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Complexes of Nickel(II) with 1-Nitroso-2-naphthol and 2-Nitroso-1-naphthol (Monooximes of 1,2-Naphthoquinones)

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The complexes $Ni(nqo)_2$, $Ni(nqo)_2 \cdot 2NH_3$, $Ni(nqo)_2 \cdot 2py$ *and* $Na[Ni(nqo)_3]$, *where nqoH = 1-nitroso-2-naphthol or 2-nitroso-1-naphthol, have been prepared. The magnetic susceptibilities and electronic and mass spectra of the complexes have been investigated. The complexes* $Ni(nqo)_2$ *show some degree of association the extent of which depends on the method used for their preparation.*

Introduction

Complex formation of nickel(II) with 1-nitroso-2-naphthol (1-nqoH) and 2-nitroso-1-naphthol (2-nqoH) (the abbreviation nqoH will be used to denote either 1-nqoH or 2-nqoH) has been investigated earlier [1] but apart from a recent investigation by Gurrieri and Siracusa [2], the study of the composition and properties of the products has received little attention. In previous papers we have described complexes of 2-nitrosophenols with copper(II) [3–5], nickel(II) [4–7], iron(II) and iron(III) [5–8]. In continuation of these studies this paper reports some complexes of nickel(II) derived from 1-nitroso-2-naphthol and 2-nitroso-1-naphthol.

Experimental

Analytical data are given in Table I.

Interaction of 1-Nitroso-2-naphthol with Nickel Chloride

Gurrieri and Siracusa method [2]

1-Nitroso-2-naphthol (8.0 g, 2.4 mol equiv) in ethanol–water (1:1) (400 cm^3) was added dropwise with stirring to a solution of nickel chloride hexahydrate (4.5 g, 1 mol equiv) in water (200 cm^3). After 48 h bis(2-naphthoquinone-1-oximato)nickel(II) (7.2 g, 91%) (Solid A) was filtered off, washed with water (3 × 100 cm^3) and ethanol (3 × 100 cm^3), extracted (Soxhlet) with methanol until extracts were very pale orange, and dried at 20 °C/0.1 mm.

At pH = 10

1-Nitroso-2-naphthol (4.3 g, 2 mol equiv) in ethanol (250 cm^3) was added dropwise with stirring to a

TABLE I. Analytical and Magnetic Data.

No.	Formula	μ_{eff}/B.M. (*ca.* 295 K)	Found (%)				Requires (%)			
			C	H	N	Ni	C	H	N	Ni
1	$Ni(1\text{-}nqo)_2$ (Solid A)	2.67	59.3	3.2	6.9	14.4	59.6	3.0	7.0	14.5
2	$Ni(1\text{-}nqo)_2$ (Solid B)	2.69	59.6	3.0	6.9	14.3	59.6	3.0	7.0	14.5
3	$Ni(1\text{-}nqo)_2 \cdot 2NH_3$	3.21	54.4	4.7	13.3	13.3	55.0	4.1	12.8	13.4
4	$Ni(1\text{-}nqo)_2 \cdot 2py$	3.32	64.6	3.9	10.3	10.2	64.2	3.9	10.0	10.4
5	$Na[Ni(1\text{-}nqo)_3]$	2.97	60.9	3.2	7.1	9.7	60.3	3.0	7.0	9.8
6	$Ni(2\text{-}nqo)_2$ (Solid C)	2.46	59.2	3.1	7.0	14.6	59.6	3.0	7.0	14.5
7	$Ni(2\text{-}nqo)_2$ (Solid D)	2.55	59.3	2.9	7.2	14.2	59.6	3.0	7.0	14.5
8	$Ni(2\text{-}nqo)_2 \cdot 2NH_3$	3.15	54.8	4.2	13.0	13.1	55.0	4.1	12.8	13.4
9	$Ni(2\text{-}nqo)_2 \cdot 2py$	3.44	64.4	4.1	10.0	9.7	64.2	3.9	10.0	10.4
10	$Na[Ni(2\text{-}nqo)_3]$	3.07	60.3	3.0	7.1	9.3	60.3	3.0	7.0	9.8

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solution of nickel chloride hexahydrate (3.0 g, 1 mol equiv) and ammonium acetate (30 g), in ethanol–water (2:3) (500 cm^3) which had been brought to pH 10 with ammonium hydroxide. After 48 h *bis-(2-naphthoquinone-1-oximato)diamminenickel(II)* (4.8 g, 89%) was filtered off, washed with water (3 × 100 cm^3) and ethanol (3 × 100 cm^3), extracted (Soxhlet) with methanol until extracts were very pale orange, and dried at 100 °C/0.1 mm.

