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Synthesis and structure of tetracoordinated nickel(II) complexes of deprotonated chelated aminoazo ligands: X-ray crystal structure of *bis*[1-isopropyl-3-methyl-4-(4-methylphenylazo)-5-(4-methoxyphenylamidato)pyrazole] nickel(II)

Alexander L. Nivorozhkin* and Hans Toftlund
Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

Leonid E. Nivorozhkin and Irina A. Kamenetskaya
Insititute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov on Don, Russia

Alla S. Antsishkina and Michail A. Porai-Koshits
N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 117090 Moscow, Russia

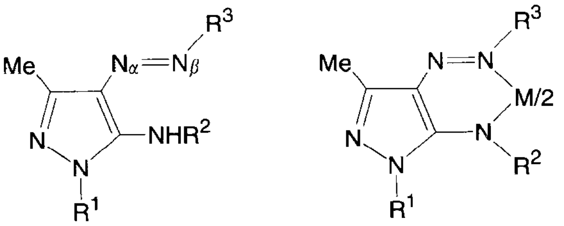
Summary

Tetracoordinate nickel(II) complexes NiL_2 derived from the deprotonated forms of aminoazoligands HL were prepared and investigated by spectroscopy and magnetic susceptibility measurements. The magnetic moments, which lie in the 3.1–3.6 B.M. range correspond to the occurrence both in solution and in the solid state of the high spin (S = 1) form and a tetrahedral configuration at the metal centre. The u.v. spectra exhibit three ligand field bands at 1020–1280 nm characteristic of high spin nickel(II) complexes. The large isotropic chemical shifts found in the ^1H n.m.r. spectra are consistent with partial delocalization of unpaired electron spin density to the ligand HOMO. The X-ray single crystal structure of NiL^4_2[L^4 = 1-isopropyl-3-methyl-4-(4-methylphenylazo)-5-(4-methoxyphenylamino)-pyrazole] reveals that the metal is coordinated by four nitrogen atoms in tetrahedral configuration with an angle of 90° between the N(1)NiN(2) and N(6)NiN(7) planes belonging to the different almost planar metallocycles. The rates of $R \rightleftarrows S$ interconversion of the tetrahedral configuration for NiL^4_2 and NiL^5_2 [L^5 = 1-isopropyl-3-methyl-4-phenylazo-d_5-5-(4-methoxyphenylamino)pyrazole] are slow on the n.m.r. timescale. In contrast to NiL^1_2–Ni^6_2, NiL^7_2, which contains coordinated NH-groups instead of NAr-groups, is planar.

Introduction

Metal–chelate complexes containing a coordinated arylazo-group have attracted much attention as commercial azo dyes with increased light fastness and resistance to oxidation compared to nonmetallated dyes$^{(1)}$. These usually incorporate one or two deprotonated hydroxy-, mercapto- or amino-groups in the *ortho* positions of adjacent aromatic rings so that five- and/or six-membered metallocycles are formed. The azo group has two potential coordination sites for a metal centre, and the problem of structural isomerism associated with the occurrence of different metal coordination modes has been frequently discussed$^{(2)}$. However, a complete structural assignment is often complicated due to the azo-hydrazone tautomerism of the coordinated ligand and *E*/*Z* isomerism of the azo group.

Compared to the complexes derived from tridentate ligands, those based on bidentate ligands constitute a simple model to provide insight into the coordination abilities of the azo-group. In this paper, we address these properties with respect to tetracoordinate nickel(II) metal–chelate complexes NiL_2 prepared from 1,3-substituted 4-arylazo-5-aminopyrazoles (Scheme 1). Pyrazole-containing azo-dyes are known to be one of the ubiquitous class of organic dyes$^{(1)}$. Moreover, tetracordinate metal–chelate complexes with a [$Ni(NR)_4$] ligand environment display intriguing stereochemistry related to the configuration around the metal centre depending on the particular type of coordinated nitrogen-containing functional group$^{(3,4)}$. This is illustrated by the extensively investigated tetrahedral β-aminopropeneiminato [NiN(azomethine)R_4] and planar formazanato [NiN(azo)R_4] complexes. Relatively less studied aminoazo metal–chelates are structurally intermediate between these two types. The X-ray structure of the hydrazonoimine nickel(II) complex of glyoxal$^{(5)}$ revealed a planar metal configuration which is also retained in solution. Annelation of the pyrazole fragment to a metallocyclic ring is known$^{(4)}$ to considerably stabilize tetrahedral geometry in [NiN_2S_2] complexes. We have been interested in determining how this influences the geometry of aminoazo complexes.



