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Nickel(II) and palladium(II) complexes of some *ortho*-quinone monoximes. A study of the monomer–dimer equilibrium involving the nickel complexes

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Abstract

Two series of palladium(II) complexes of *o*-benzoquinone monoximes, [Pd(qo)$_2$] and [Pd(qo)Cl]$_2$, are described where qo represents the anion of the *o*-benzoquinone-2-oximes. The ligands bear the following substituents: 4-Me-6-Bu^t, 4-Bu^t-6-Me, 4,6-diBu^t and 4-CMe$_2$Ph. The dimeric complexes are new examples of μ-dichloro compounds. The temperature and concentration dependent equilibria shown by the [Ni(qo)$_2$] compounds in non-coordinating solvents are shown for the first time to involve only paramagnetic red dimers and diamagnetic green monomers. The substituents in these Ni(II) complexes are 4-Me, 4-Cl, 4-Bu^t, 4,6-diMe and 4,6-diBu^t. Some of the equilibrium constants, enthalpies and entropies of dissociation are calculated. The techniques used include electronic spectra, ^{1}H NMR and magnetic susceptibility determinations. Some of the parent nitrosophenols are characterised by their UV, IR and ^{1}H NMR spectra.

Introduction

The syntheses of several palladium(II) [1] and nickel(II) [2–4] complexes of *o*-nitrosophenols** have been described. Their IR spectra, especially the presence of ν(C=O), indicate that the ligands have the *o*-benzoquinone-monoxime structure which has been proved by X-ray diffraction crystal structure determination to occur in several similar metal complexes [6].

The association between the [Ni(qo)$_2$] units is indicated by the paramagnetism [4] of the solids, molecular weight determination [4] in chloroform solution and the presence of some binuclear species in the mass spectrum [4, 7]. An unexplained reversible red to green colour change has been reported [3] to occur on heating benzene, but not ethanol, solutions of [Ni(qo)$_2$].

Many examples of equilibria involving Ni(II) bis-chelates are known [8]. The compounds nearest in type to those discussed here are the NiN$_2$O$_2$ complexes typified by the Ni bis salicylaldimines and the Ni bis β-ketoimino compounds. In none of these compounds is the equilibrium the one found here which involves dimers and monomers only.

Experimental

Preparation of 2-nitrosophenols

Method 1, via the decomposition of the copper(II) complex [9], was used to prepare 4,6-diBu^t-2-NOphenol (yield 48%), 4-Bu^t-6-Me-2-NOphenol (yield 50%), 6-Bu^t-4-Me-2-NOphenol† (yield 50%) and 4-CMe$_2$Ph-2-NOphenol (yield 45%).

Method 2, via the nitrite ester nitrosation of the potassium salt of the phenol [10], was used to prepare potassium 4,5-diMe-2-NOphenolate (yield 57%). The same method applied to 4-chloro- and 4-chloro-5-methylphenol gave less pure products which nevertheless gave pure nickel complexes.

Palladium(II) chelates

[Pd(qo)$_2$] (**1**–**4**) were prepared by adding the nitrosophenol (0.002 mol) in ethanol to a stirred solution of dichlorodibenzonitrilepalladium(II) [11] (0.38 g, 0.001 mol). After stirring for 14 h at room temperature the

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**The use of this more familiar name for the protonated ligand is justified by the existence of tautomerism [5]. 6-Bu^t-4-Me-*o*-benzoquinone-2-oxime and 6-Bu^t-4-Me-2-nitrosophenol are tautomers. The abbreviation qo represents the anion.

†The potassium salt of this phenol is reported in ref. 10.

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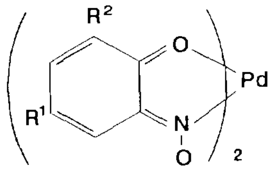
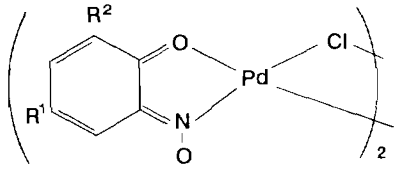
black precipitate was washed with ethanol, recrystallised from ethanol and dried *in vacuo* over phosphoric anhydride.



