Inorganica Chimica Acta, 202 (1992) 67–72

The preparation, properties and X-ray crystal structure of the nickel(II) hydroquinonylphosphine complex *cis*-$[Ni(pphqH)_2] \cdot H_2O \cdot 2(CH_3)_2NCHO$*

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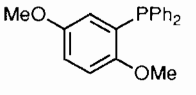
(Received March 10, 1992; revised June 26, 1992)

Abstract

The preparation and redox chemistry of the O,P-chelated, hydroquinonylphosphine complex *cis*-$[Ni(pphqH)_2]$ is reported, along with the crystal structure of *cis*-$[Ni(pphqH)_2] \cdot H_2O \cdot 2(CH_3)_2NCHO$. The complex is isostructural with *cis*-$[Pd(pphqH)_2]$. Differences in the reactivity, physical properties and redox chemistry of *cis*-$[Ni(pphqH)_2]$ and its palladium and platinum congeners are discussed.

Introduction

We have recently reported the preparation and properties of the O,P-chelated, hydroquinonylphosphine complexes *cis*-$[M(pphqH)_2]$ (M = Pd or Pt) and their stepwise conversions into the non-chelated parahydroquinonyl and parabenzoquinonyl complexes $[M(pphqH_2)_2X_2]$ and $[M(ppq)_2X_2]$ (X = Cl, Br or I) [1]. Electrochemical investigations of these Pd and Pt complexes revealed that all redox processes, ligand-centred and metal-centred, were irreversible. Nickel at the top of the Group 10 triad has a much more accessible redox chemistry based around the Ni(III)/Ni(II) and Ni(II)/Ni(I) couples [2, 3]. Thus, the potential existed for reversible metal-based redox processes and possibly for intramolecular electron redistribution in hydroquinonyl and quinonyl phosphine complexes of Ni(II). Furthermore, although few nickel complexes have been reported with an O_2P_2-donor set, examples of *cis–trans* square planar structural equilibria and also of tetrahedral–square planar structural equilibria have been established [2, 4, 5]. Similar equilibria were possible in the O,P-chelated, hydroquinonyl phosphine complex $[Ni(pphqH)_2]$. In this paper the preparation, reactivity, electrochemistry and X-ray crystal structure of $[Ni(pphqH)_2]$ are described and analogous data obtained from studies of the palladium and platinum congeners are compared with that of the nickel complex.



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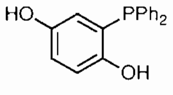

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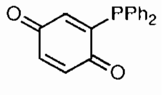

ppq

Experimental

All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques. Solvents were distilled from an appropriate drying agent under an atmosphere of dry dinitrogen [6]. The ligand diphenylphosphinohydroquinone hydrobromide ($pphqH_2 \cdot HBr$) was prepared as detailed elsewhere [1]. Other chemicals were procured from commercial sources and were used as obtained.

^1H NMR spectra were recorded on a Bruker AM500 (500 MHz) spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CXP300 spectrometer operating at 121.46 MHz and were referenced relative to external 0.05% KH_2PO_4 in D_2O. IR spectra and UV–Vis spectra were recorded on Perkin–Elmer 500B and Hitachi U-3200 spectrometers, respectively. Elemental analyses were performed by the UNSW Microanalytical Service. Cyclic voltammograms were recorded with a PAR173 potentiostat and a PAR175 universal programmer cou-

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*Nomenclature: q = paraquinonyl, hq = parahydroquinonyl (e.g. hqH_2 = hydroquinone), pp = diphenylphosphino, Fc = ferrocene.

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pled to a Houston 2000 X-Y recorder for output. A standard three electrode configuration was used with an Ag/AgCl reference electrode (BAS), a platinum disk (BAS, 1.0 mm diameter) working electrode and a platinum wire auxiliary electrode. All potentials are quoted relative to the ferricenium/ferrocene couple which was measured in the same solution as an internal standard. Bulk electrolyses were used to determine the numbers of electrons transferred at each electrochemical step and were performed at a platinum mesh working electrode.