ML

Scheme 1. HL^1, R^1 = Ph, $R^2 = C_6H_4OMe$-*p*, $R^3 = C_6H_4Me$-*p*; HL^2, R^1 = Ph, $R^2 = C_6H_4COOMe$-*p*, $R^3 = C_6H_4Me$-*p*; HL^3, R^1 = Ph, R^2 = Ph, $R^3 = C_6H_4Me$-*p*; HL^4, R^1 = *i*-Pr, $R^2 = C_6H_4OMe$-*p*, $R^3 = C_6H_4Me$-*p*; HL^5, R^1 = *i*-Pr, $R^2 = C_6H_4OMe$-*p*, $R^3 = C_6D_5$; HL^6, R^1 = *i*-Pr, $R^2 = CH_2Ph$, $R^3 = C_6H_4Me$-*p*; HL^7, R^1 = *i*-Pr, R^2 = H, R^3 = Ph.

Experimental

Instrumentation

U.v. spectra were recorded on a Shimadzu UV 3100 spectrophotometer and n.m.r. spectra using Varian XL-100 (100 MHz) and Bruker AC 250 (250 MHz) spectrometers. Chemical shifts are reported relative to TMS as

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* Author to whom all correspondence should be directed.

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the internal standard. Electron impact mass spectra were obtained on a Varian MAT 311A instrument and i.r. spectra on a Perkin-Elmer 580 spectrometer. Magnetic moments were determined in the solid state by the Faraday method and in solution using the Evans method with TMS as a reference.

Synthesis of the arylaminopyrazoles HL^1–HL^6

HL^1–HL^6 were prepared in a three step reaction sequence consisting of the reaction of the appropriate aryldiazonium salts with 1,3-substituted 5-pyrazolones yielding 4-arylhydrazono-5-pyrazolones. These were converted to the corresponding 5-chloro derivatives using $POCl_3$. Nucleophilic substitution of the chlorine atom in the 4-arylazo-5-chloropyrazole with amines gave the final products. The last reaction was carried out using the following general procedure, which is a modified version of that reported in reference(6).

1,3-substituted 4-arylazo-5-aminopyrazoles HL^1–HL^6

The corresponding 4-arylazo-5-chloropyrazole (20 mmol) was fused with the appropriate amine (20 mmol) in a sealed glass tube at 140–150° C for 5–6 h. The resulting dark-brown solid was dissolved in DMF (20 cm^3) and treated with 20% NaOH (10 cm^3). After adding H_2O (20 cm^3), the solution was extracted with Et_2O (2×50 cm^3). The Et_2O layer was washed with H_2O, dried over Na_2SO_4 and evaporated *in vacuo*. Column chromatography of the residual oil (Al_2O_3, benzene as eluent, orange fraction collected) gave analytically pure HL^1–HL^6 as yellow-orange or red crystals in 40–45% yield after recrystallization from benzene–hexane (1:1).

1-Phenyl-3-methyl-4-(4-methylphenylazo)-5-(4-methoxyphenylamino)pyrazole HL^1

M.p. 144–146° C. Found: C, 72.2; H, 5.6; N, 17.9; $C_{24}H_{23}N_5O$ calcd: C, 72.5; H, 5.8; N, 17.6%. I.r. (cm^{-1}, Nujol): 3220 (w, NH), 1610 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 9.34 (br s, 1H, NH), 7.95–6.55 (m, 13H, aromatic H), 3.72 (s, 3H, OCH_3), 2.52 (s, 3H, pyr. CH_3), 2.30 (s, 3H, tolyl CH_3).

1-Phenyl-3-methyl-4-(4-methylphenylazo)-5-(4-carbomethoxyphenylamino)pyrazole HL^2

M.p. 157–158° C (literature(6) 158° C). Found: C, 70.9; H, 5.5; N, 16.6; $C_{25}H_{23}N_5O_2$ calcd: C, 70.6; H, 5.45; N, 16.5%. I.r. (cm^{-1}, Nujol): 3230 (w, NH), 1720 (C=O), 1620 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 9.39 (br s, 1H, NH), 7.71–6.60 (m, 13H, aromatic H), 3.75 (s, 3H, $COOCH_3$), 2.55 (s, 3H, pyr. CH_3), 2.30 (s, 3H, tolyl CH_3).

1-Phenyl-3-methyl-4-(4-methylphenylazo)-5-phenylaminopyrazole HL^3

M.p. 115–117° C. Found: C, 75.0; H, 5.5; N, 19.2; $C_{23}H_{21}N_5$ calcd: C, 75.2; H, 5.8; N, 19.1%. I.r. (cm^{-1}, Nujol): 3250 (w, NH), 1610 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 9.25 (br s, 1H, NH), 7.90–6.50 (m, 14H, aromatic H), 2.50 (s, 3H, pyr. CH_3), 2.34 (s, 3H, tolyl CH_3).

