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Nickel(II)-induced activation of a carbon–nitrogen single bond(s) of a co-ordinated ligand by hydroxylated substrates: generation of mono- and bi-nuclear complexes with modified ligand frameworks†

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In the presence of some hydroxylated compounds as substrates, complexations of nickel(II) with the pentadentate N_4S ligand methyl 2-{2-bis[(3,5-dimethylpyrazol-1-ylmethyl)amino]propylamino}cyclopent-1-ene-1-carbodithioate (Hmmpcd) having a pair of flexible pyrazolyl arms proceeded through unusual reaction paths involving C–N bond cleavage process. For example, the product **1** obtained in methanol as substrate is a square planar compound with a modified ligand structure that includes a methoxy group provided by the solvent. With an acidic substrate *viz.* phenol the product is also a square planar compound **2** with one of the pendant arms of Hmmpcd being replaced by a hydrogen atom. On the other hand, in the presence of a basic substrate *viz.* ethanolamine the ligand undergoes more extensive breakdown to generate a binuclear complex **3** with a bridging pyrazolyl group. These complexes **1**–**3** were characterised by X-ray crystallography and ^{1}H NMR spectroscopy. Compound **1** displayed a reversible one-electron $\mathrm{Ni^{II}} \longrightarrow \mathrm{Ni^{I}}$ reduction at $E_{\frac{1}{2}} \approx -1.0$ V *vs.* Ag–AgCl reference as established by cyclic voltammetry and combined coulometry/EPR experiments. Such reversibility of electron transfer is unusual for a square-planar nickel(II) compound in an acyclic ligand environment. Stabilisation of the reduced nickel(I) species by methoxy group co-ordination provides a probable explanation for this reversible electron transfer.

Methyl 2-{2-bis[(3,5-dimethylpyrazol-1-ylmethyl)amino]propylamino}cyclopent-1-ene-1-carbodithioate (Hmmpcd) is a pentadentate N_4S ligand with a pair of appended pyrazolyl arms and a carbodithioate functionality behaving more like an electronic analogue of thiol, when co-ordinated to metal ions.[1,2] With copper(II) and zinc(II)[2] and cobalt(II)[3] ions it forms five-co-ordinated complexes of distorted square pyramidal and trigonal bipyramidal geometries. In the case of nickel(II), however, the co-ordination behaviour of this and related ligands is not that straightforward. Reaction proceeds through solvolytic cleavage of an otherwise unreactive C–N single bond of the co-ordinated ligand in alcohol as solvent to generate square planar products with modified ligand structure that includes an alkoxy group provided by the solvent.[4] Herein we report our studies on the interactions of the N_4S ligand Hmmpcd with $Ni(ClO_4)_2\cdot 6H_2O$ under diverse reaction conditions in the presence of hydroxylated compounds as substrates. Both mono- and binuclear square planar complexes with modified ligand structures are obtained by metal-induced C–N bond cleavage of the ligand. Compounds have been characterised by crystal structure analyses and spectroscopic methods. Redox and spectroelectrochemical studies are also reported.

Experimental

Materials

The ligand Hmmpcd was prepared as reported earlier.[2] Solvents were purified and dried from appropriate reagents[5] and distilled prior to use. All other chemicals were reagent grade, available commercially and used as received.

Preparations‡

$[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ 1. A solution of nickel(II) perchlorate hexahydrate (0.18 g, 0.50 mmol) in 10 cm^3 methanol was added dropwise to a stirred solution of Hmmpcd (0.22 g, 0.50 mmol), also in methanol (15 cm^3), to form a green solution. The solution was stirred at room temperature for *ca.* 2 h, when a moss-green microcrystalline compound was obtained. The product was collected by filtration, washed with chilled methanol–diethyl ether (2 : 1 v/v, 4 × 10 cm^3) and finally dried over $CaCl_2$ under reduced pressure. The product was recrystallised from acetone–*n*-hexane. Yield: 0.18 g (66%). Found: C, 40.0; H, 5.5; N, 10.3. Calc. for $C_{18}H_{29}ClN_4NiO_5S_2$: C, 40.1; H, 5.4; N, 10.4%. IR (KBr disk): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$/pyrazole ring, 1555s; $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N} + \mathrm{C}\overset{\cdots}{-}\mathrm{C})$, 1460s; ν_{asym}(Cl–O), 1100s; δ(O–Cl–O), 630 cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 5.98 (s, 1 H, Me_2pz ring), 5.46 and 5.06 (ABq, 2 H, CH_2, $J_{AB} = 11.1$), 4.34 and 4.10 (ABq, 2 H, CH_2, $J_{AB} = 9.3$), 4.20 (m, 1 H, one of CH_2), 3.76 (pseudotriplet, 1 H, one of CH_2, $J_{AB} = 12.0$ Hz), 3.54 (m, 1 H, CH), 3.48 (s, 3 H, OCH_3), 2.68–2.62 (m, 4 H, cyclopentene ring), 2.60 (s, 3 H, SCH_3), 2.34 and 2.26 (pair of s, 6 H, CH_3/Me_2pz ring), 1.84–1.77 (m, 2 H, cyclopentene ring) and 1.23 (d, 3 H, CH_3). Λ_M (25 °C, CH_3CN) 129 S cm^2 mol^{-1}.

