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Synthesis and structure of 1,10-phenanthroline *bis*{[2-(2-pyrrole)-methylimino]4-methylphenolato}nickel(II)

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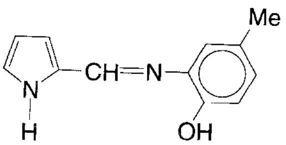
Summary

Electrochemical oxidation of nickel in an acetonitrile solution containing 2-pyrrole-[N-(2-hydroxy-4-methylphenyl)methylimine] (H_2L) and 1,10-phenanthroline (phen) yielded $Ni(HL)_2 \cdot phen$, whose crystal structure was determined by XRD. The nickel atom has a distorted octahedral geometry, and is coordinated to the phenolic oxygen and imino nitrogen atoms of two Schiff base ligands. The i.r. and u.v.–vis. spectra of the complex are discussed and related to the structure.

Introduction

The synthesis of metal complexes with Schiff bases containing weakly acid groups can be satisfactorily achieved via an electrochemical procedure, starting from the metal as the anode of an electrolytic cell. Following this method, the preparations of Schiff base metal complexes derived from H-pyrrole-2-aldehyde or salicylaldehyde and amines have been reported$^{(1-5)}$. In addition to its simplicity and high yield, this procedure allows one-step preparation of mixed complexes when a second ligand is added to the cell. We now report the electrochemical synthesis and crystal structure of $[Ni(HL)_2phen]$ containing both the anionic form of 2-pyrrole-[N-(2-hydroxy-4-methylphenyl)-methylimine] (H_2L) and 1,10-phenanthroline (phen).

H_2L



Experimental

MeCN, H-pyrrole-2-aldehyde, 2-hydroxy-4-methylaniline and 1,10-phenanthroline (commercial products) were used as supplied. Nickel (Ega Chemie) was used as 2 × 2 cm plates. The Schiff base was prepared by condensing equimolecular amounts of H-pyrrole-2-aldehyde and 2-hydroxy-4-methylaniline in $CHCl_3$, using a Dean-Stark trap. After removal of the H_2O produced in the reaction, the solution was concentrated and the isolated solid was washed with diethylether and dried *in vacuo*. Its purity was checked by recording its i.r. and ^1H n.m.r. spectra.

The electrochemical method used to obtain the compound was similar to that described by Tuck$^{(6)}$. The nickel anode was suspended from a platinum wire and the cathode was a platinum wire. Both the Schiff base (0.33 g) and 1,10-phenanthroline (0.13 g) were dissolved in MeCN (50 ml), and a small amount of Me_4NClO_4 (ca. 10 mg) was added to the solution as a current carrier. Direct current was obtained from a purpose built d.c. power supply. An applied voltage of 24 V allowed a current of 20 mA. During the electrolysis, N_2 was bubbled through the solution to provide an inert atmosphere and to stir the solution phase. Under these conditions the cell can be summarized as: $Pt(-)/CH_3CN + H_2L + phen/M(+)$. After 2 h, the clear solution was filtered to remove any particles of metal and then left to concentrate *in vacuo* at room temperature. After cooling, crystals were obtained and characterized as $Ni(HL)_2 \cdot phen$ by elemental analysis. (Found: N, 13.9; C, 66.7; H, 5.3; calcd.: N, 13.2; C, 67.8; H, 4.7%).

X-ray data collection and reduction

An amber prismatic crystal of $[Ni(C_{12}H_{11}N_2O)_2(C_{12}H_8N_2)]$ was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range: $6.5° < \theta < 13.5°$ on an Enraf-Nonius CAD4 four cycle diffractometer$^{(7)}$. Data were collected at 293 K using MoK_α radiation ($\lambda = 0.70930$ Å) and the $\omega/2\theta$ scan technique. Lorentz, polarization and empirical absorption correction was applied$^{(8)}$. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