Preparation of cis-[Ni(pphqH)$_2$]

Sodium carbonate (0.1 g) was added to a solution of the ligand pphqH$_2$·HBr (0.13 g, 0.34 mmol) and oven dried NiCl$_2$·6H$_2$O (25 mg) in methanol (10 cm^3) and the resulting green solution stirred for 16 h. The yellow solid which precipitated was collected and repeatedly washed with water to remove the excess sodium carbonate, and then was washed with diethyl ether and dried *in vacuo* to give the crude product as a yellow powder (80 mg, 70%). Recrystallization from warm dimethylformamide gave orange–red crystals of the product (15 mg, 12%) – elemental analysis, ^{1}H NMR and X-ray structure determination all revealed one water and two dimethylformamide molecules of crystallization, i.e. [Ni(pphqH)$_2$]·H$_2$O·2(CH$_3$)$_2$NCHO.

M.p. 240 °C (dec.). IR (paraffin mull): 3331s, 3057s, 2673w, 2620w, 1732w, 1654s, 1593s, 1516vs, 1508vs, 1440vs, 1316m, 1265m, 1153s, 1122s, 1101m, 1071m, 1041m, 1028m, 999m, 817w, 751m, 725s, 696s, 666m, 560m, 539m, 454w, 375w, 299w cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$SO): δ 8.39 (s, O*H*), 7.46–7.39 (m, *Ph*, 8H), 7.29–7.24 (m, *Ph*, 12H), 6.65 (dd, *J* 9, 3 Hz, C$_6$*H*$_3$O(OH)), 6.44 (d, *J* 9 Hz, C$_6$*H*$_3$O(OH)), 6.11 (m (br), C$_6$*H*$_3$O(OH)) plus peaks for (CH$_3$)$_2$NCHO: δ 7.95 (s, C*H*O), 2.89 (s, C*H*$_3$), 2.73 (s, C*H*$_3$). ^{31}P NMR ((CD$_3$)$_2$SO): δ 33.16. UV–Vis ((CH$_3$)$_2$NCHO): λ_{max} 394 nm (ϵ_{max} = 5190 l mol^{-1} cm^{-1}). *Anal.* Found: C, 61.71; H, 5.39; N, 3.38. Calc. for C$_{36}$H$_{28}$NiO$_4$P$_2$·H$_2$O·2C$_3$H$_7$NO: C, 62.32; H, 5.44; N, 3.46%.

Reactions of cis-[Ni(pphqH)$_2$] with HCl or HBr

The reactions were performed in 5 mm NMR tubes. Red [Ni(pphqH)$_2$] (20 mg) was suspended in d$_6$-acetone (0.5 cm^3) and one drop of either aqueous HCl (12 M) or aqueous HBr (40%) was added). In both cases the red nickel complex dissolved giving a light green solution. ^{1}H and ^{31}P NMR analyses of both solutions showed that the ligand was present in the solutions as its free phosphine oxide (pphqH$_2$·oxide) [1].

Data for pphqH$_2$·oxide. ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.92–7.88 (m, *Ph*, 8H), 7.81–7.74 (m, *Ph*, 12H), 7.40 (dd, *J* 8.7, 6.6 Hz, C$_6$*H*$_3$O(OH)), 7.31 (dd, *J* 8.7, 2.5 Hz, C$_6$*H*$_3$O(OH)), 6.55 (dd, *J* 14.4, 2.5, C$_6$*H*$_3$O(OH)). ^{31}P NMR ((CD$_3$)$_2$CO): δ 41.14.