$[Ni\{(N_3S)H\}]ClO_4$ 2. To a solution of Hmmpcd (0.22 g, 0.5

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3859/

‡ During these syntheses the N_4S ligand undergoes C–N bond(s) cleavage as shown in Scheme 1. The modified forms of the ligand are represented by their respective donor atoms set.

mmol) in *n*-propanol (15 cm^3) containing 0.12 g (1.25 mmol) of phenol was added with stirring a solution of nickel(II) perchlorate hexahydrate (0.18 g), in the same solvent (20 cm^3). The reaction mixture changed immediately to green. It was heated at reflux for *ca.* 1 h and then cooled to room temperature when a green microcrystalline solid was obtained. This was collected by filtration, washed with chilled methanol–ether (2 : 1 v/v) and dried *in vacuo*. The product was recrystallised from methanol. Yield: 0.1 g (40%). Found: C, 38.6; H, 5.1; N, 11.1. Calc. for $C_{16}H_{25}ClN_4NiO_4S_2$: C, 38.8; H, 5.0; N, 11.3%. IR (KBr disk): ν(C$\overset{..}{-}$C) + ν(C$\overset{..}{-}$N)/pyrazole ring, 1560s; ν(C$\overset{..}{-}$N + C$\overset{..}{-}$C), 1480s; ν_{asym}(Cl–O), 1100s; δ(O–Cl–O), 630s cm^{-1}. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 5.93 (s, 1 H, Me_2pz ring), 5.08–4.80 (m, 3 H, CH_2, NH), 3.69–3.40 (m, 3 H, CH_2, CH), 2.68–2.61 (m, 4 H, cyclopentene ring), 2.60 (s, 3 H, SCH_3), 2.30 and 2.25 (pair of s, 6 H, CH_3/Me_2pz ring), 1.86 (m, 2 H, cyclopentene ring) and 1.26 (d, 3 H, CH_3). Λ_M (25 °C, CH_3CN) 138 S cm^2 mol^{-1}.

[(N_2S)Ni(μ-Me_2pz)Ni(N_2S)]ClO_4 3. *Method 1.* A solution of Hmmpcd (0.22 g, 0.5 mmol) in acetonitrile (15 cm^3) was combined with 2 cm^3 ethanolamine. Nickel(II) perchlorate hexahydrate (0.18 g, 0.5 mmol) dissolved in 10 cm^3 acetonitrile was added. The mixture was heated to reflux for *ca.* 4 h during which time it turned from green to orange-red. It was filtered and the filtrate left to stand in the air. After three days a red crystalline compound was collected by filtration, washed with methanol–ether (1 : 1 v/v), dried *in vacuo* and finally recrystallised from acetonitrile. Yield: 0.12 g (31%). Found: C, 39.1; H, 5.6; N, 10.9. Calc. for $C_{25}H_{41}ClN_6Ni_2O_4S_4$: C, 38.9; H, 5.3; N, 10.9%. IR (KBr disk): ν(N–H), 3235m; ν(C$\overset{..}{-}$C) + ν(C$\overset{..}{-}$N)/pyrazole ring, 1570s, 1580m; ν(C$\overset{..}{-}$C + C$\overset{..}{-}$N), 1465s; ν_{asym}(Cl–O), 1100s; δ(O–Cl–O), 630s cm^{-1}. Λ_M (25 °C, CH_3CN) 120 S cm^2 mol^{-1}.

Method 2. To a stirred solution of compound **2** (0.1 g, 0.2 mmol) in acetonitrile (15 cm^3) was added 0.6 cm^3 ethanolamine and the resulting green solution heated at reflux for *ca.* 1 h during which time it turned orange-red. It was filtered and the filtrate concentrated to *ca.* 10 cm^3. On standing at room temperature the solution yielded red crystalline solid. The remaining work-up was as described in method 1. Yield: 0.05 g (30%).

CAUTION: Perchlorate salts of metal complexes are potentially explosive.[6] Complexes reported above were isolated in small amounts and handled with care.

Physical methods

The ^1H NMR spectra were recorded on a Bruker model Avance DPX 300 spectrometer. Spectroelectrochemical measurements were carried out by means of a Fuso model 312 polarograph with HECS 321B potential sweep unit. Spectral measurements were performed using a Photal MCPD-1000 spectro-multichannel photodetector with a Photal MC-934 external light source unit. An NEC PC-9801 VX personal computer and a Photal MC-920 plotter were used for control and data retrieval.[7,8] Electrochemical measurements were done with a Bioanalytical system model 100 B/W workstation. Cyclic voltammograms were recorded at 25 ± 1 °C in acetonitrile under purified dinitrogen with the electroactive component at *ca.* 10^{-3} mol dm^{-3}. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte. A three-electrode configuration was employed with Ag–AgCl as reference, a glassy carbon working and a platinum wire counter electrode. For coulometry a platinum gauze working electrode was used. Satisfactory coulometric experiments were done in CH_3CN solution at −40 °C or below and the yellow catholyte solutions were immediately frozen at liquid nitrogen temperature before EPR measurements. Scrupulously dried and freshly distilled deoxygenated acetonitrile was used throughout as solvent. Potentials are reported relative to Ag–AgCl and are not corrected for junction potentials. For EPR spectroscopy, a JEOL model JES-RE3X spectrometer combined with ESR data system JEOL ES-PRIT 300 was used. All other measurements were done as described earlier.[2,9,10] Elemental analyses for C, H and N were performed at Indian Association for the Cultivation of Science (IACS) with a Perkin-Elmer 2400 elemental analyser.