1-isopropyl-3-methyl-4-(4-methylphenylazo)-5-(4-methoxyphenylamino)pyrazole HL^4

M.p. 81–83° C. Found: C, 69.2; H, 6.8; N, 19.5; $C_{21}H_{25}N_5O$ calcd: C, 69.4; H, 6.9; N, 19.3%. I.r. (cm^{-1}, Nujol): 3240 (w, NH), 1615 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 8.94 (br s, 1H, NH), 7.41 (AA'BB', 4H, ^3J 7.5 Hz, $\Delta\nu$ 40.2 Hz, tolyl H), 6.93 (AA'BB', 4H, ^3J 8.4 Hz, $\Delta\nu$ 19.5 Hz, anisyl H), 3.98 (h, 1H, ^3J 6.7 Hz, CH), 3.76 (s, 3H, OCH_3), 2.50 (s, 3H, pyr. CH_3), 2.36 (s, 3H, tolyl CH_3), 1.25 (d, 6H, ^3J 6.7 Hz, $2CH_3$).

1-isopropyl-3-methyl-4-phenylazo-d_5-5-(4-methoxyphenylamino)pyrazole HL^5

M.p. 135–137° C. Found: C, 67.3; H, 7.7; N, 19.7; $C_{20}H_{18}D_5N_5O$ calcd: C, 67.8; H, 8.0; N, 19.8%. I.r. (cm^{-1}, Nujol): 3245 (w, NH), 1610 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 9.12 (br s, 1H, NH), 7.38 (AA'BB', 4H, ^3J 6.7 Hz, $\Delta\nu$ 40.0 Hz, anisyl H), 3.96 (h, 1H, ^3J 6.7 Hz, CH), 3.76 (s, 3H, OCH_3), 2.48 (s, 3H, pyr. CH_3), 1.24 (d, 6H, ^3J 6.7 Hz, $2CH_3$).

1-isopropyl-3-methyl-4-(4-methylphenylazo)-5-benzylaminopyrazole HL^6

M.p. 97–99° C. Found: C, 72.5; H, 7.2; N, 19.8; $C_{21}H_{25}N_5$ calcd: C, 72.6; H, 7.25; N, 20.2%. I.r. (cm^{-1}, Nujol): 3270 (w, NH), 1610 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 7.86 (br t, 1H, NH), 7.56–7.05 (m, 5H, benzyl aromatic H), 6.75 (AA'BB', 4H, ^3J 8.7 Hz, $\Delta\nu$ 37.5 Hz, tolyl H), 4.55 (d, 2H, ^3J 6.1 Hz, CH_2), 4.50 (h, 1H, ^3J 6.6 Hz, CH), 2.43 (s, 3H, pyr. CH_3), 2.33 (s, 3H, tolyl CH_3), 1.40 (d, 6H, ^3J 6.6 Hz, $2CH_3$).

Preparation of 1-isopropyl-3-methyl-4-phenylazo-5-aminopyrazole HL^7

This compound was obtained by the reaction of 1-isopropyl-3-methyl-5-aminopyrazole with phenyldiazonium chloride in AcOH following the literature method(7) for the synthesis of 1-phenyl-3-methyl-4-phenylazo-5-aminopyrazole. M.p. 132–134° C (from EtOH). Found: C, 64.4; H, 7.1; N, 30.0; $C_{13}H_{17}N_5$ calcd: C, 64.2; H, 7.0; N, 28.8%. I.r. (cm^{-1}, Nujol): 3480, 3330 (NH_2), 1610 (C=N). ^1H n.m.r. ($CDCl_3$, 100 MHz): δ 7.65–7.15 (m, 5H, aromatic H), 6.10 (br s, 2H, NH_2), 3.85 (h, 1H, ^3J 6.6 Hz, CH), 2.45 (s, 3H, CH_3), 1.28 (d, 6H, ^3J 6.6 Hz, $2CH_3$).

Preparation of the complexes

To HL (20 mmol) in absolute EtOH (2 cm^3) were added a solution of the corresponding metal acetate (10 mmol) in EtOH (1 cm^3) and freshly prepared NaOEt (20 mmol) in EtOH (1 cm^3). The reaction mixture was boiled under reflux for 15 min and cooled in a refrigerator. The resulting precipitate was collected and recrystallized from toluene to give ML_2 as crystalline solids in 70–80% yields. Analytical data for ML_2 are given in Table 1.

X-ray structural determination

Crystals of NiL^4_2 suitable for X-ray crystallography were obtained by slow cooling of a saturated toluene–octane (1:1) solution placed in a 5 mm diameter glass ampoule. The crystals were monoclinic, space group C2/c, $a =$

Table 1. Analytical and magnetic moment data for the complexes.