X-ray structure determination

Dark orange–red crystals of the complex were grown from dimethylformamide. After many unsatisfactory attempts crystals which were only just suitable for X-ray analysis were obtained. A small crystal which contained crystallites growing on one side was selected as the best available for data collection. The crystallites could not be removed. Crystallographic data are given in Table 1. Cell dimensions were derived from the angular measurement of 25 strong reflections in the range $25 < 2\theta < 30°$. Three standard reflections (800, 080, 006) monitored every 100 reflections indicated negligible crystal instability. Lorentz and polarization corrections were applied [7]. An absorption correction was not applied because of the presence of intergrowth crystallites.

The structure was solved using SHELXS-86 [7] and refined using SHELXS-76 [7]. All benzene rings were constrained to be regular hexagons with bond lengths fixed at 1.395 Å and were refined isotropically. All other non-H atoms were refined with anisotropic thermal parameters. Neutral atom scattering factors and anom-

TABLE 1. Crystal data, data collection and refinement of *cis*-[Ni(pphqH)$_2$]·H$_2$O·2(CH$_3$)$_2$NCHO

Empirical formula	C$_{42}$H$_{44}$N$_2$NiO$_7$P$_2$
M_r	809.47
Space group	monoclinic, $P2_1/c$ (No. 14)
a (Å)	15.711(13)
b (Å)	13.724(23)
c (Å)	19.083(20)
β (°)	111.05(7)
V (Å^3)	3840(8)
D_c (g cm^{-3})	1.40
Z	4
Crystal size (mm)	$0.21 \times 0.24 \times 0.42$
Radiation, λ (Å)	Mo Kα, 0.71069
μ (cm^{-1})	6.45
F(000)	1696
Diffractometer	Nicolet P$\bar{3}$
Temperature (K)	153 ± 5
Scan type	ω–2θ
Scan speed (° min^{-1})	5.86
Data limits (°)	$4 < 2\theta < 45$
Reflections measured	h, k, $\pm l$
Crystal decay (%)	<3
Absorption correction	none applied
Total observed data	5018
Unique data	1856 ($I > 2.5\sigma I$)
No. variables	247
$R(\Sigma\Delta F/\Sigma\|F_o\|)$	0.0920
$R_w[\Sigma w^{1/2}(\Delta F)/\Sigma w^{1/2}F_o]$	0.0872
Weight (w)	$[2.2983/(\sigma^2 F + 0.00088F^2)]$
Maximum shift/error	0.111
Residual ē density (ē Å^{-3})	0.64

TABLE 2. Final positional and isotropic thermal parameters (Å$^2 \times 10^3$) for *cis*-[Ni(pphqH)$_2$]·H_2O·2$(CH_3)_2NCHO$