Crystallography

Diffraction quality crystals of compound **1** were grown by slow diffusion of *n*-hexane into a dichloromethane solution of it, and for **3** from Et_2O–CH_3CN. Crystals of **2** were obtained from methanol by slow evaporation. A suitable crystal of compound **2** (brown tablet, 0.12 × 0.40 × 0.43 mm) was mounted on a glass fibre without protection. For crystals of **1** (pleotropic, yellow to dark blue, 0.11 × 0.14 × 0.14 mm) and **3** (rose-pink, 0.08 × 0.14 × 0.45 mm) epoxy cement was used for mounting. The intensity data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatised Mo-Kα radiation, $\lambda = 0.71073$ Å, and the cell dimensions were determined from setting angles of 25 centred reflections in the ranges $13 \le \theta \le 14$, $13 \le \theta \le 15$ and $15 \le \theta \le 16°$ for **1**, **2** and **3**, respectively. Table 1 contains a summary of relevant crystal data and the final residuals. The nickel atom positions were located from Patterson maps and the other non-hydrogen atoms by means of DIRDIF[11] calculation. A small empirical absorption correction[12] was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **3**, however, non-hydrogen atoms other than oxygen were refined anisotropically. Hydrogen atoms were included at calculated positions, updated after each cycle of refinement, with *d*(C–H) fixed at 0.95 Å and *B*(H) at $1.2B_{eq}$(C). No solvent of crystallisation was present in any of these crystals. The perchlorate oxygen atoms had large and appreciably high anisotropic thermal parameters, but the apparent partial disorders could not be modelled. The TEXSAN program,[13] incorporating complex atomic scattering factors,[14] was used in all calculations. The crystallographic numbering schemes are shown in Figs. 1–3, which were drawn with ORTEP[15] with 30% probability ellipsoids.

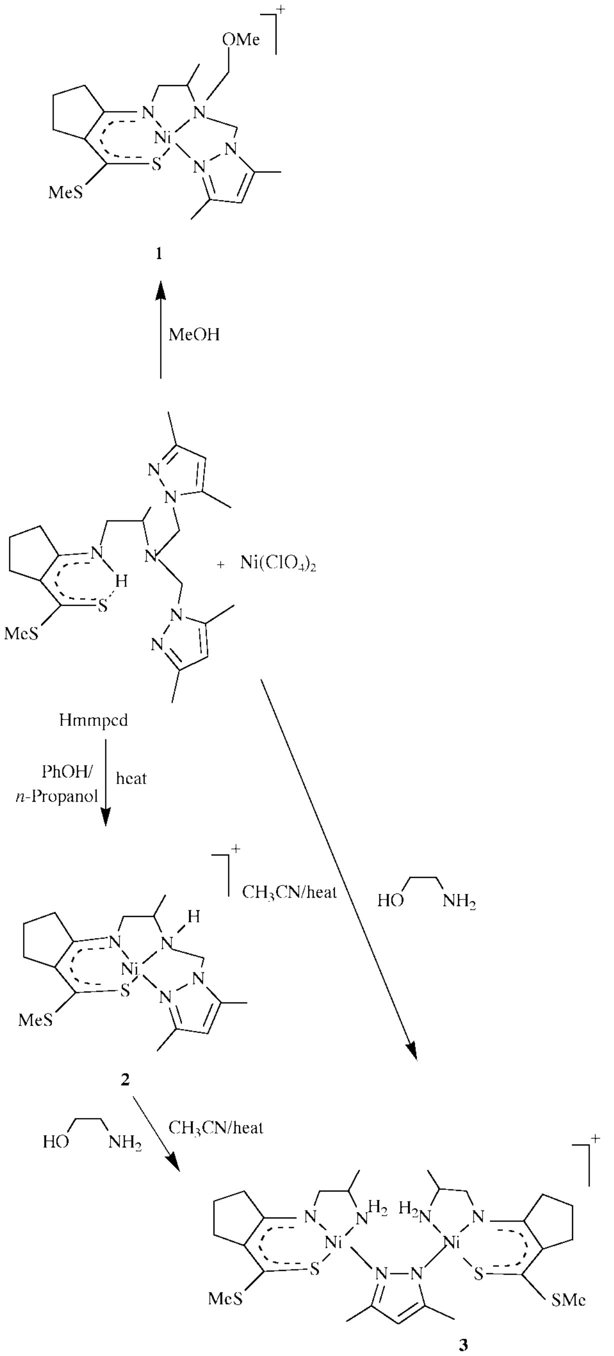
CCDC reference number 186/1629.

See http://www.rsc.org/suppdata/dt/1999/3859/ for crystallographic files in .cif format.