Interaction of 2-Nitroso-1-naphthol with Nickel Chloride

Gurrieri and Siracusa method

2-Nitroso-1-naphthol (4.0 g, 2.4 mol equiv) in ethanol–water (1:1) (200 cm^3) was added dropwise with stirring to a solution of nickel chloride hexahydrate (2.2 g, 1 mol equiv) and concentrated aqueous ammonia (0.2 cm^3) in water (100 cm^3). After 48 h bis(1-naphthoquinone-2-oximato)nickel(II) (3.2 g, 86%) (Solid C) was filtered off, washed with water (3 × 100 cm^3) and ethanol (3 × 100 cm^3), extracted (Soxhlet) with methanol until extracts were very pale orange, and dried at 20 °C/0.1 mm.

At pH = 10

2-Nitroso-1-naphthol (4.3 g, 2 mol equiv) in ethanol (200 cm^3) was added dropwise with stirring to a solution of nickel chloride hexahydrate (3.0 g, 1 mol equiv) and ammonium acetate (30 g), in ethanol–water (1:2) (500 cm^3) which had been brought to pH 10 with ammonium hydroxide. After 48 h *bis(1-naphthoquinone-2-oximato)diamminenickel(II)* (4.4 g, 82%) was filtered off, washed with water (3 × 100 cm^3) and ethanol (6 × 150 cm^3), extracted (Soxhlet) with methanol until last extracts were very pale orange, and dried at 100 °C/0.1 mm.

Pyrolysis of Bis(naphthoquinone oximato)diamminenickel(II)

Bis(2-naphthoquinone-1-oximato)diamminenickel(II) (3.1 g) was heated at 200–250 °C/0.1 mm for 1 h. Bis(2-naphthoquinone-1-oximato)nickel(II) (2.9 g, 92%) (Solid B) was obtained, washed with ether (6 × 100 cm^3), extracted (Soxhlet) with methanol until extracts were very pale orange, and dried at 100 °C/0.1 mm.

Similarly, bis(1-naphthoquinone-2-oximato)diamminenickel(II) (3.5 g) gave bis(1-naphthoquinone-2-oximato)nickel(II) (3.3 g, 87%) (Solid D).

Interaction of Bis(naphthoquinone oximato)nickel(II) with Pyridine

Bis(2-naphthoquinone-1-oximato)nickel(II) (Solid A) (2.8 g) was heated under reflux with pyridine (80 cm^3) for 3 h. The clear solution was concentrated (10 cm^3), diethyl ether (100 cm^3) was added with stirring and orange-brown *bis(2-naphthoquinone-1-oximato)nickel(II)-dipyridine* (3.2 g, 82%) was filtered off, washed with ether (4 × 150 cm^3) and dried at 100 °C/0.1 mm. A similar reaction using Solid B gave a product with similar analyses, identical X-ray powder diffraction patterns, and identical i.r. spectra to that of the product obtained from Solid A.

Similarly, bis(1-naphthoquinone-2-oximato)nickel(II) (Solid C) gave *bis(1-naphthoquinone-2-oximato)-nickel(II)-dipyridine* (80%). Solid D gave under similar conditions a product with similar analyses, identical X-ray powder diffraction patterns, and identical i.r. spectra to that of the product obtained from Solid C.

Synthesis of Sodium Tris(naphthoquinone oximato)-nickelate(II)

Bis(2-naphthoquinone-1-oximato)nickel(II) (Solid A) (3.1 g, 1 mol equiv) was heated under reflux with sodium 2-naphthoquinone-1-oximate (1.5 g, 1 mol equiv) in methanol (150 cm^3) for 9 h. *Sodium tris-(2-naphthoquinone-1-oximato)nickelate(II)* (4.1 g, 88%) was filtered off, washed with boiling methanol (3 × 200 cm^3) and dried at 100 °C/0.1 mm. A similar reaction using Solid B gave a product with similar analyses, identical X-ray powder diffraction patterns,

TABLE II. Thermogravimetric Analysis.