1–4



5–8

	R^1	R^2
1 and **5**	Me	Bu^t
2 and **6**	Bu^t	Me
3 and **7**	Bu^t	Bu^t
4 and **8**	CMe_2Ph	H

Palladium(II)-μ-dichloro complexes

$[Pd(qo)Cl]_2$ (**5–8**) were prepared by adding a chloroform solution of the 2-nitrosophenol (0.0021 mol) dropwise, with stirring, to a suspension of $PdCl_2$ (0.35 g, 0.0020 mol) in chloroform at room temperature. After 48 h the suspension was filtered, the filtrate concentrated and an excess of dry ether was added. The blue-green product was dried at 20 °C/1 mm Hg over phosphoric anhydride.

Nickel(II) chelates

$[Ni(4\text{-}Meqo)_2]$, $[Ni(4\text{-}Clqo)_2]$, $[Ni(4\text{-}Bu^tqo)_2]$ and $[Ni(4,6\text{-}diMeqo)_2]$ were prepared by the method described by Charalambous *et al.* [4].

$[Ni(4\text{-}Cl\text{-}5\text{-}Meqo)_2]$. Potassium 4-Cl-5-Me-2-nitrosophenolate (1.05 g, 5 mmol) in water (150 cm^3) was added to a stirred solution of nickel chloride hexahydrate (0.57 g, 2.5 mmol) in water (150 cm^3). The resultant dihydrate was filtered off, washed with H_2O, EtOH and dried over phosphoric anhydride. The anhydrous product was obtained by drying at 130 °C/1 mm Hg.

$[Ni(4,6\text{-}diBu^tqo)_2]$. A solution of 4,6-diBu^t-2-NO-phenol (0.50 g, 2.1 mmol) in ethanol (50 cm^3) was added to a stirred solution of nickel chloride hexahydrate (0.273 g, 1.0 mmol) in ethanol (50 cm^3). After 12 h at room temperature an excess of distilled water was added, the product filtered off and dried over phosphoric anhydride at 110 °C/2 mm Hg.

Analytical and physical data

Elementary analyses were carried out in the microanalytical laboratories of this department. The UV–Vis spectra were recorded on Beckman Acta Mark IV and Perkin-Elmer Lambda 15 machines, $\epsilon \pm 1\%$. The variable temperature results were obtained using either machine and a Beckman RIIC Tem 2 unit, $T \pm 1$ °C. ^1H NMR spectra were recorded on a Perkin-Elmer R34 spectrometer (220 MHz) and the variable temperature results, $T \pm 4$ °C, on a Bruker WP 80 (80 MHz). This latter was also used in Evan's method [16] to determine the temperature dependency of the magnetic susceptibility of $[Ni(4,6\text{-}diBu^tqo)_2]$ in toluene solution. IR spectra were recorded on Perkin-Elmer 735 and 783 spectrophotometers using Nujol or HCB mulls. The 100–500 cm^{-1} region was recorded on a Beckman IR 720M using Nujol mulls on polythene discs. The molecular weights were determined in chloroform at 37 °C using a Perkin-Elmer Hitachi model 115 molecular weight apparatus.

Results and discussion

UV spectra

Table 1 illustrates the many similarities between the spectra of two nickel(II) chelates in toluene solution at 70 °C and those of square planar palladium(II) chelates. The spectra of the nickel(II) chelates also resemble those of NiN_2O_2 bis chelates of known square planar geometry. There are absorbances at 617 and 630 nm in this work, 585–606 nm in β-ketoamines [12] and 615–640 nm in salicylaldimines [13]; there are absorbances at 485 and 480 nm in this work, 481–490 nm in β-ketoamines chelates and shoulders at 470 and 490 nm in salicylaldimine chelates.