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}[a] or U_{11}[b]
Ni(1)	0.2633(2)	0.0243(2)	0.5234(1)	24
P(1)	0.2065(4)	−0.1183(4)	0.4952(3)	25
P(2)	0.2632(4)	0.0675(4)	0.4146(3)	23
O(1)	0.2731(7)	0.0001(9)	0.6239(6)	24
O(2)	0.3048(8)	0.150(1)	0.5569(6)	27
O(3)	0.1412(8)	−0.3488(9)	0.6896(7)	31
O(4)	0.3586(9)	0.4201(9)	0.3644(7)	37
C(11)	0.2033(7)	−0.1544(8)	0.5836(5)	18(5)
C(12)	0.1701(7)	−0.2427(8)	0.5994(5)	25(5)
C(13)	0.1768(7)	−0.2640(8)	0.6727(5)	21(5)
C(14)	0.2166(7)	−0.1969(8)	0.7301(5)	18(5)
C(15)	0.2498(7)	−0.1086(8)	0.7142(5)	17(4)
C(16)	0.2431(7)	−0.0873(8)	0.6410(5)	34(6)
C(21)	0.2730(7)	−0.2129(7)	0.4714(6)	17(4)
C(22)	0.3671(7)	−0.1984(7)	0.4956(6)	29(5)
C(23)	0.4231(7)	−0.2708(7)	0.4842(6)	34(5)
C(24)	0.3851(7)	−0.3575(7)	0.4485(6)	37(6)
C(25)	0.2911(7)	−0.3720(7)	0.4243(6)	33(5)
C(26)	0.2350(7)	−0.2997(7)	0.4357(6)	21(5)
C(31)	0.0906(6)	−0.1286(9)	0.4261(6)	20(5)
C(32)	0.0729(6)	−0.1507(9)	0.3509(6)	12(4)
C(33)	−0.0167(6)	−0.1518(9)	0.2998(6)	42(6)
C(34)	−0.0886(6)	−0.1308(9)	0.3239(6)	46(6)
C(35)	−0.0709(6)	−0.1087(9)	0.3992(6)	35(6)
C(36)	0.0187(6)	−0.1076(9)	0.4503(6)	32(5)
C(41)	0.3030(7)	0.1888(8)	0.4347(5)	24(5)
C(42)	0.3160(7)	0.2573(8)	0.3854(5)	20(5)
C(43)	0.3451(7)	0.3513(8)	0.4106(5)	23(5)
C(44)	0.3611(7)	0.3769(8)	0.4850(5)	31(5)
C(45)	0.3481(7)	0.3084(8)	0.5342(5)	24(5)
C(46)	0.3190(7)	0.2144(8)	0.5091(5)	30(5)
C(51)	0.3411(6)	0.0020(9)	0.3811(7)	25(5)
C(52)	0.3145(6)	−0.0797(9)	0.3349(7)	30(5)
C(53)	0.3793(6)	−0.1335(9)	0.3171(7)	29(5)
C(54)	0.4708(6)	−0.1055(9)	0.3455(7)	34(6)
C(55)	0.4974(6)	−0.0237(9)	0.3918(7)	34(5)
C(56)	0.4325(6)	0.0300(9)	0.4095(7)	32(5)
C(61)	0.1535(6)	0.0776(8)	0.3424(6)	17(4)
C(62)	0.1359(6)	0.0742(8)	0.2654(6)	22(5)
C(63)	0.0470(6)	0.0856(8)	0.2145(6)	36(6)
C(64)	−0.0244(6)	0.1005(8)	0.2406(6)	32(5)
C(65)	−0.0068(6)	0.1040(8)	0.3176(6)	26(5)
C(66)	0.0822(6)	0.0926(8)	0.3685(6)	27(5)
C(1)	0.658(2)	0.567(2)	0.305(1)	56
C(2)	0.566(2)	0.435(2)	0.338(2)	101
C(3)	0.501(2)	0.587(2)	0.281(2)	94
N(1)	0.580(1)	0.530(2)	0.310(1)	66
O(11)	0.674(1)	0.643(1)	0.2824(9)	58
C(4)	0.113(1)	0.008(2)	0.017(1)	47
C(5)	0.119(2)	0.177(2)	0.042(1)	44
C(6)	0.110(2)	0.112(2)	−0.083(1)	52
N(2)	0.116(1)	0.097(1)	−0.006(1)	35
O(22)	0.115(1)	−0.015(1)	0.0820(9)	57
O(5)	0.3415(9)	0.352(1)	0.2284(7)	48

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] e.s.d.s given in parentheses for isotropic temperature factor U_{11}.

TABLE 3. Selected bond lengths (Å) and angles (°) for *cis*-[Ni(pphqH)$_2$·H_2O·2$(CH_3)_2NCHO$[a]