Compound	M.p. (°C)	Empirical formula	Found (Calcd.)(%)			μ_{eff} (B.M.)	μ_{eff} (B.M.)[a]	m/z (M^+)
NiL^1	218	$C_{48}H_{44}N_{10}O_2Ni$	67.4	5.2	16.4	3.25	3.31	850
			(67.7)	(5.2)	(16.3)			
NiL^2	206	$C_{50}H_{44}N_{10}O_4Ni$	65.9	5.1	15.5	3.12	3.24	906
			(66.2)	(4.9)	(15.4)			
NiL^3	322 (dec.)	$C_{46}H_{40}N_{10}Ni$	69.7	5.0	17.3	3.68	3.55	790
			(69.8)	(5.1)	(17.7)			
NiL^4	216	$C_{42}H_{48}N_{10}O_2Ni$	64.0	6.2	17.8	3.19	3.40	782
			(64.4)	(6.2)	(17.9)			
NiL^5	225	$C_{40}H_{34}D_{10}N_{10}O_2Ni$	62.3	7.3	18.4	3.69	3.61	764
			(62.8)	(7.1)	(18.3)			
NiL^7	238	$C_{26}H_{32}N_{10}Ni$	57.7	5.9	25.5	0	0	542
			(57.5)	(5.9)	(25.8)			
ZnL^4	219	$C_{42}H_{48}N_{10}O_2Zn$	63.7	6.1	17.9			789
			(63.8)	(6.1)	(17.7)			
ZnL^5	202	$C_{40}H_{34}D_{10}N_{10}O_2Zn$	62.5	7.1	18.3			771
			(62.2)	(7.1)	(18.1)			

[a] In $CDCl_3$ solution.

Table 2. Bond lengths (Å) with e.s.d.s in parentheses for NiL^4_2.

Ni(1)—N(1)	1.929(8)	Ni(1)—N(2)	1.954(8)
Ni(1)—N(6)	1.932(8)	Ni(1)—N(7)	1.949(7)
N(1)—C(4)	1.33(1)	N(1)—C(15)	1.44(1)
N(2)—N(3)	1.29(1)	N(2)—C(8)	1.45(1)
N(3)—C(1)	1.31(1)	N(4)—N(5)	1.41(1)
N(4)—C(2)	1.29(1)	N(5)—C(4)	1.37(1)
N(5)—C(5)	1.48(1)	C(1)—C(2)	1.44(1)
C(1)—C(4)	1.44(2)	C(2)—C(3)	1.51(2)
C(5)—C(6)	1.55(2)	C(5)—C(7)	1.53(1)
C(8)—C(9)	1.39(2)	C(8)—C(13)	1.36(1)
C(9)—C(10)	1.38(2)	C(10)—C(11)	1.38(2)
C(11)—C(12)	1.39(2)	C(11)—C(21)	1.55(2)
C(12)—C(13)	1.39(2)	C(15)—C(16)	1.38(1)
C(15)—C(20)	1.36(1)	C(16)—C(17)	1.40(2)
C(17)—C(18)	1.37(2)	C(18)—C(19)	1.38(2)
C(18)—O(1)	1.40(1)	C(19)—C(20)	1.38(2)
O(1)—C(52)	1.43(1)	N(6)—C(25)	1.34(1)
N(6)—C(36)	1.45(1)	N(7)—N(8)	1.30(1)
N(7)—C(29)	1.44(1)	N(8)—C(22)	1.34(1)
N(9)—N(10)	1.41(1)	N(9)—C(23)	1.30(2)
N(10)—C(25)	1.36(1)	N(10)—C(26)	1.46(2)
C(22)—C(23)	1.40(1)	C(22)—C(25)	1.40(1)
C(23)—C(24)	1.53(2)	C(26)—C(57)	1.54(3)
C(26)—C(55)	1.58(3)	C(29)—C(30)	1.39(2)
C(29)—C(34)	1.37(2)	C(30)—C(31)	1.37(2)
C(31)—C(32)	1.36(2)	C(32)—C(33)	1.40(2)
C(32)—C(42)	1.52(2)	C(33)—C(34)	1.39(2)
C(36)—C(37)	1.35(2)	C(36)—C(41)	1.38(2)
C(37)—C(38)	1.40(2)	C(38)—C(39)	1.37(2)
C(39)—C(40)	1.31(2)	C(39)—O(2)	1.39(2)
C(40)—C(41)	1.42(2)	O(2)—C(56)	1.44(2)

Table 3. Bond angles (°) with e.s.d.s in parentheses for NiL^4_2.