Results and discussion

The N_4S ligand Hmmpcd with flexible pyrazolyl arms can wrap up copper(II), zinc(II) and cobalt(II) ions forming complexes of distorted five-co-ordination geometries.[2,3] As displayed in Scheme 1, the interaction of this ligand with nickel(II) is quite unusual. The reaction in methanol proceeds through solvolytic cleavage of an otherwise unreactive C–N single bond to generate the square planar product [Ni{(N_3S)CH_2OCH_3}]ClO_4 **1** with modified ligand structure that accommodates a methoxy group provided by the solvent. Choice of solvents other than alcohol does not help in the isolation of the expected five-co-ordinated nickel(II) complex and leads only to gummy intractable solid(s) of unknown composition. This indicates the inherent reluctance shown by nickel(II) in attaining five-co-ordination when subjected to hard–soft donor environments.[16]

In an effort to understand more about the role of nickel(II) in this unprecedented C–N bond activation process, other hydroxylated compounds have been also tried as substrate. With an acidic substrate like phenol the reaction proceeds through an altogether different path and instead of the anticipated product [Ni{(N_3S)CH_2OPh}]ClO_4 with incorporated phenoxo group an interesting square planar compound [Ni{(N_3S)H}]ClO_4 **2** is generated by the complete removal of a CH_2Me_2pz arm from the co-ordinating ligand. On the other hand, when a basic hydroxylated compound *viz.* ethanolamine is used as substrate the product obtained is a binuclear com-



Scheme 1

pound $[(N_2S)Ni(\mu\text{-}Me_2pz)Ni(N_2S)]ClO_4$ **3** with a bridging pyrazolyl group. An identical product is obtained when di- or tri-ethanolamine is used as substrate. The reaction, however, fails to occur if triethylamine is used instead. Thus with amino-alcohols the reaction proceeds with extensive breakdown of the co-ordinating ligand, generating the precursor tridentate amine[2] and Me_2pz molecules both remained co-ordinated. Paul and Nag[17] prepared analogous binuclear nickel(II) complexes from μ-azido precursors by cycloaddition reactions.

Syntheses of compounds **1**–**3** thus involve C–N bond cleavage process. Controlled experiments have shown that the presence of nickel(II) ion is obligatory for such reactions to proceed. In fact, compound **2** containing a metal bound pyrazolyl arm on being treated with ethanolamine undergoes further C–N bond cleavage to produce **3** (method 2). Similar metal ion-induced disintegration of pyrazole containing ligands has been reported recently.[18]

The complexes are air-stable in the solid state and have varying degrees of solubilities in common organic solvents. In solution, the mononuclear complexes are greenish brown and susceptible to decomposition on prolonged standing in the air. The orange-red binuclear complex **3** on the other hand is quite stable in solution. The complexes are all 1 : 1 electrolytes in acetonitrile.[19]

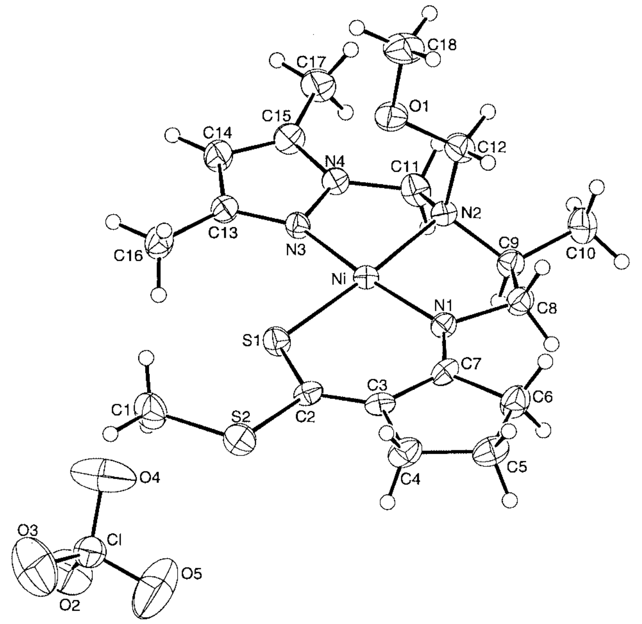


Fig. 1 An ORTEP drawing of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1** showing the atom-labelling scheme.

The IR spectra of the complexes have many prominent bands characteristic of the co-ordinated N_4S ligand framework.[2] One of these bands with a distinctive sharp feature appears at *ca.* 1560 cm^{-1} and is due to the $\nu(C\overset{..}{-}N)$ stretching mode of the co-ordinating pyrazolyl group in the mononuclear complexes (**1**, **2**). The corresponding band due to the bridging pyrazolyl group in the binuclear complex **3** appears at a slightly higher frequency. Compound **2** also displays a medium intensity band at 3180 cm^{-1} due to ν(N–H) vibrations, thus indicating removal of a CH_2Me_2pz arm from the co-ordinated Hmmpcd. As expected, all these complexes have two strong bands at 1100 and 630 cm^{-1}, characteristic of ionic perchlorate.[20]

Descriptions of structures

X-Ray crystallographic analyses of complexes **1**–**3** have enabled us to confirm the ligand breakdown processes as described in Scheme 1. Figs. 1–3 display the ORTEP views of these complexes. Their selected metric parameters are given in Table 2. Both the mononuclear complexes **1** and **2** crystallise in monoclinic space group $P2_1/c$ with four molecular weight units per cell. Each asymmetric unit in **1** consists of a modified ligand form, tetradentate in nature, providing an N_3S donor environment around Ni and possesses a pendant arm that includes a methoxy ether moiety. In compound **2** the modified ligand form provides the same co-ordination moiety as in **1** but lacks the pendant arm due to complete detachment of a CH_2Me_2pz group from the parent N_4S ligand. The geometries around the nickel(II) centres are square planar. In both molecules the Ni–N distances have large disparity with Ni–N(2) bond lying *trans* to the Ni–S(1) has maximum length 1.969(4) Å (1.939(4) Å in **2**) out of the three. The S(1)–C(2) distance 1.713(6) Å (1.713(4) Å in **2**) is indicative of thiolate character of the metal bound sulfur,[21,22] a feature typical of ligands based on the 2-aminocyclopent-1-ene-1-carbodithioate moiety.[1,2,4] The Ni–S(1) distance 2.121(2) Å (2.138(1) Å in **2**) in these complexes is remarkably short, compared to average Ni–S distances reported[21,23–25] and capable of exerting strong *trans* labilising influence as reflected in the elongation of the Ni–N(2) bonds.[26] The bond