Ni(1)–P(1)	2.138(6)	Ni(1)–P(2)	2.159(6)
Ni(1)–O(1)	1.90(1)	Ni(1)–O(2)	1.87(1)
P(1)–C(11)	1.78(1)	P(1)–C(21)	1.82(1)
P(1)–C(31)	1.83(1)	P(2)–C(41)	1.77(1)
P(2)–C(51)	1.81(1)	P(2)–C(61)	1.78(1)
O(1)–C(16)	1.37(2)	O(5)–O(4)	2.67(2)
O(3)–C(13)	1.38(2)	O(5)–O(1)^{i}	2.78(2)
O(2)–C(46)	1.34(2)	O(5)–O(11)^{ii}	2.88(2)
O(4)–C(43)	1.36(2)	O(3)–O(22)^{iii}	2.70(2)
P(1)–Ni(1)–P(2)	98.8(2)	P(1)–Ni(1)–O(1)	88.2(4)
P(1)–Ni(1)–O(2)	172.5(4)	P(2)–Ni(1)–O(1)	172.8(4)
P(2)–Ni(1)–O(2)	87.4(4)	O(1)–Ni(1)–O(2)	85.7(5)
Ni(1)–P(1)–C(11)	99.6(4)	Ni(1)–P(1)–C(21)	119.4(4)
Ni(1)–P(1)–C(31)	118.0(5)	C(11)–P(1)–C(21)	104.6(6)
C(11)–P(1)–C(31)	107.5(5)	C(21)–P(1)–C(31)	106.1(5)
Ni(1)–P(2)–C(41)	99.9(4)	Ni(1)–P(2)–C(51)	115.9(5)
Ni(1)–P(2)–C(61)	115.5(4)	C(41)–P(2)–C(51)	108.2(5)
C(41)–P(2)–C(61)	105.1(6)	C(51)–P(2)–C(61)	110.7(5)
Ni(1)–O(2)–C(16)	119.0(8)	Ni(1)–O(2)–C(46)	119.7(8)

[a] Symmetry codes: (i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

alous dispersion corrections were inlaid [7] and taken from ref. 8. Two dimethylformamide molecules and a water molecule of solvation were located and displayed large anisotropic thermal parameters reflecting some disorder in their positions. With the exception of the water molecule, for which no H atoms were attached, H atoms were placed in fixed calculated positions. The disorder of the solvent molecules together with the small imperfect crystal used for data collection have contributed to the high final *R* factor: $R = 0.0920$ and $R_w = 0.0872$.

Final positional and isotropic thermal parameters are given in Table 2, and selected bond lengths and angles are given in Table 3. See also 'Supplementary material'.

Results and discussion

We have established that the route of choice to the palladium(II) or platinum(II) quinonylphosphine complexes, $[MX_2(ppq)_2]$, and hydroquinonylphosphine complexes, $[MX_2(pphqH_2)_2]$ and $[M(pphqH)_2]$ (M = Pd or Pt; X = halide), is via the complexes $[MX_2(pphqMe_2)_2]$ in which each hydroquinonyl moiety is protected as its dimethyl ether [1]. Ether cleavage with BBr_3 gave the corresponding hydroquinonylphosphine $[MX_2(pphqH_2)_2]$ complexes which could be either oxidized to the quinonyl complexes $[MX_2(ppq)_2]$ or treated with base to give the O,P-chelated hydroquinonylphosphine complexes $[M(pphqH)_2]$ in excellent overall yields (60–85%) [1]. This indirect synthetic route could not be used for the synthesis of nickel hydroquinonylphosphine and quinonylphosphine complexes as the desired nickel complexes of the bulky phosphine ligand pphqMe$_2$ could not be isolated from reactions of nickel dichloride with this phosphine. However we found that reaction of nickel dichloride with ppqhqH$_2$·HBr in dry methanol in the presence of excess sodium carbonate gave the O,P-chelated hydroquinonylphosphine nickel complex, [Ni(pphqH)$_2$], directly as an amorphous yellow powder in typically 80% yield. [Ni(pphqH)$_2$] was insoluble in most common solvents (e.g. dichloromethane, acetone, ethylacetate, methanol, ethanol, acetonitrile) but was soluble in dimethyl sulfoxide or dimethylformamide from which it could be recrystallized as dark orange–red crystals. Decomposition occurred when either HCl or HBr were added to a suspension of the complex in acetone in contrast to the analogous complexes [M(pphqH)$_2$] (M = Pd, Pt) which cleanly form the complexes [M(pphqH)$_2$X$_2$] (M = Pd, Pt; X = Cl or Br) [1].