Structure solution and refinement

The structure was solved by direct methods$^{(9)}$, which revealed the position of all nonhydrogens atoms, and refined on F by a full-matrix, least-squares procedure using anisotropic displacement parameters for nickel and coordinating atoms, and isotropic for remaining non-hydrogen atoms. Hydrogen atoms were located on a $\Delta\rho$ map and added to the structure factor calculation as fixed contributions ($B_{iso} = 4.0$ Å^2), but their positional parameters were not refined. In the final cycle, a secondary extinction correction was applied$^{(10)}$. After all shift/e.s.d. ratios became less than 0.001, the refinement converged to the agreement factors listed in Table 1. Atomic scattering factors from *International Tables for X-ray Crystallography*$^{(11)}$. Molecular graphics from SCHAKAL$^{(12)}$. These and other crystallographic data have been deposited as Supplementary Publication No. CSD-57376 (copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik D-7514 Eggenstein-Leopoldshafen).

Physical measurements

The carbon, nitrogen and hydrogen contents of the complex were determined on a Carlo-Erba EA 1108 microanalyser. Infrared spectra were recorded as KBr mulls on a Perkin-Elmer 180 spectrophotometer. Solid reflectance spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic measurements were made using a DMS VSM1660.

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Table 1. Crystal data, data-collection and structure refinement parameters of [Ni($C_{12}H_{11}N_2O$)$_2$($C_{12}H_8N_2$)].

Crystal shape	Prismatic
Size	0.15 × 0.20 × 0.32 mm
Chemical formula	$C_{36}H_{30}NiN_6O_2$
Formula weight	636.7
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a	11.172(2) Å
b	17.870(3) Å
c	15.158(4) Å
β	92.26(1)°
Vol. of unit cell	3024.6(5) Å^3
Z	4
D_x (g cm^{-3})	1.400
F(000)	1328
Linear absorption coefficient	6.848 cm^{-1}
Minimum, maximum and average absorption correction	0.547/1.094/0.943
Maximum value of (sin θ)/λ reached in intensity measured	0.682 Å^{-1}
Range of *h*, *k*, *l*	0, 15; 0, 24; −20, 20
Standard reflections	−1, −5, 6; 4, −5, 3; 2, −6, −5
Interval standard reflections measured	7200s
Total no. of reflections measured (θ range)	8621 (3–29°)
No. of unique reflections (R_{int})	7851 (0.033)
No. of observed reflections	2706
Criterion for observed reflections	$I > 3\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$
Parameters refined	407
Value of *R*	0.054
Value of *ωR*	0.058
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.001
Max. $\Delta\rho$ in final diff. electron density map	0.335 eÅ^{-3}
Error in an observation of unit weight	2.300
Secondary extintion coefficient	1.017 × 10^{-9}

Results and discussion

The electrochemical oxidation of a nickel anode in an acetonitrile solution of the Schiff base H_2L and an additional ligand (1,10-phenanthroline) proved to be a simple one-step route to [Ni(HL)$_2$phen], where HL^- is the monoanionic form of the Schiff base. The compound thus obtained was a crystalline solid, insoluble in common nonpolar solvents but soluble in polar organic solvents such as acetonitrile or dimethyl sulphoxide. The value of the electrochemical efficiency, E_f, defined as moles of metal dissolved per Faraday of charge (mol F^{-1}), was 0.5 mol F^{-1}. This, and the formation of H_2 at the cathode, are in accordance with the following mechanism

$$\text{Cathode: } 2H_2L + 2e^- \longrightarrow H_{2(g)} + 2HL^-$$

$$\text{Anode: } Ni + phen + 2HL^- \longrightarrow [Ni(HL)_2phen] + 2e^-$$

X-ray structure of the compound

Bond lengths and angles are listed in Tables 2 and 3, respectively. The molecular structure and the numbering scheme used are illustrated in Figure 1. The nickel atom is coordinated to the phenolic oxygen and nitrogen atoms of two bidentate Schiff bases monoanions, and to a bidentate phenanthroline molecule. The pyrrole nitrogen atoms of each Schiff base molecule are not coordinated to the metal. The environment around the nickel atom is octahedral, with the imine nitrogen atoms in *cis*-positions, showing angular distortion due to the bidentate character of the ligands and principally to the small bite of phenanthroline. This bond angle $N_{(phen)}$—Ni—$N_{(phen)}$, 78.1(2)°, is similar to that found in [Ni(phen)$_3$]$^{2+}$, 80.1(14)°(13).