Table 1 Crystal data and refinement details of complexes **1**, **2** and **3**

	1	**2**	**3**
Chemical formula	$C_{18}H_{29}ClN_4NiO_5S_2$	$C_{16}H_{25}ClN_4NiO_4S_2$	$C_{25}H_{41}ClN_6Ni_2O_4S_4$
M	539.7	495.67	770.73
Symmetry	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	*Iba*2 (no. 45)
a/Å	11.779(4)	7.856(1)	18.732(2)
b/Å	13.233(3)	20.912(1)	11.284(1)
c/Å	14.732(3)	12.727(1)	16.048(2)
β/°	100.03(2)	99.38(1)	
U/Å^3	2261(2)	2063(8)	3392(1)
Z	4	4	4
D_c/g cm^{-3}	1.585	1.596	1.509
F(000)	1128	1032	1608
μ/cm^{-1}	11.9	13.0	14.7
Transmission coefficients	0.885–1.000	0.800–1.000	0.941–1.000
No. unique data	3643	3744	1553
No. observed data	2238	2940	1238
T/°C	21	22	21
R (*wR*′)	0.044 (0.045)	0.048 (0.060)	0.049 (0.062)

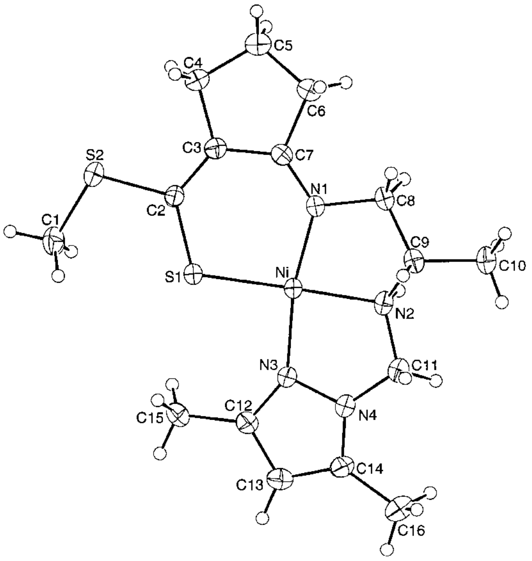


Fig. 2 Molecular structure of [Ni{(N_3S)H}]ClO_4 **2** with the atomic numbering.

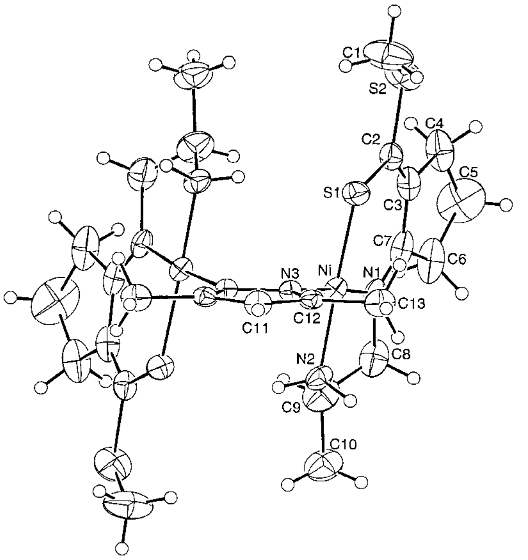


Fig. 3 An ORTEP diagram of [(N_2S)Ni(μ-Me_2pz)Ni(N_2S)]ClO_4 **3**.

Table 2 Selected bond distances (Å) and angles (°) for the complexes **1**, **2** and **3**

	1	**2**	**3**
Ni–N(1)	1.855(5)	1.874(4)	1.874(9)
Ni–N(2)	1.969(4)	1.939(4)	1.913(8)
Ni–N(3)	1.917(5)	1.926(4)	1.916(8)
Ni–S(1)	2.121(2)	2.138(1)	2.140(3)
S(1)–C(2)	1.713(6)	1.713(4)	1.680(1)
S(1)–Ni–N(2)	176.5(1)	175.1(1)	173.0(4)
S(1)–Ni–N(3)	92.0(1)	93.6(1)	87.4(3)
N(2)–Ni–N(3)	85.0(2)	84.4(1)	88.0(4)
N(1)–Ni–N(3)	170.4(2)	169.1(1)	173.6(4)
N(1)–Ni–N(2)	86.8(2)	85.0(2)	86.7(5)
N(1)–Ni–S(1)	96.4(1)	97.2(1)	98.2(3)
Ni–S(1)–C(2)	111.0(2)	111.2(2)	111.1(5)
Ni–N(1)–C(7)	133.0(4)	131.0(3)	126.5(8)
Ni–N(1)–C(8)	112.1(3)	112.6(3)	110.8(8)
Ni–N(2)–C(9)	104.0(3)	108.1(3)	106.9(9)
Ni–N(2)–C(11)	107.2(3)	111.2(3)	—
Ni–N(3)–N(4)/ Ni–N(3)–N(3′)[a]	111.5(3)	111.6(3)	120.8(2)

[a] Atom N(4) in complexes **1** and **2** corresponds to N(3′) in **3**.

angles S(1)–Ni–N(2) and N(1)–Ni–N(3) in **1** are 176.5(1) and 170.4(2)°, respectively. Corresponding bond angles in **2** (Table 2) are almost identical. The Ni atom is displaced negligibly 0.002(1) Å (0.003(1) Å in **2**) from the least squares plane containing the N_3S donor atoms, thus indicating almost ideal square planar geometry around the nickel centres in these mononuclear complexes.