Physical measurements obtained on the dark orange–red crystals of [Ni(pphqH)$_2$] obtained from dimethylformamide solution are consistent with the presence of a square planar Ni(II) complex both in solution and solid phases, and with one water and two dimethylformamide molecules of crystallization in the solid. Most notably the complex is diamagnetic thus ruling out tetrahedral coordination and confirming square planar coordination of the nickel atom. The ^{1}H NMR spectrum recorded in deutero-dimethyl sulfoxide displayed a singlet for the hydroquinonyl OH protons, two multiplets for the phenyl protons, a distinct multiplet for each of the three hydroquinonyl ring protons, and the requisite three peaks for dimethylformamide. The hydroquinonyl OH peak at δ 8.39 disappears on shaking with added D$_2$O. The position and pattern of the three hydroquinonyl ring proton multiplets is indicative of the structure in palladium or platinum [MX$_2$(pphqH$_2$)$_2$] and [M(pphqH)$_2$] complexes [1]. The position and pattern of these multiplets in the nickel complex is similar to that found for the complexes *cis*-[M(pphqH)$_2$] (M = Pd or Pt) suggesting the assignment of *cis* coordination about the nickel atom. An extra 'virtual' coupling in each hydroquinonyl multiplet arising from strong coupling between the two phosphorus atoms was observed in the spectra of the palladium and platinum complexes [1]. That this virtual coupling was not found for the nickel complex is consistent with the usual sequence of ^2J (P–M–P) couplings within a transition metal triad which is 1st row ≪ 2nd row < 3rd row [9]. In the ^{31}P{^{1}H} NMR spectrum a singlet at δ 33.16 was observed indicating equivalent hydroquinonylphosphine ligands. The ^{31}P chemical shift compares with δ 40.70 for *cis*-[Pd(pphqH)$_2$] and δ 18.59 for *cis*-[Pt(pphqH)$_2$] [1]. As it is expected that the coordination shift for a ligand in a series of analogous complexes should increase vertically up a group [10], the ^{31}P chemical shift found for [Ni(pphqH)$_2$] appears at first sight to be anomalous. However, we note the reported ^{31}P chemical shift for complexes of the alkoxyphosphine PPh$_2$CH$_2$C(CF$_3$)$_2$OH (LH): *cis*-NiL$_2$, δ 34.7; *trans*-NiL$_2$, δ 14.5; *cis*-PdL$_2$, δ 40.6; *cis*-PtL$_2$, δ 17.3 [4]. Comparison with this data confirms assignment of the complex as *cis*-[Ni(pphqH)$_2$]. It is noteworthy that *cis–trans* structural isomerism was not observed in the NMR spectra of the complex. [Ni(PPh$_2$CH$_2$C(CF$_3$)$_2$O)$_2$] is reported to be an equilibrium mixture of *cis* and *trans* isomers at ambient temperature [4]. The single band found at 394 nm ($\epsilon_{max} \sim 5190$ l mol^{-1} cm^{-1}) in the visible spectrum of the complex in dimethylformamide solution is typical of the visible spectra displayed by other square planar nickel systems with the *cis*-O$_2$P$_2$ ligand donor set [4, 5].

The dark orange–red crystals of *cis*-[Ni(pphqH)$_2$]·H$_2$O·2(CH$_3$)$_2$NCHO grown from dimethylformamide were further characterized by X-ray crystallography. The X-ray structural determination revealed that the complex crystallized in the space group *P*2$_1$/*c* with four molecules in the unit cell. The unit cell also contained four water and eight dimethylformamide molecules of crystallization. The complex and the atom labelling scheme are shown in Fig. 1. Comparison with the crystal structure of [Pd(pphqH)$_2$]·H$_2$O·2(CH$_3$)$_2$SO shows that the neutral nickel complex and its palladium congener are isostructural [1]. The nickel complex displays a distorted square planar coordination with two *cis*-coordinated hydroquinonylphosphine ligands and is planar to within 0.2 Å. The mean planes through the hydroquinonylphosphine moieties are on average tilted at 4.0° in the same direction to the NiO$_2$P$_2$ plane. The Ni–P distances (2.138(6) and 2.159(6) Å) and Ni–O distances (1.90(1) and 1.87(1) Å) are similar to those found in other structurally characterized nickel–phosphine complexes with O$_2$P$_2$ coordination [4, 5, 11–13] and compare with