Compound No[a]	Wt. of Sample (mg)	T/°C[b,c]	Weight Loss (mg)		Decomposition Temperature (°C) of Ni(nqo)$_2$
			Found	Calc[d]	
3	102	205	8	8	330
4	97	200	29	27	335
8	107	230	8	8	320
9	81	220	22	23	315

[a] Nos. from Table I. [b] Temperature of loss of ammonia (3,8) or pyridine (4,9). [c] Maxima on the (rate of weight loss) against temperature curve. [d] Calc. for 2 mol equiv of ammonia or pyridine.

and identical i.r. spectra to that of the product obtained from Solid A.

Similarly, bis(1-naphthoquinone-2-oximato)nickel(II) (Solid C) gave *sodium tris(1-naphthoquinone-2-oximato)nickelate(II)* (63%). Solid D gave under similar conditions a product with similar analyses, identical X-ray powder diffraction patterns, and identical i.r. spectra to that of the product obtained from Solid C.

Measurements

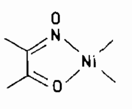
X-ray powder pattern photographs, thermogravimetric analysis data (Table II), magnetic susceptibility data, and i.r., electronic and mass spectra were obtained as described earlier [6, 8].

Results and Discussion

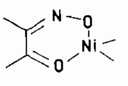
Gurrieri and Siracusa reported the synthesis of a complex of formula $Ni(1\text{-}nqo)_2 \cdot 2H_2O$ [2]. This was obtained by the interaction of 1-nitroso-2-naphthol with nickel chloride in aqueous ethanol. Although only limited experimental details were given the preparation of this complex was attempted by the route indicated. However, such attempts always led to a product for which elemental analysis suggested the formula $Ni(1\text{-}nqo)_2$ (Solid A). The absence of water in the product, which was dried at 20 °C, was also indicated by i.r. spectroscopy and thermogravimetric analysis. In the present work we have also investigated the interaction of nickel chloride with 1-nitroso-2-naphthol in the presence of ammonium hydroxide and ammonium acetate. Under these conditions the complex $Ni(1\text{-}nqo)_2 \cdot 2NH_3$ was obtained initially which on heating at *ca.* 200°/0.1 mm afforded a complex of composition $Ni(1\text{-}nqo)_2$ (Solid B). The i.r. spectrum and X-ray powder pattern of this solid were different from those of Solid A obtained directly from 1-nitroso-2-naphthol and nickel chloride. Furthermore the magnetic behaviour of Solids A and B were different. These differences suggest that there are two or more different forms of $Ni(1\text{-}nqo)_2$ either in terms of crystal packing or different molecular structures.

In complexes of type $Ni(1\text{-}nqo)_2$ several different structures are possible because (a) the NO group may be bonded to the metal either through the nitrogen atom (I) or through the oxygen atom (II) and (b) association of $Ni(1\text{-}nqo)_2$ units to give dimeric or polymeric species may occur (*e.g.* III). Added to these there is the possibility of isomeric structures due to the asymmetric nature of the ligand.

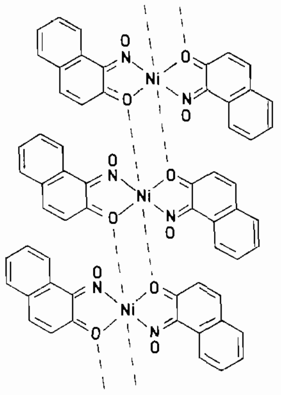
Both solids A and B on treatment with the sodium salt of 1-nitroso-2-naphthol, gave the complex $Na[Ni(1\text{-}nqo)_3]$ and on heating with pyridine gave the complex $Ni(1\text{-}nqo)_2 \cdot 2py$. Furthermore both solids have very similar mass spectra. These observations eliminate the possibility of linkage isomerism as the reason for the different nature of the solids A and B, and suggest that most probably their different nature is due to differences in the extent of association of the unit $Ni(1\text{-}nqo)_2$.



I



II



III

Because of insolubility in non-disruptive organic solvents no conclusions regarding association could be drawn from molecular-weight measurements. However, magnetic susceptibility measurements of the solids A and B and studies of their mass spectra indicate that association of the unit $Ni(1\text{-}nqo)_2$ occurs in both cases.