The binuclear complex **3** has two crystallographically related nearly identical nickel centres (Fig. 3). The structure shows extensive breakdown of the co-ordinated N_4S ligand when allowed to react with ethanolamine to generate the precursor tridentate (N_2S) amine.[2] The co-ordination geometry around each metal centre is square planar with one sulfur and two nitrogen atoms coming from the tridentate amine while the fourth site is occupied by a nitrogen atom contributed by the bridging pyrazolyl moiety. The Ni···Ni separation here 3.288(2) Å is quite close to those in other square planar dinickel complexes,[27–29] but appears considerably shorter compared to that (3.920(1) Å) where the nickel(II) co-ordination sites are octahedral.[21,30] An extremely short Ni···Ni separation 2.501(2) Å has been reported recently[29] in a mixed oxidation state nickel(II,III) complex where the individual metal centres are square pyramidal. Both nickel atoms, as in the mononuclear complexes (**1**, **2**), are displaced by 0.004(1) Å out of their respective least squares planes (defined by S(1), N(1), N(2) and N(3) as shown in Fig. 3) which are inclined to each other by an acute dihedral angle of 59.1°. The Ni–N(3) (μ-pyrazolyl nitrogen) distance is 1.916(8) Å and the Ni–N(3)–N(3′) angle is

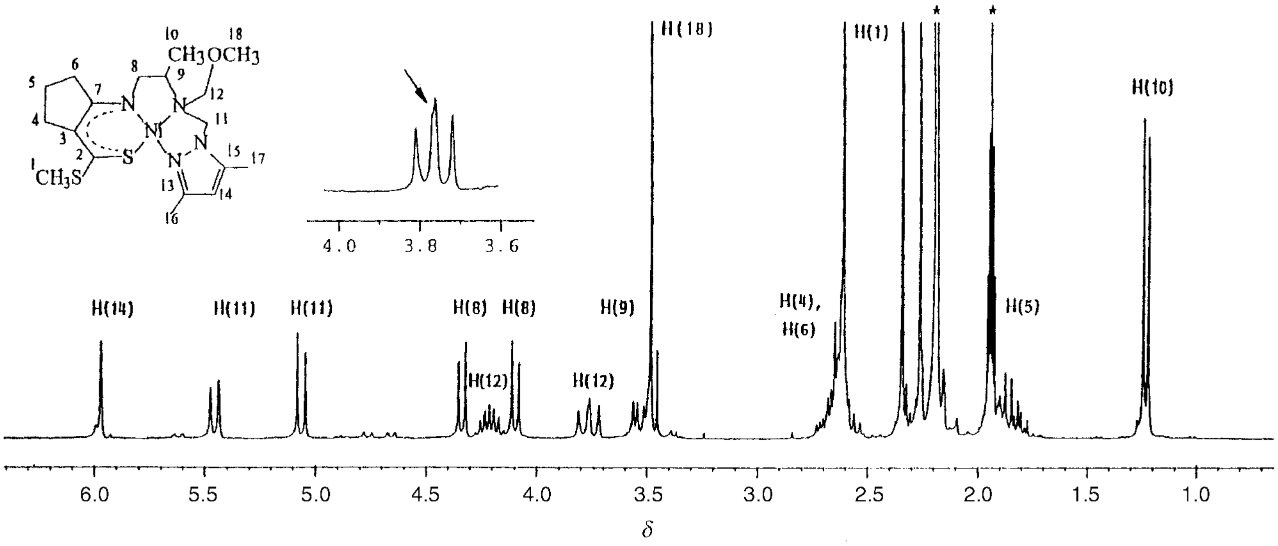


Fig. 4 300 MHz ^1H NMR spectrum of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1** in acetonitrile-d_3 solution at 25 °C. Asterisks indicate protio solvent impurities.

120.8(2)°. The pyrazolyl ring plane is appreciably inclined relative to the nickel co-ordination planes. The resulting dihedral angle is 100.2°. The middle carbon atom C(11) of the μ-pyrazolyl ring lies on a crystallographic twofold axis of this centrosymmetric molecule.

^1H NMR spectroscopy

The assignments for the ^1H NMR spectrum of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1**, discussed below, are labelled in Fig. 4. A sharp singlet appearing at δ 3.48 confirms the replacement of a pyrazolyl moiety by a OCH_3 group in the modified ligand form. The methylenic protons H(11) which appear as a singlet (at δ *ca.* 5) for free Hmmpcd are diastereotopic in the complex due to rigidity of the metal bound pyrazolyl arm and show up as an AB spin system with $\delta_A = 5.46$ and $\delta_B = 5.06$ ($J_{AB} = 11.1$ Hz). The protons of the $CH_2(8)$ group are also anisochronous and constitute another AB quartet at δ 4.34 and 4.10 due to their geminal coupling ($J_{AB} = 9.3$ Hz), indicating structural rigidity of the ethylenic backbone of the co-ordinated ligand. Corresponding peaks due to the methine H(9) and methyl H(10) protons of this backbone appear as a multiplet and a doublet at δ 3.54 and 1.23, respectively as per expectation.