N(1)—Ni(1)—N(2)	94.8(3)	N(1)—Ni(1)—N(6)	114.3(3)
N(1)—Ni(1)—N(7)	119.6(3)	N(2)—Ni(1)—N(6)	115.0(3)
N(2)—Ni(1)—N(7)	120.8(3)	N(6)—Ni(1)—N(7)	94.0(3)
Ni(1)—N(1)—C(4)	121.5(6)	Ni(1)—N(1)—C(15)	112.7(6)
C(4)—N(1)—C(15)	123.1(8)	Ni(1)—N(2)—N(3)	128.1(6)
Ni(1)—N(2)—C(8)	117.8(6)	N(3)—N(2)—C(8)	113.4(8)
N(2)—N(3)—C(1)	120.1(8)	N(5)—N(4)—C(2)	105.6(8)
N(4)—N(5)—C(4)	112.2(8)	N(4)—N(5)—C(5)	115.6(8)
C(4)—N(5)—C(5)	126.7(8)	N(3)—C(1)—C(2)	124.5(9)
N(3)—C(1)—C(4)	131.1(9)	C(2)—C(1)—C(4)	101.4(8)
N(4)—C(2)—C(1)	112.9(9)	N(4)—C(2)—C(3)	120.3(9)
C(1)—C(2)—C(3)	126.8(9)	N(1)—C(4)—N(5)	131.0(9)
N(1)—C(4)—C(1)	124.1(9)	N(5)—C(4)—C(1)	104.8(8)
N(5)—C(5)—C(6)	109.5(9)	N(5)—C(5)—C(7)	108.7(9)
C(6)—C(5)—C(7)	111.0(1)	N(2)—C(8)—C(9)	120.9(9)
N(2)—C(8)—C(13)	119.3(9)	C(9)—C(8)—C(13)	1196.8(9)
C(8)—C(9)—C(10)	120.0(1)	C(9)—C(10)—C(11)	121.0(1)
C(10)—C(11)—C(12)	118.0(1)	C(10)—C(11)—C(21)	121.0(1)
C(12)—C(11)—C(21)	121.0(1)	C(11)—C(12)—C(13)	121.0(1)
C(8)—C(13)—C(12)	120.0(1)	N(1)—C(15)—C(1)	116.7(9)
N(1)—C(15)—C(20)	122.9(9)	C(16)—C(15)—C(20)	120.2(9)
C(15)—C(16)—C(17)	119.9(9)	C(16)—C(17)—C(18)	119.0(1)
C(17)—C(18)—C(19)	122.0(1)	C(17)—C(18)—O(1)	122.0(1)
C(19)—C(18)—O(1)	117.0(1)	C(18)—C(19)—C(20)	119.0(1)
C(15)—C(20)—C(19)	121.0(1)	C(18)—O(1)—C(52)	116.7(9)
Ni(1)—N(6)—C(25)	121.8(7)	Ni(1)—N(6)—C(36)	117.0(6)
C(25)—N(6)—C(36)	120.8(8)	Ni(1)—N(7)—N(8)	128.5(6)
Ni(1)—N(7)—C(29)	121.0(6)	N(8)—N(7)—C(29)	110.3(8)
N(7)—N(8)—C(22)	119.1(8)	N(10)—N(9)—C(23)	105.5(9)
N(9)—N(10)—C(25)	110.9(8)	N(9)—N(10)—C(26)	117.6(9)
C(25)—N(10)—C(26)	128.2(9)	N(8)—C(22)—C(23)	123.0(9)
N(8)—C(22)—C(25)	131.0(9)	C(23)—C(22)—C(25)	105.9(9)
N(9)—C(23)—C(22)	112.0(1)	N(9)—C(23)—C(24)	122.0(1)
C(22)—C(23)—C(24)	126.0(1)	N(6)—C(25)—N(10)	129.9(9)
N(6)—C(25)—C(22)	124.3(9)	N(10)—C(25)—C(22)	105.8(9)
N(10)—C(26)—C(57)	112.0(1)	N(10)—C(26)—C(55)	106.0(1)
C(57)—C(26)—C(55)	110.0(2)	N(7)—C(29)—C(30)	121.7(9)
N(7)—C(29)—C(34)	119.9(9)	C(30)—C(29)—C(34)	118.0(1)
C(29)—C(30)—C(31)	120.0(1)	C(30)—C(31)—C(32)	123.0(1)
C(31)—C(32)—C(33)	117.0(1)	C(31)—C(32)—C(42)	123.0(1)
C(33)—C(32)—C(42)	119.0(1)	C(32)—C(33)—C(34)	120.0(1)
C(29)—C(34)—C(33)	121.0(1)	N(6)—C(36)—C(37)	121.0(1)
N(6)—C(36)—C(41)	119.0(9)	C(37)—C(36)—C(41)	120.0(1)
C(36)—C(37)—C(38)	120.0(1)	C(37)—C(38)—C(39)	119.0(1)
C(38)—C(39)—C(40)	121.0(1)	C(38)—C(39)—O(2)	114.0(1)
C(40)—C(39)—O(2)	125.0(1)	C(39)—C(40)—C(41)	120.0(1)
C(36)—C(41)—C(40)	120.0(1)	C(39)—O(2)—C(56)	115.0(1)

36.075(10), $b = 11.277(4)$, $c = 21.519(10)$ Å; $\beta = 111.87(4)^\circ$, $V = 8125(1)$ Å^3, $Z = 8$, $D_c = 1.28$ g cm^{-3}. The unit cell parameters and intensities of 6389 reflections were recorded with an Enraf-Nonius CAD-4 diffractometer (MoK_α graphite monochromator, $\lambda = 0.71069$ Å, $\mu(\mathrm{Mo}K_\alpha) = 2.8$ cm^{-1}, θ/ω scan, $\theta = 25^\circ$). The structure was solved by the heavy-atom method and refined by full-matrix least-squares on 2823 observed $[I > 2\sigma(I)]$ intensities using

