble to enable measurements to be taken over a range of concentrations, shows some degree of association at higher concentrations. The solution spectra of all the compounds were recorded, with the object of gaining further information about their structure in solution. However, because *d–d* bands are obscured by charge transfer bands, which tail into the visible region, no structural information was forthcoming. The *d–d* bands usually appear as poorly resolvable shoulders and have high extinction coefficients compared with those normally observed for *d–d* transitions.

In the solid state further evidence for the structures of the complexes Ni(5-MeOqo)$_2$ · PhNH$_2$, K[Ni(5-MeOqo)$_3$] and Ni(4-Clqo)$_2$ · PhNH$_2$ has been obtained from studies of their magnetic moments of the pyridine adduct and of the complex K[Ni(5-MeOqo)$_3$] are as expected for a magnetically dilute complex of octahedral symmetry (Table II). The complex Ni(5-MeOqo)$_2$ and the aniline adducts have subnormal moments at room temperature, consistent with the proposed dimeric structures for these compounds.

The mass spectrum of Ni(5-MeOqo)$_2$ (Table III) provides convincing evidence for the presence of a dimer [Ni(5-MeOqo)$_2$]$_2$ in the vapour state. The spectrum shows a fragment of m/e greater than that of the monomer Ni(5-MeOqo)$_2$, whose isotope pattern indicates a dimetallic species. The fragmentation pattern of this complex resembles that of the complexes Ni(4-xqo)$_2$ (X = Cl, Br, CH$_3$ and t-C$_4$H$_9$)[2,3] in exhibiting elimination of radicals such as NO, qo and even-electron molecules such as CO. In addition but not unexpectedly there are several reactions involving the methoxy group.

In complexes derived from 2-nitrocophenols the NO group may coordinate to the metal through either the nitrogen atom or the oxygen atom. X-ray crystallographic studies indicate that in the complexes K[Ni(4-Clqo)$_3$] · (CH$_3$)$_2$CO, Cu(4-Meqo)$_2$ · py and ferroverdin the ligand is bonded to the metal through the nitrogen. The i.r. spectra (Table IV) of the compounds reported here are similar (1300–900 cm^{-1}, i.e. the region of νNO) to the spectrum of K[Ni(4-Clqo)$_3$] · (CH$_3$)$_2$CO suggesting that in these complexes also the bonding involves the nitrogen of the NO group. In the i.r. spectrum of α-form of 5-methoxy-2-nitrosophenol, which is known from X-ray crystallographic studies to have the *o*-quinone mono-oxime structure,[14] the νCO is observed at 1650 cm^{-1}. In the complexes Ni(5-MeOqo)$_2$ and K[Ni(5-MeOqo)$_3$] the νCO shifts to *ca.* 1600 cm^{-1}. The spectra of the complexes Ni(5-MeOqo)$_2$ and Ni(5-MeOqo)$_2$ PhNH$_2$ are more complex than those of K[Ni(5-MeOqo)$_3$] and Ni(5-MeOqo)$_2$ · 2py in this region. This complexity is most probably due to the presence of qo$^-$ groups which are not only involved in chelation but also in intermolecular bridging (III). The same trend is observed in the analogous series of complexes derived from 4-chloro-2-nitrosophenol (Table IV) and in other similar series of complexes.[15]

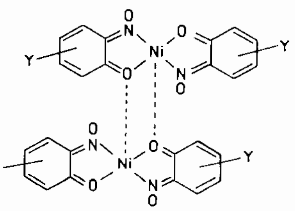
TABLE III. Ion Abundances[a] for Ni(5-MeOqo)$_2$.

Ion	m/e[b]	Relative Abundance
[Ni(5-MeOqo)$_2$]$_2$–64	660[d]	1
Ni(5-MeOqo)$_2$ ^{1,2c}	362[e]	100
Ni(5-MeOqo)$_2$–15	347	2
Ni(5-MeOqo)$_2$–28	334	<1
Ni(5-MeOqo)$_2$–30	332[f]	1
Ni(5-MeOqo)$_2$–32	330[g]	<1
Ni(5-MeOqo)$_2$–43	319	1
Ni(5-MeOqo)$_2$–45	317	1
Ni(5-MeOqo)$_2$–58 ^{1,3}	304	8
Ni(5-MeOqo)$_2$–73 ^{2,3}	289	2
Ni(5-MeOqo)$_2$–86	276	18
Ni(5-MeOqo)$_2$–101	261	8
Ni(5-MeOqo)	210	13
Ni(5-MeOqo)–28	182	7
Ni(5-MeOqo)–58	152	21

[a] Metal-containing ions only are recorded. [b] The m/e values given are for ions containing ^{58}Ni. [c] Italicized number superscripts indicate identified metastable transitions and relate the daughter ion to its precursor. [d] Found, 660.0295 (calc. 660.0300). [e] Found, 362.0044 (calc. 362.0040). [f] Found, 332.0107 (calc. 332.0105). [g] Found, 330.0147 (calc. 330.0151).

TABLE IV. Infrared Absorptions in the Region 1700–1470 cm^{-1}.

Compound	ν, cm^{-1}				
K[Ni(4-Clqo)$_3$] · (CH$_3$)$_2$CO	1612	1535	1510		
Ni(4-Clqo)$_2$ · 2py	1603	1530	1500		
Ni(4-Clqo)$_2$	1610	1545	1520	1485	
K[Ni(5-MeOqo)$_3$]	1600	1530	1510		
Ni(5-MeOqo)$_2$ · 2py	1605	1550	1540	1500	
Ni(5-MeOqo)$_2$	1600	1555	1540	1530	1485



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Acknowledgements

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