IR spectra

All the compounds show the characteristic ν(CO) absorptions: 1614–1600 cm in the palladium chelates, 1620 cm^{-1} in the nickel chelates. In addition the [Pd(qo)Cl] complexes also exhibit absorptions in the region of 300 cm^{-1} characteristic [14] of chlorine-bridged binuclear complexes. These are therefore formulated $[Pd_2(\mu\text{-}Cl)_2(qo)_2]$. The individual absorptions are 314 and 282 cm^{-1} for compound **5**; 290 and 298 cm^{-1} for compound **6**; 285(br) cm^{-1} for compound **7**; 290 and 280 cm^{-1} for compound **8**.

Equilibrium studies

The $[Ni(qo)_2]$ complexes are associated in chloroform solution. In this work the degree of polymerisation (osmometric) was found to be *c*. 2 for the 4-Bu^t chelate. These solutions are red in colour. A molecular weight determination using the Rast method [15] showed [Ni(4-

TABLE 1. UV spectra of the *o*-benzoquinone-2-monoximate complexes $[\mathrm{Pd(qo)_2}]$, $[\mathrm{Pd(qo)Cl}]_2$ and $[\mathrm{Ni(qo)_2}]^a$

Compound	R^1	R^2	Absorption maxima (nm) (ε (10^2 $mol^{-1}m^2$))					
1	Me	Bu^t	700sh (3.2)^b	605 (4.6)	560sh (3.8)	456 (4.0)	383 (22.8)	370sh (18.0)
5	Me	Bu^t	672sh (3.6)^c	604 (4.6)			380sh (17.6)	350 (23.1)
2	Bu^t	Me	700sh (3.0)	597 (4.8)	550sh (4.0)	480sh (4.0)	385 (26.8)	366sh (11.7)
6	Bu^t	Me	680sh (3.0)	602 (4.2)			380sh (15.6)	353 (20.2)
3	Bu^t	Bu^t	680sh (4.2)	592 (6.0)	560sh (5.2)	440 (5.2)	383 (31.6)	370sh (25.2)
7	Bu^t	Bu^t	640sh (4.0)	604 (4.8)	564 (3.6)	485 (5.2)	380sh (16.0)	350 (24.0)
$[\mathrm{Ni(qo)_2}]^a$	Bu^t	Bu^t		617 (4.6)		485 (5.2)	376 (22.2)	
4	CMe_2Ph	H	660sh (3.8)	580 (5.8)	550sh (5.2)	472sh (4.2)	382 (27.6)	366sh (22.4)
8	CMe_2Ph	H	632sh (4.8)	592 (6.2)	560sh (4.8)		384sh (18.4)	350 (29.6)
$[\mathrm{Ni(qo)_2}]^a$	CMe_2Ph	H		630 (5.1)		480 (5.1)	369 (23.8)	

Solvent - toluene. sh = shoulder. ^{a}Measured at 70 °C. ^{b}A further shoulder appeared at 650 nm (4.0). ^{c}All values of ε are calculated per mole of metal, e.g. on the basis of [Pd(qo)Cl].

Bu^tqo)$_2$] to be monomeric at the melting point of naphthalene (80 °C). At this temperature the melt was dark green. This red (cold) → green (hot) colour change has been noted before [3].

The UV–Vis spectra of several $[\mathrm{Ni(qo)_2}]$ complexes in toluene solution were examined over the temperature range −22 to 70 °C so that the spectra are not temperature sensitive at the extremes. The families of spectra, see Fig. 1*, typically show four isosbestic points indicating the presence of only two absorbing species. The changes in molar absorbance at about 625 nm were used to follow the equilibria. The equilibrium constant K was calculated at each temperature between the maximum and minimum temperatures.

$$\underset{a-x}{[\mathrm{Ni(qo)_2}]_2} \rightleftharpoons \underset{2x}{[2\ \mathrm{Ni(qo)_2}]}: K = 4x^2/(a-x)$$

Plots of ln K_T versus $1/T$ gave straight lines, gradient $\Delta H/R$. ΔS_{298} was calculated from K_{298} and ΔH.