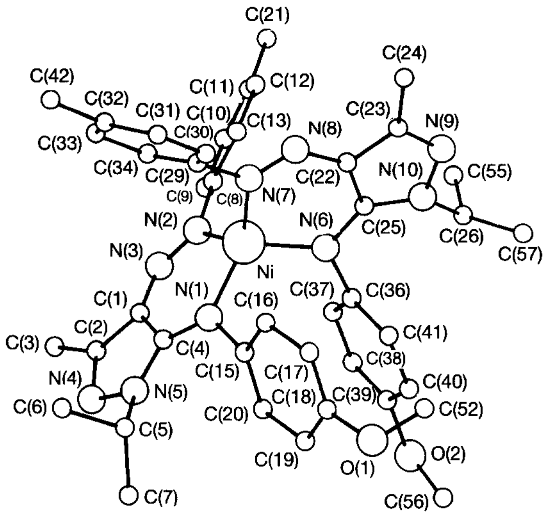

Figure 1. Molecular structure of NiL$_2^4$.

the SHELX programs, anisotropically [Ni, N(1), N(2), N(6) and N(7)] and isotropically (other non-H atoms) to $R = 0.063$, $R_w = 0.068$. Bond lengths and angles are given in Tables 2 and 3. The molecular structure of NiL$_2^4$ is shown in Figure 1.

Results and discussion

Synthesis of the azoaminopyrazoles

Preparation of the 4-azo-5-aminopyrazoles from the corresponding 5-chloro derivatives by nucleophilic substitution requires severe reaction conditions, *viz.* fusing of the reaction components at high temperature (140–150° C). The reaction was found not to occur even in strongly polar solvents such as DMF and DMSO, as on previous observations(8). An alternative synthetic strategy to activate a chlorine atom and carry out the reaction in solution has been reported using 2-alkylated pyrazoles bearing a positive charge on the adjacent nitrogen atom(8).

The protons of the amino group form a weak hydrogen bond to the N_β atoms of the azo group and display broadened signals in the ^1H n.m.r. spectra with chemical shifts in the range of 7.8–9.4 p.p.m. which disappear under deuteration. The strength of the hydrogen bond increases on going from alkyl to aryl R^2 substituents, as may be deduced from the higher-field shift of the NH proton signal by 1.5 p.p.m. for $R^2 = \mathrm{Alk}$ compared to $R^2 = \mathrm{Ar}$. The presence of spin–spin coupling between the NH and NCH_2 protons ($^3J = 6.1$ Hz) in the case of HL^6, confirms the occurrence of the azo-tautomeric form of HL, in contrast to 4-hydroxy-5-arylazopyrazoles possessing a hydrazono structure with a labile hydrogen atom localized at the azo-group nitrogen(9).

U.v. spectra and magnetic properties of the ML$_2$ complexes

The ML$_2$ complexes were prepared by the reaction of HL with the corresponding metal acetates in a 2:1 ratio in EtOH in the presence of an equimolar amount of sodium ethoxide as a base to achieve deprotonation of the amino-group. NiL$_2^6$ has not been obtained in analytically pure form. The complexes are dark brown (M = Ni) or dark red (M = Zn) solids with good solubility in chloroform and toluene and high m.ps. Under neutral reaction conditions the formation of copper(II) and palladium(II) complexes with 3-phenyl-4-arylazo-5-aminopyrazole and 3,5-diamino-4-phenylazopyrazole containing protonated amino groups was reported(10).

The magnetic moments of NiL$_2^1$–NiL$_2^5$ determined in solution and in the solid state (Table 1) are very similar, at 3.1–3.6 B.M., and indicate a high-spin structure with strong spin-orbital coupling, whereas NiL$_2^7$ is diamagnetic. The u.v. spectral data obtained in chloroform are given in Table 5. NiL$_2^7$ exhibits a u.v. spectrum typical of diamagnetic planar nickel(II) complexes. Two ligand field (LF) bands at 579 and 684 nm may be assigned to ^1E and $^1B_2$ transitions in D_{4h} symmetry. The LMCT band is observed at 486 nm, in the same range as for the zinc complexes ZnL$_2^4$ and Zn$_2^5$. In contrast, NiL$_2^1$–NiL$_2^5$ display LMCT absorptions shifted by 50–60 nm to lower wavelengths. Their LF spectra are also essentially different from that of NiL$_2^7$ and contain a relatively weak two- or three-component absorption in the near i.r. region centred at ca. 1020, 1160 and 1270 nm and associated with d–d transitions in a high-spin state with T_d symmetry. These are clearly detected for NiL$_2^2$, NiL$_2^4$ and NiL$_2^5$ but not well resolved for NiL$_2^1$ and NiL$_2^3$. Similar spectral features were reported for the tetrahedral aromatic aminoazo nickel(II) metal–chelates(11) and those derived from hydrazonoimines of glyoxal(12). For these compounds, the third mostly i.r. shifted component has not been observed. In the case of NiL$_2$ it appears as a rather flattened shoulder. Reliable assignment of the above d–d bands referring to $^3A_2$, $^3T_1(P)$ and $^3T_2$ transitions is complicated and requires a single crystal study(13).