Analogous behaviour was also observed in the case of the system 2-nitroso-1-naphthol/nickel chloride. Thus interaction of 2-nitroso-1-naphthol and nickel chloride in aqueous ethanol, according to the method of Gurrieri and Siracusa, led to a complex of formula $Ni(2\text{-}nqo)_2$ (Solid C). In the presence of ammonium hydroxide and ammonium acetate the system 2-nitroso-1-naphthol/nickel chloride gave initially the complex $Ni(2\text{-}nqo)_2$, $2NH_3$ which on heating at *ca.* 200°/0.1 mm gave a solid of formula $Ni(2\text{-}nqo)_2$ (Solid D) whose i.r. spectrum and X-ray powder pattern were different from those of Solid C. Both the solids C and D on heating with pyridine afforded complexes of formula $Ni(2\text{-}nqo)_2 \cdot 2py$ which were shown to be identical by i.r. spectroscopy and X-ray powder photography. Furthermore, solids C and D on treatment with the sodium salt of 2-nitroso-1-naphthol gave the same product, ($Na[Ni(2\text{-}nqo)_3]$) and both solids have very similar mass spectra.

The room-temperature magnetic moments (Table I) of the complexes $Ni(nqo)_2 \cdot 2NH_3$, $Ni(nqo)_2 \cdot 2py$ and $Na[Ni(nqo)_3]$ lie between 3.0–3.4 B.M. and are within the range expected for nickel(II) in an approximately octahedral field.

In contrast the room-temperature magnetic moments of the complexes $Ni(nqo)_2$ are subnormal being in the range 2.5–2.6 B.M. which indicates the presence of an overall antiferromagnetic interaction between adjacent nickel atoms. Susceptibility measurements have been recorded at temperatures between 300–99 K on several different samples of the complexes which were obtained from the two methods of preparation. Unfortunately it was not possible to reproduce exactly the susceptibilities for each compound and the results quoted below are the average values of several series of measurements. However, the decreasing magnetic moment with temperature and the large negative Weiss constant (*ca.* −150 K) supports the antiferromagnetic behaviour of the complexes within the temperature range used and indicate association of $Ni(nqo)_2$ units.

Further evidence for association is provided by mass spectrometry. The mass spectra of the compounds A and C are given in Table III. The spectra of the compounds B and D were very similar to those of A and B respectively and are not presented in the tables. In all cases the peak with highest m/e value corresponds to $[Ni_2(nqo)_4 - 64]^+$ and there is a peak corresponding to $[Ni_2(nqo)_3]^+$. Such species whose dimetallic nature is clearly indicated by their isotopic pattern suggest that the compounds have some degree of association in the vapour state. Similar ions have also been observed in the spectra of several nickel(II) complexes derived from 2-nitrosophenols. The fragmentation pattern of the compounds $Ni(nqo)_2$ resembles that of 2-nitrosophenol complexes [4, 7, 8] in exhibiting loss of ligand radicals and elimination of ligand fragments duch as O, CO and NO (Scheme).

The presence of peaks corresponding to loss of oxygen from $[Ni_2(nqo)_4]^+$ and $[Ni(nqo)_2]^+$ suggests

$Ni(1\text{-}nqo)_2$ (Solid A)

T (°K)	333.5	299.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8
$10^6 \chi_A$	2713	2994	3075	3157	3317	3519	3615	3734	3765
μ_{eff}	2.69	2.67	2.59	2.49	2.40	2.30	2.12	1.96	1.73

$Ni(1\text{-}nqo)_2$ (Solid B)

T (°K)	333.5	299.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8
$10^6 \chi_A$	2817	3013	3135	3991	3498	3681	3850	3989	4056
μ_{eff}	2.74	2.69	2.62	2.55	2.46	2.35	2.19	2.02	1.79

$Ni(2\text{-}nqo)_2$ (Solid C)

T (°K)	333.5	299.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8
$10^6 \chi_A$	2363	2526	2590	2714	2910	2910	3152	4151	5182
μ_{eff}	2.51	2.46	2.38	2.31	2.25	2.17	2.10	2.06	2.02

$Ni(2\text{-}nqo)_2$ (Solid D)

T (°K)	333.5	299.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8
$10^6 \chi_A$	2564	2704	2825	2970	3184	3360	3645	4031	4568
μ_{eff}	2.62	2.55	2.49	2.42	2.35	2.24	2.13	2.03	1.90

Scheme. Illustration of Elimination of Ligand Fragments in $Ni(nqo)_2$.