Perhaps the most significant aspect of this spectrum is the appearance of two multiplets centred at δ 4.20 and 3.76 each corresponding to a single proton. We assigned these peaks as arising from the inequivalent protons of the $C(12)H_2$ group which is attached to a chiral nitrogen centre and consequently are diastereotopic due to symmetry reasons. Each doublet of this AB quartet appears as multiplets due to possible interactions from the adjoining proton(s).

In order to resolve these complex connectivities between the adjoining proton(s) a ^1H–^1H COSY NMR experiment was carried out at ambient temperature and the spectrum obtained is displayed in Fig. 5. Altogether six prominent cross peaks are obtained of which four are due to the geminal couplings of H(11), H(8) and H(12) methylenic protons (proton labellings are as shown in Fig. 4) and also due to the coupling between protons of the cyclopentene ring. Besides, there are two long range connectivities in this molecule, one involving the proton corresponding to the multiplet (with seven line structure) at δ 4.2 and the H(10) methyl protons and the other, between the proton corresponding to the (pseudo) triplet at δ 3.76 and the H(9) methine proton. The results clearly suggest the diastereotopic nature of the H(12) methylene protons which initially form two doublets at δ 4.20 and 3.76 due to symmetry reasons described earlier. As confirmed by the 2-D experiment, one of these doublets (at δ 3.76) further splits into a pair of overlapping doublets (as shown in Fig. 4 inset) due to interactions ($J_{AB} = 12.0$ Hz) from the H(9) proton. The other doublet (at δ 4.20) probably splits into a pair of overlapping quartets by interaction from the nearby H(10) methyl protons, thus constituting a multiplet of probable seven-line structure.

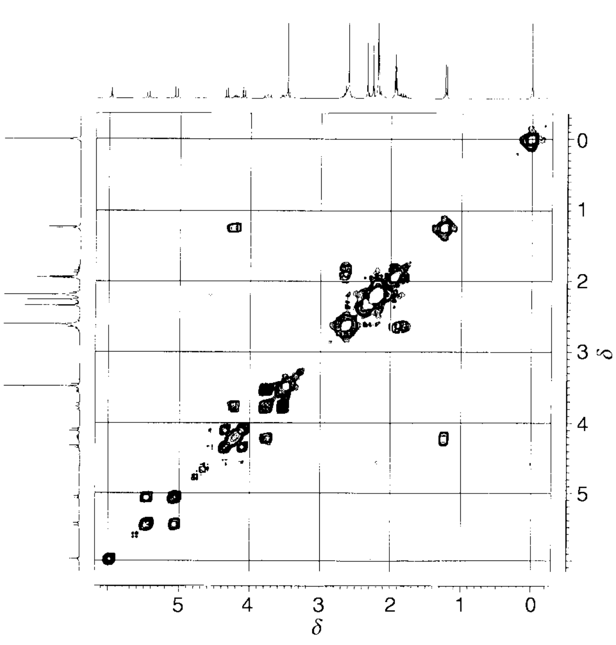


Fig. 5 ^1H–^1H 2-D COSY NMR spectrum (300 MHz, 25 °C, acetonitrile-d_3) of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1**.

The ^1H NMR spectrum of $[Ni\{(N_3S)H\}]ClO_4$ **2** has features (Fig. 6A) that clearly indicate the absence of a pyrazolyl arm in the modified ligand structure. The methoxy group appearing at δ 3.48 for **1** is absent for this molecule as are also the multiplets due to the methylenic protons of the CH_2OCH_3 arm. Instead, there is a broad new peak at δ 4.83 due to the NH proton which remained coupled with the diastereotopic H(11) methylenic protons forming a pair of multiplets in the δ 5.08–4.80 region. When exchanged with D_2O, these multiplets are clearly resolved (shown in Fig. 6B) into a pair of doublets at δ 5.03 and 4.89 corresponding to an AB quartet ($J_{AB} = 10.2$ Hz). All the remaining protons in this molecule have features almost similar to those observed for **1**.

Redox properties and spectroelectrochemical studies

In acetonitrile (0.1 mol dm^{-3} NEt_4ClO_4) the cyclic voltam-

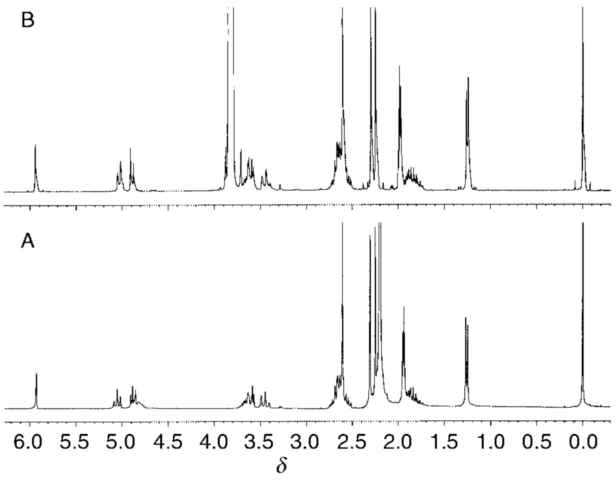


Fig. 6 300 MHz ^{1}H NMR spectrum of $[Ni\{(N_3S)H\}]ClO_4$ **2** at 25 °C: (A) in acetonitrile-d_3 solution, (B) exchanged with D_2O.