^1H n.m.r. spectroscopy

The ^1H n.m.r. spectra of NiL$_2^1$–NiL$_2^6$ display large isotropic chemical shifts (Table 5) in the range from 35 to −23 p.p.m. characteristic of high spin (S = 1) tetracoordinated nickel(II) complexes, due to the partial delocalization of the unpaired electron spin density to the ligand HOMO. The assignment of the signals was based on their integral intensities, literature data and structural variations.

The completely deuterated phenylazo-d$_5$ group in NiL$_2^5$ allowed assignment of the most down-field shifted signals at about 30 p.p.m. to the aromatic protons of the 5-NAr group, whereas those belonging to the 4-arylazo group appear at about 25 p.p.m. The resonances of the 1-NPh group are rather narrow and almost unshifted from the usual diamagnetic region, which may be caused by the essential acoplanarity of the phenyl ring with respect to the neighbouring conjugated π-electron system involving metallocyclic and pyrazole rings. The 3-CH_3 proton signals appear at the high field region (ca. −22 p.p.m.) for all the complexes, in accordance with data reported for the analogous paramagnetic tetrahedral 4-aldimino-5-thiopyrazolato nickel(II) metal–chelates(14).

For NiL$_2^4$ and NiL$_2^5$, which contain a diastereotopic 1-isopropyl substituent, the methyl group protons show a spectral pattern consisting of two singlets [with fine structure due to $^3J(CH_3CH)$ spin–spin coupling masked by paramagnetic broadening], corresponding to the slow R$\leftrightarrows$S inversion of the tetrahedral configuration at the metal centre. We were unable to achieve a coalescence point or any essential exchange broadening at temperatures as high as 55° C in $CDCl_3$ and 120° C in $C_6D_5NO_2$. Steric overcrowding of the ligands in proximity to the metal centre in tetracoordinate complexes is known to destabilize

Table 4. Electronic spectra of the ML_2 complexes.

Compound	λ_{max}, nm [(log ε(dm^3 mol^{-1} cm^{-1})] in $CHCl_3$ Intraligand	LMCT	LF
NiL^1_2	346(4.39), 396(4.47)	425sh (4.45)	~1000(1.59), ~1150(1.58)[a]
NiL^2_2	310(4.57), 327sh (4.56), 390(4.55)	432sh (4.43)	1033(1.56), 1170(1.63), 1279(1.60)
NiL^3_2	350(4.45), 392(4.49)	423sh (4.45)	1012(1.61), ~1150(1.60)[a]
NiL^4_2	348(4.82), 359sh (4.81) 385(4.77)	446(4.72)	1029(1.67), 1165(1.75), 1261(1.69)
NiL^5_2	340(4.16), 387(4.12)	438(4.04)	1022(1.82), 1153(1.84), 1278(1.79)
NiL^7_2	311(4.36), 368(4.20)	486(3.66)	579(3.53), 684(2.40)
ZnL^4_2	330(4.09), 382(4.26)	470(4.40)	
ZnL^5_2	330(4.08), 384(4.30)	474(4.48)	

[a] Accompanied by a flattened shoulder.

Table 5. ^{1}H n.m.r. data for the complexes (δ, p.p.m., $CDCl_3$, 25° C, 250 MHz).

Compound	R^1	R^2	R^3	CH_3
NiL^1	8.20–6.23 (m, 10H)	29.95 (br s, 8H, arom.) 8.61 (6H, $2OCH_3$)	24.06 (8H, arom.) 16.11 (6H, $2CH_3$)	−22.24
NiL^2	7.98–6.78 (m, 10H)	36.23, 31.70 (8H, arom.) 6.78 (6H, $2COOCH_3$)	23.90 (8H, arom.) 15.42 (6H, $2CH_3$)	−22.04
NiL^3	8.14–6.52 (m, 10H)	33.51, 30.32 (8H, arom.)	23.97 (8H, arom.) 15.87 (6H, $2CH_3$)	−22.13
NiL^4	−1.59, −1.10 (12H, $4CH_3$)	32.18, 29.54 (8H, arom.) 8.95 (6H, $2OCH_3$)	24.18 (8H, arom.) 16.33 (6H, $2CH_3$)	−22.58
NiL^5	−1.53, −1.13 (12H, $4CH_3$)	31.85, 29.57 (8H, arom.) 8.97 (6H, $2OCH_3$)		−22.49
NiL^7	3.24 (h, 2H, ^3J 6.0 Hz, 2CH) 1.03 (d, 12H, ^3J 6.0 Hz, $4CH_3$)	5.02 (br s, 2H, NH)	7.90–7.50 (m, 10H)	1.68
ZnL^4	3.63 (h, 2H, ^3J 6.5 Hz, 2CH) 1.03 (dd, 12H, ^3J 6.5 Hz, $\Delta\nu$ 32.9 Hz, $4CH_3$)	7.17 (AA′BB′, 8H, ^3J 8.3 Hz, $\Delta\nu$ 77.3 Hz, arom.) 3.71 (s, 6H, $2OCH_3$)	6.54–6.37 (m, 8H) 2.25 (s, 6H, $2CH_3$)	2.41
ZnL^5	3.62 (h, 2H, ^3J 6.6 Hz, 2CH) 1.02 (dd, 12H, ^3J 6.6 Hz, $\Delta\nu$ 32.5 Hz, $4CH_3$)	6.58–6.40 (m, 8H) 3.71 (s, 6H, $2OCH_3$)		2.41