The basal plane may be considered as formed by the four nitrogen donor atoms, which are nearly planar with the metal atom (maximum deviation from the best plane 0.004 Å). The oxygen atoms are in the axial positions. The bond angles defined by *trans* atoms lie within the range 169.5–175.2°, which are close to those expected for an octahedral geometry.

The bond lengths Ni—$N_{(imino)}$, 2.163(5) and 2.190(5), are slightly longer than those found in hexacoordinated salicylaldiminates nickel(II) complexes [2.066(3)–2.050(6) Å](4,14), but similar to those reported for several hexacoordinated compounds of nickel with nonsalicylaldimines Schiff bases [2.14(2)–2.16(1) Å](15,16). This has been observed for zinc(II) complexes with similar ligands(17). The bond lengths Ni—$O_{(phenolato)}$, 2.008(4) and 2.002(5) Å are close to those reported for the above hexacoordinated nickel(II) [2.005(4)–2.032(3) Å](4,14,15). The values of 2.121(5) and 2.136(5) for Ni—$N_{(phen)}$ are similar to those found in the octahedral compound [Ni(phen)$_3$]$^{2+}$, 2.06(4) and 2.15(3) Å(13). The phenyl ring of each Schiff base is essentially planar. This plane is twisted with respect to the pyrrolic ring plane, with dihedral angles of 24.3 and 28.4°. Therefore, the phenolate oxygen atom of each Schiff base

Table 2. Bond lengths(Å) with e.s.d.s in parentheses.

Ni—O(11)	2.008(4)	Ni—O(21)	2.002(5)
Ni—N(11)	2.163(5)	Ni—N(21)	2.190(5)
Ni—N(31)	2.136(5)	Ni—N(32)	2.121(6)
O(11)—C(11)	1.343(7)	O(21)—C(21)	1.340(9)
N(11)—C(16)	1.441(8)	N(11)—C(17)	1.298(8)
N(12)—C(18)	1.378(9)	N(12)—C(111)	1.39(1)
N(21)—C(26)	1.432(8)	N(21)—C(27)	1.295(8)
N(22)—C(28)	1.386(9)	N(22)—C(211)	1.355(9)
N(31)—C(31)	1.336(9)	N(31)—C(312)	1.362(9)
N(32)—C(310)	1.32(1)	N(32)—C(311)	1.356(9)
C(11)—C(12)	1.410(9)	C(11)—C(16)	1.402(9)
C(12)—C(13)	1.397(9)	C(13)—C(14)	1.39(1)
C(14)—C(15)	1.39(1)	C(14)—C(141)	1.50(1)
C(15)—C(16)	1.405(9)	C(17)—C(18)	1.41(1)
C(18)—C(19)	1.40(1)	C(19)—C(110)	1.38(1)
C(21)—C(22)	1.41(1)	C(21)—C(26)	1.403(9)
C(22)—C(23)	1.37(2)	C(23)—C(24)	1.39(1)
C(24)—C(25)	1.39(1)	C(24)—C(241)	1.51(1)
C(25)—C(26)	1.40(1)	C(27)—C(28)	1.422(9)
C(28)—C(29)	1.40(1)	C(29)—C(210)	1.40(1)
C(31)—C(32)	1.39(2)	C(32)—C(33)	1.36(1)
C(33)—C(34)	1.40(1)	C(34)—C(35)	1.46(1)
C(34)—C(312)	1.39(2)	C(35)—C(36)	1.33(1)
C(36)—C(37)	1.44(1)	C(37)—C(38)	1.41(1)
C(37)—C(311)	1.42(2)	C(38)—C(39)	1.35(1)
C(39)—C(310)	1.42(1)	C(110)—C(111)	1.36(2)
C(210)—C(211)	1.37(1)	C(311)—C(312)	1.43(2)

Table 3. Bond angles(°) with e.s.d.s in parentheses.