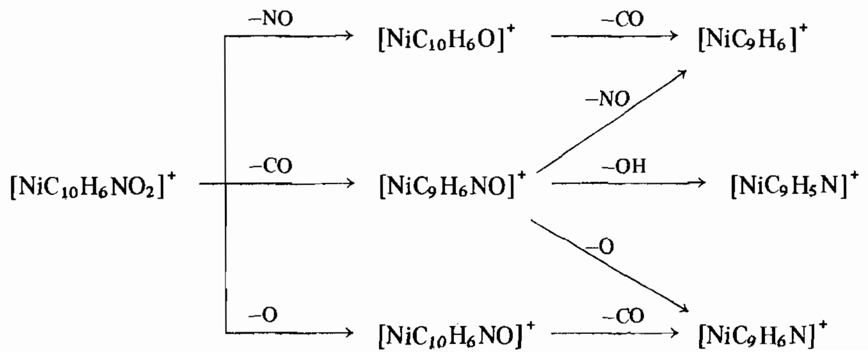


TABLE III. Ion Abundances[a] for $Ni(nqo)_2$.

Ion	m/e	$Ni(1\text{-}nqo)_2$[b] (%)	$Ni(2\text{-}nqo)_2$ (%)	Assignment
$[Ni_2(nqo)_4 - 64]^+$	740	2	2	$C_{40}H_{24}N_4O_4Ni$
$[Ni_2(nqo)_3]^+$	632	2	3	$C_{30}H_{18}N_3O_6Ni$
$[Ni(nqo)_2]^+$	402^{1}[c]	100	100	$C_{20}H_{12}N_2O_4Ni$[d]
$[Ni(nqo)_2 - 30]^+$	372	2	1	$C_{20}H_{12}NO_3Ni$
$[Ni(nqo)_2 - 32]^+$	370	14	2	$C_{20}H_{12}N_2O_2Ni$
$[Ni(nqo)_2 - 58]^+$	$344^{1,2}$	50	55	$C_{19}H_{12}NO_2Ni$
$[Ni(nqo)_2 - 86]^+$	316^{2}	10	26	$C_{18}H_{12}NONi$
$[Ni(nqo)_2 - 90]^+$	312	8	15	$C_{18}H_{10}N_2Ni$
$[Ni(nqo)]^+$	230^{3}	18	–	$C_{10}H_6NO_2Ni$[d]
$[Ni(nqo) - 28]^+$	202	15	4	C_9H_6NONi
$[Ni(nqo) - 30]^+$	200	15	4	$C_{10}H_6ONi$
$[Ni(nqo) - 44]^+$	186	60	16	C_9H_6NNi
$[Ni(nqo) - 45]^+$	185^{3}	70	12	C_9H_5NNi[d]
$[Ni(nqo) - 58]^+$	172	90	24	C_9H_6Ni[d]
$[Ni]^+$	58	12	10	

[a] Metal-containing species only; all species are corrected for isotopic abundance and the m/e values are given for the ions containing ^{58}Ni. [b] The spectrum also contains metal-containing peaks at m/e 290 (28%), 282 (50%), 255 (20%), 252 (15%). [c] Number superscripts indicate identified metastable transitions and relate the daughter ion to its precursor. [d] Confirmed by exact mass measurements.

that in the complexes $Ni(nqo)_2$ the NO group of the ligand is bonded to the metal through the nitrogen atom (I). This conclusion contrasts with an earlier suggestion [2], based on interpretation of i.r. spectra, stating that in the complexes $M(nqo)_2$ (M = Ni, Cu, Mn) the bonding of the ligand to the metal involves the oxygen of the NO group (II). However, X-ray crystallographic studies of several complexes of 2-nitrosophenols [5] and especially recent structure determinations of copper complexes of nitrosonaphthols [10] indicate M–N bonding and cast doubts on the conclusions drawn from the i.r. data.

The diffuse reflectance spectra of all the complexes were recorded. In all cases the presence of strong absorption at low energies, due to change transfer or ligand bands, rendered the spectra useless as diagnostic tools for probing the coordination environment of the metal.

Acknowledgements

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