a planar configuration compared to tetrahedral and increase the barriers against R ⇆ S interconversion(4). For example, related $\Delta G^{\neq}$ values for β-aminopropeneiminato complexes with $[Ni(NAr)_4]$ ligand environment were found to lie in the 70–75 kJ mol^{-1} range and even higher(15). Annelation of a pyrazole heteroaromatic ring to the metallocyclic fragment could also contribute to the enhancement of inversion barriers(4).

Similarly, R ⇆ S interconversion for ZnL_2 complexes is slow on the n.m.r. timescale. The protons of the 1-N-*i*-Pr group in the case of ZnL^5_2 and ZnL^4_2 give a pair of doublets with diastereotopic splittings $\Delta\nu$ of 32.5 and 32.9 Hz, respectively, at 250 MHz. Increasing the temperature up to 150° C in $C_6D_5NO_2$ does not result in the occurrence of an exchange pattern. The barriers to interconversion for zinc(II) complexes are usually higher than those of nickel(II) chelates by 20–60 kJ mol^{-1} and lie in the 60–100 kJ mol^{-1} range. To the best of our knowledge, activation barriers for sterically crowded ZnN_4 complexes have not been reported. These may be large enough to allow a preparative separation of enantiomers.

The importance of steric requirements in tuning the geometry at the metal centre in tetracoordinated $[MN_4]$ metal–chelate complexes is also inferred from comparison of the NiL^1–NiL^5 complexes, which have a $[Ni(NAr)_4]$ coordination sphere, with NiL^7_2, which is of the $[Ni(NAr)_2(NH)_2]$ type. The latter is diamagnetic and planar both in solution and in the solid state according to the magnetic susceptibility and u.v. spectral data. Its ^{1}H n.m.r. spectrum does not show any essential isotropic chemical shifts and is similar to the zinc(II) complexes. The NH-resonances were observed at about 5 p.p.m. and were suppressed upon deuteration.

Molecular structure of NiL^4_2

The structure of the NiL^4_2 is shown in Figure 1. The configuration at the metal centre is tetrahedral, the angle θ between the NiN(1)N(2) and NiN(6)N(7) planes being 90.0(3)°. The nickel atom is coordinated to the two nitrogens of the deprotonated amino groups and the two β-nitrogens of the azo groups bound to the methoxyphenyl substituents, forming two six-membered metallocyclic rings. The metallocycles possess almost entirely planar conformations with a small folding along the N(1)···N(2) (4°) and N(6)···N(7) (7°) axes. The pyrazole rings are nearly coplanar with neighbouring metallocyclic rings. The toluene rings are twisted about 80° out of the adjacent metallocyclic ring planes and also to each other while the planes of the methoxyphenyl rings are twisted by 51

[N(1)—$C_6H_4OCH_3$] and 61° [N(6)—$C_6H_4OCH_3$] relative to the NiN(1)N(2) and NiN(6)N(7) planes, respectively, being close to a parallel mutual orientation with a corresponding dihedral angle of 13°. The methoxy-group C(39)O(2)C(56) is almost coplanar with the parent phenyl ring, the angle between the C(39)O(2)C(56) plane and that of the aromatic ring being 7°. The second group C(18)O(1)C(52) is rotated by 49°.

The Ni—N_{azo} bond lengths Ni—N(2) 1.954(8) Å and Ni—N(7) 1.949(7) Å are ca. 0.02 Å larger than those of Ni—N(amino) Ni—N(1) 1.929(8) Å and Ni—N(6) 1.932(8) Å. Similar bond lengths in planar nickel(II) complexes derived from N,N′-polymethylene bridged hydrazonoimines of glyoxal and 1-phenylbutane-1,2,3-trione(16) are 0.025–0.1 Å longer. Both azo groups have an essentially double bond character, the corresponding bond lengths being N(2)—N(3) 1.29(1) Å and N(7)—N(8) 1.30(1) Å.

Preliminary results(17) on the X-ray single crystal structure of the complex CuL^2_2 reveal a pseudo-tetrahedral configuration around the copper centre ($\theta = 68°$), which is coordinated to the N_β atoms of the azo groups.

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