O(11)—Ni—O(21)	175.2(2)	O(11)—Ni—N(11)	81.3(2)
O(11)—Ni—N(21)	96.9(2)	O(11)—Ni—N(31)	92.9(2)
O(11)—Ni—N(32)	89.5(2)	O(21)—Ni—N(11)	95.4(2)
O(21)—Ni—N(21)	79.9(2)	O(21)—Ni—N(31)	90.9(2)
O(21)—Ni—N(32)	94.1(3)	N(11)—Ni—N(21)	95.3(2)
N(11)—Ni—N(31)	169.5(3)	N(11)—Ni—N(32)	93.0(3)
N(21)—Ni—N(31)	94.2(2)	N(21)—Ni—N(32)	170.2(3)
N(31)—Ni—N(32)	78.1(2)	C(16)—N(11)—C(17)	116.4(5)
C(18)—N(12)—C(111)	108.5(6)	C(26)—N(21)—C(27)	116.05(5)
C(31)—N(31)—C(312)	117.8(6)	C(310)—N(32)—C(311)	118.2(7)
O(11)—C(11)—C(12)	120.9(6)	O(11)—C(11)—C(16)	121.4(6)
C(12)—C(11)—C(16)	117.7(6)	C(11)—C(12)—C(13)	121.2(6)
C(12)—C(13)—C(14)	120.1(6)	C(13)—C(14)—C(15)	119.7(6)
C(13)—C(14)—C(141)	120.8(6)	C(15)—C(14)—C(141)	119.5(6)
C(14)—C(15)—C(16)	120.8(7)	N(11)—C(16)—C(11)	115.1(5)
N(11)—C(16)—C(15)	124.5(6)	C(11)—C(16)—C(15)	120.4(6)
N(11)—C(17)—C(18)	130.6(6)	N(12)—C(18)—C(17)	126.8(6)
N(12)—C(18)—C(19)	107.3(6)	C(17)—C(18)—C(19)	125.8(7)
C(18)—C(19)—C(110)	107.1(6)	O(21)—C(21)—C(22)	122.1(6)
O(21)—C(21)—C(26)	120.8(6)	C(22)—C(21)—C(26)	117.0(6)
C(21)—C(22)—C(23)	122.1(7)	C(22)—C(23)—C(24)	120.7(7)
C(23)—C(24)—C(25)	118.1(7)	C(23)—C(24)—C(241)	122.1(7)
C(25)—C(24)—C(241)	119.8(7)	C(24)—C(25)—C(26)	122.1(7)
N(21)—C(26)—C(21)	114.9(6)	N(21)—C(26)—C(25)	125.2(6)
C(21)—C(26)—C(25)	120.0(6)	N(21)—C(27)—C(28)	128.8(6)
N(22)—C(28)—C(27)	125.7(6)	N(22)—C(28)—C(29)	107.8(7)
C(27)—C(28)—C(29)	126.5(7)	C(28)—C(29)—C(210)	107.2(7)
N(31)—C(31)—C(32)	121.9(7)	C(31)—C(32)—C(33)	120.4(7)
C(32)—C(33)—C(34)	118.5(8)	C(33)—C(34)—C(35)	122.9(8)
C(33)—C(34)—C(312)	118.5(7)	C(35)—C(34)—C(312)	118.6(7)
C(34)—C(35)—C(36)	121.2(8)	C(35)—C(36)—C(37)	121.0(9)
C(36)—C(37)—C(38)	123.3(7)	C(36)—C(37)—C(311)	119.0(8)
C(38)—C(37)—C(311)	117.7(7)	C(37)—C(38)—C(39)	119.2(8)
C(38)—C(39)—C(310)	119.9(8)	C(19)—C(110)—C(111)	109.4(7)
N(12)—C(111)—C(110)	107.6(7)	C(29)—C(210)—C(211)	106.9(7)
N(22)—C(211)—C(210)	110.4(7)	N(32)—C(310)—C(39)	122.6(8)
N(32)—C(311)—C(37)	122.4(8)	N(32)—C(311)—C(312)	118.4(7)
C(37)—C(311)—C(312)	119.2(7)	N(31)—C(312)—C(34)	122.9(7)
N(31)—C(312)—C(311)	116.5(7)	C(34)—C(312)—C(311)	120.6(7)