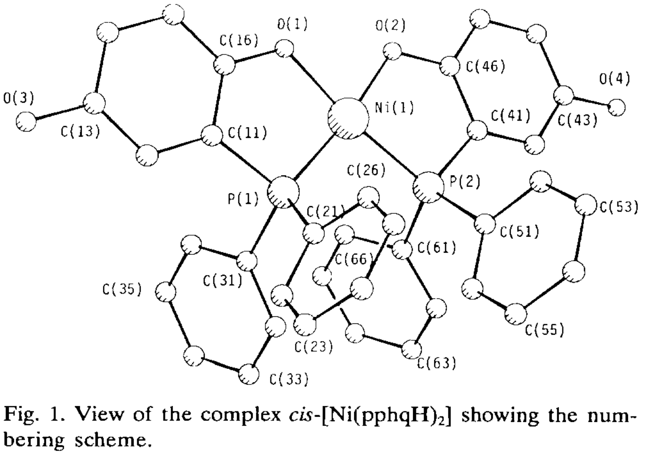

Fig. 1. View of the complex *cis*-[Ni(pphqH)$_2$] showing the numbering scheme.

2.227(1) for the Pd–P and 2.059(1) Å for the Pd–O bond lengths in *cis*-[Pd(pphqH)$_2$] [1]. The angles around the nickel atom (P–Ni–O 87.4(4) and 88.2(4)°; P–Ni–P 98.8(2)°; O–Ni–O 85.7(5)°) reflect the small O,P-bite of the hydroquinonylphosphine ligand and presumably distortion caused by the minimization of steric interactions between the phenyl groups on adjacent phosphine moieties. The structure is held together by a network of hydrogen bonds (Table 3). The coordinated hydroquinonyl oxygen O(1) is H-bonded to a molecule of water O(5). The non-chelated hydroquinonyl oxygen O(4) on an adjacent complex is H-bonded bo the same water molecule. In addition that water molecule is also H-bound to the oxygen O(11) of one of the dimethylformamide molecules. This H-bonding generates infinite chains of the complex H-bonded through water molecules which run essentially parallel to the *c* axis of the unit cell. The oxygen O(2) of the other coordinated hydroquinonyl is not involved in any H-bonding (O(2)...O(5) 3.11(2) Å). The non-chelated hydroquinonyl oxygen O(3) of that same unit is H-bonded to the remaining dimethylformamide molecule through O(22). Typically, square planar nickel complexes with bulky phosphine ligands exhibit *trans* geometries. It is possible that, in the solid state at least, the extended H-bonding network would not be likely with a *trans* geometry and that the *cis* geometry is therefore favoured because of the stabilization conferred on the system by the H-bonded network. Interestingly, the crystal structure of [Pd(pphqH)$_2$]·H$_2$O·2(CH$_3$)$_2$SO revealed a different pattern of H-bonding: in this structure the water molecule was found symmetrically H-bound to both coordinated hydroquinonyl oxygen atoms and the dimethyl sulfoxide molecules were H-bound to the two non-coordinated hydroquinonyl OH groups [1].