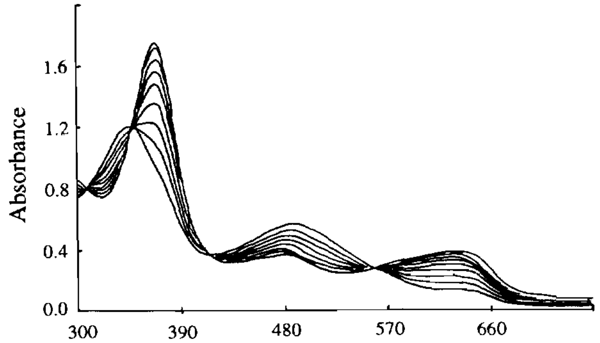


Fig. 1. The electronic spectra of $[\mathrm{Ni(4\text{-}CMe_2Phqo)_2}]$ over the temperature range 19–70 °C. Temperatures: 19, 25, 30, 35, 40, 45, 50, 60, 70 °C. Solutions: 7.36×10^{-5} mol dm^{-3} in toluene.

TABLE 2. Thermodynamic data for the dimer ⇌ monomer equilibrium $[\mathrm{Ni(qo)_2}]_2 \rightleftharpoons 2[\mathrm{Ni(qo)_2}]$

qo	K_{298}	ΔH (kJ mol^{-1})	ΔG_{298} (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
4,6-diMeqo	5.83×10^{-5}	47.3	24.1	78
4-Clqo	3.53×10^{-4}	72.5	19.95	177
4-Meqo	1.58×10^{-3}	84.6	15.98	230
4-Bu^tqo	3.03×10^{-3}	92.4	14.37	262

The results given in Table 2 are for those four complexes sufficiently soluble at the lowest temperatures to give a 2×10^{-4} mol dm^{-3} solution of $[\mathrm{Ni(qo)_2}]$. With so few results it is merely worth noting the opposing effects of ΔH and ΔS upon ΔG, the inductive effect of the 4-substituents upon ΔH, i.e. as +I increases 4-Cl, 4-Me, 4-Bu^t so does ΔH. The ΔS values are all positive as expected for dissociation reactions.

The steric effect

The sterically congested complex $[\mathrm{Ni(4,6\text{-}diBu^tqo)_2}]$ differs from the other Ni(II) complexes in that freshly prepared, dilute toluene solutions change colour from red, through grey to green. The first-order rate constant, calculated from the changes in absorption at 488 nm is k (291 K) = 1.7×10^{-4} s^{-1}.

The change was shown to be due to dissociation by comparing the UV spectra of equilibrated solutions in the concentration range 1.00×10^{-2} to 5.00×10^{-5} mol dm^{-3}. The spectra obtained closely resembled Fig. 1 in that there are four isosbestic points, a reduction in absorbance at c. 480 nm and a new maximum at 620 nm. Thus in this case too the red complex is a dimer and the green is a monomer.

The diamagnetism of the green monomeric Ni(II) complexes

Using Evan's method [16] the complex $[\mathrm{Ni(4,6\text{-}diBu^tqo)_2}]$ in toluene at 80 °C is shown to be diamagnetic

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*These spectra represent only a limited temperature range.

and therefore square planar. The toluene methyl proton resonance was used as both the reference and indicator signals. At 22 °C the red solution was clearly paramagnetic, $\delta\nu = 15$ Hz, making $\mu_{\mathrm{eff}} = 2.68$ μB. At 65 °C the separation was only 5 Hz and at 80 °C the signal appears only as a shoulder on the solvent reference resonance.

Supplementary material

Elementary analyses, mass spectra, ^{1}H NMR, electronic and IR spectra may be obtained from the authors.

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