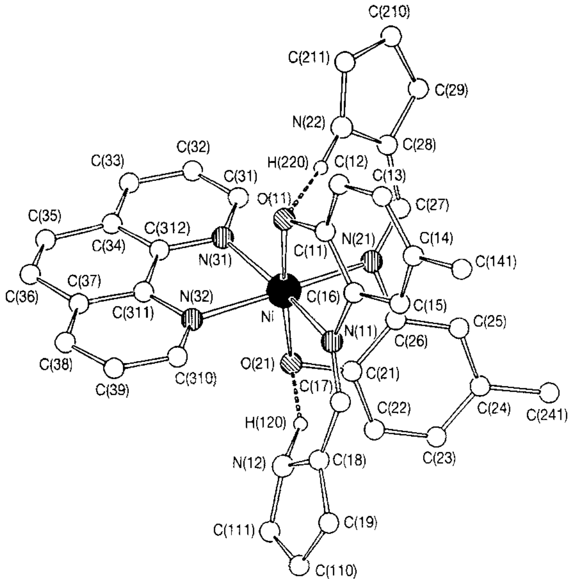

Figure 1. Crystal structure of Ni(HL)$_2$phen.

Table 4. Hydrogen bond lengths (Å) and angles(°) with e.s.d.s in parentheses.

O···H—N	O···N	O···H	H—N	O···H—N
O(21)···H(120)—N(12)	2.631(7)	1.405(4)	1.330(5)	148.4(3)
O(11)···H(220)—N(22)	2.632(7)	1.599(4)	1.045(5)	168.9(3)

anion is involved in a strong hydrogen bond with the N—H group of the other Schiff base [N···O = 2.631(7) and 2.632(7) Å] (Table 4). These values are on the low side of the range expected for N···O, 2.73–3.22 Å(11). The remaining structure features are basically identical to those found in other complexes containing similar ligands.

Spectroscopy studies

The i.r. spectrum of the complex is consistent with the X-ray data. At 3400–3200 cm^{-1}, the H$_2$L ligand shows two bands attributable to the ν(N—H) and ν(O—H) vibrations; the complex shows bands between 2850–3060 cm^{-1} characteristic of NH groups involved in hydrogen bonds. In addition, bands attributable to ν(OH) are absent, confirming that the deprotonated ligand is the one present in the complex. The ν(C=N) band, which in the ligand appears at 1630 cm^{-1}, shifts to 1590 cm^{-1} in the complex, reflecting coordination through the imine nitrogen(18). Bands at ca. 1510, 840 and 725 cm^{-1} in the complex are in agreement with the phenanthroline being coordinated to the metal atom(19).

The magnetic moment of the compound is 3.3 B.M. at room temperature (300 K), in keeping with the octahedral geometry proposed for the complex.

The diffuse reflectance spectrum of the complex in the near i.r.–vis. region shows two d–d transition bands at 19 200 and 8070 cm^{-1}, and a shoulder around 13 000 cm^{-1}. These bands may be respectively attributed to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$ transitions, in a distorted octahedral field(20). The shoulder may be attributed to the ν_1 band being split as a consequence of the distorted octahedral symmetry. The $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ transition was not observed, probably due to the presence of a strong charge transfer band in the region 23 000–26 000 cm^{-1}.

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