The redox chemistry of *cis*-[Ni(pphqH)$_2$] was investigated by electrochemical methods. Cyclic voltammograms obtained in dimethylformamide (0.1 M n-Bu$_4$NPF$_6$) revealed a quasireversible reduction at −1.75 V versus Fc$^+$/Fc ($i^a/i^c = 0.65$ and $\Delta E_p = 80$ mV at 100 mV s^{-1}, cf. 65 mV for the Fc$^+$/Fc couple), an irreversible anodic peak at 0.02 V and an irreversible cathodic peak at −0.84 V which only arises after the anodic peak is traversed (Fig. 2). Bulk electrolysis at −1.9 V confirmed that the reduction is a single electron process. Comparison of the peak heights for the oxidation and reduction processes suggests that the oxidation is also a single electron process. On scanning to more positive potentials two further irreversible anodic peaks at 0.38 and 0.52 V were also observed before the solvent discharge (not shown). Peak heights suggest that these are two-electron processes. New peaks are observed at 0.12 and 0.21 V on the return cathodic sweep after the second and third oxidation processes are traversed. It is likely that the quasireversible reduction process is the reduction of the metal centre (Ni(II) + $e \rightarrow$ Ni(I)) and that the irreversible first oxidation process arises from oxidation of the metal centre (Ni(II) $\rightarrow$ Ni(III) + e). Support for these assignments comes from the electrochemistry found for the corresponding palladium and platinum analogues of *cis*-[Ni(pphqH)$_2$]. Under the same conditions one-electron redox processes were not found in the palladium and platinum complexes: *cis*-[Pt(pphqH)$_2$] showed no reductive processes and hydroquinonyl-centred two-electron oxidations at 0.21 and 0.42 V whereas *cis*-[Pd(pphqH)$_2$] showed an irreversible reduction at −1.98 V and hydroquinonyl-centred two-electron oxidations at 0.21 and 0.45 V [1]. Although assignments of the second and third oxidation processes found for *cis*-[Ni(pphqH)$_2$] cannot be made with absolute confidence, it is likely that they arise from proton-coupled oxidation of the hydroquinonyl substituents, i.e. analogous oxidation processes to those observed in

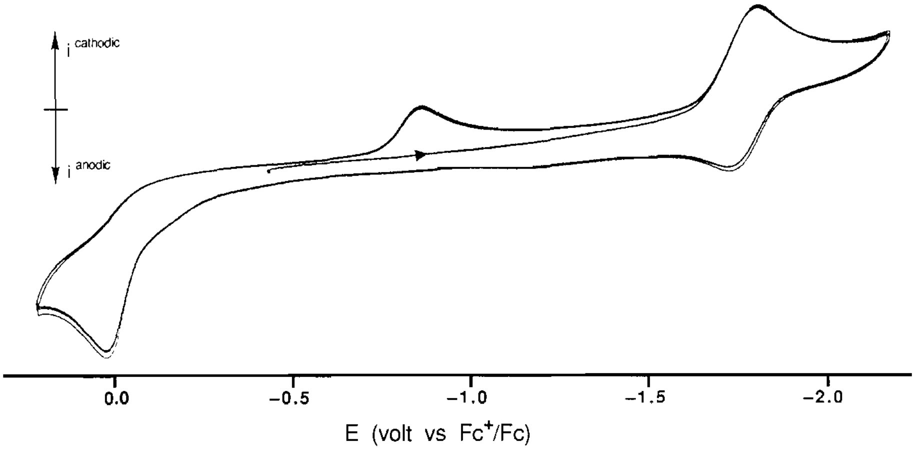

Fig. 2. Cyclic voltammogram of *cis*-[Ni(pphqH)$_2$] in dimethylformamide (0.1 M n-Bu$_4$NPF$_6$) at a platinum disk electrode (scan rate 100 mV s^{-1}).

the palladium and platinum congeners of the nickel complex [1, 14].

Supplementary material

Thermal parameters for non-hydrogen atoms, observed and calculated structure factors and a full list of bond distances and angles for *cis*-$[Ni(pphqH)_2] \cdot H_2O \cdot 2(CH_3)_2NCHO$ are available on request from author L.R.H.

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