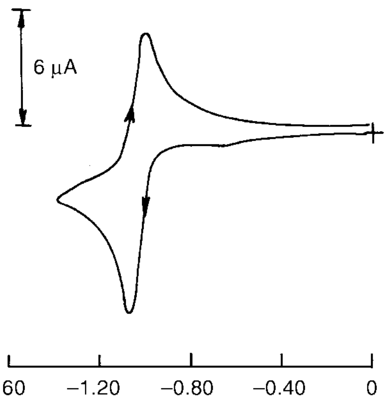


Fig. 7 Cyclic voltammogram (*vs.* Ag–AgCl) of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1** in acetonitrile (0.1 mol dm^{-3} NEt_4ClO_4) at a glassy carbon electrode (100 mV s^{-1} scan rate).

mogram of compound **1** at a glassy carbon working electrode displays (Fig. 7) a reversible reduction with $E_{\frac{1}{2}} \approx -1.0$ V ($\Delta E_p = 60$ mV) *vs.* Ag–AgCl reference. Comparison with ferrocenium–ferrocene couple as internal standard[31] suggests this process is monoelectronic. Both compounds **2** and **3** are electrochemically inactive in the range of potential (+1.5 to −2.0 V) studied. The nature of this reduction process was further examined by combined coulometry/EPR experiments. Exhaustive electrolysis at −40 °C past the reduction process ($E_w = -1.2$ V *vs.* Ag–AgCl) established one-electron stoichiometry ($n = 0.95 \pm 0.1$) for this couple. The EPR spectrum of the frozen (77 K) catholyte solution has a rhombic feature with $g_1 = 2.217$, $g_2 = 2.170$ and $g_3 = 2.054$. All these indicate a metal-centred reduction process involving $Ni^{II} \longrightarrow Ni^{I}$ electron transfer.

For square planar nickel(II) complexes in acyclic ligand environments such as above the reversibility in the $Ni^{II} \longrightarrow Ni^{I}$ reduction is not very common.[32–37] Observed peak-to-peak separations are comparable to those of the ferrocene–ferrocenium system ($\Delta E_p = 75$ mV) measured under identical experimental conditions, which indicates the molecules retain their structural integrity during the process of electron transfer on the timescale of cyclic voltammetry. Given the preference of Ni^{I} for a five-co-ordinate trigonal bipyramidal geometry,[38] it is possible that the pendant ether oxygen might bind the nickel(I) centre to fulfil the desired co-ordination number. Similar ether[39] and thioether[40,41] co-ordinated nickel complexes are known. Failure of compound **2** to undergo $Ni^{II} \longrightarrow Ni^{I}$ reduction under identical experimental conditions also supports the concept of methoxy group co-ordination during reduction. The reduced nickel(I) ion being larger in size with Jahn–Teller configuration (d^9) requires only minimum reorganisational energy to adopt an axially elongated square-pyramidal structure.[34]

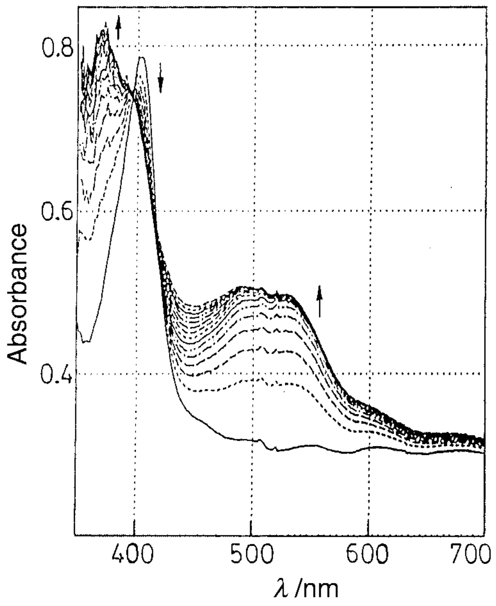


Fig. 8 Changes in the electronic absorption spectrum of $[Ni\{(N_3S)CH_2OCH_3\}]ClO_4$ **1** upon electrochemical reduction in CH_3CN. Arrows indicate spectral changes on stepping through −0.4 to −1.3 V applied potential *vs.* Ag–AgCl.

Formation of Ni^{I} during the reduction process was also established by spectroelectrochemistry. Fig. 8 depicts the electronic spectral change during the progress of electrolysis in CH_3CN (0.3 mol dm^{-3} NEt_4ClO_4) solution followed with an optically transparent thin-layer electrode (OTTLE) cell. As expected, the high energy band observed at 405 nm in **1** due to LMCT (S→Ni) is blue shifted to 370 nm on reduction. Also a feature at 618 nm (ε 85 dm^3 mol^{-1} cm^{-1}), due to a nickel(II) spin-allowed d–d transition ($^1A_{1g} \longrightarrow {}^1A_{2g}$), is lost during the reduction process and the reduced complex absorbs more strongly in the visible region with the generation of two new bands at *ca.* 530 and 485 nm, originating from nickel(I) ligand-field transitions under a planar or axially distorted geometry.[42–44]

Concluding remarks

Activation of carbon–nitrogen multiple bonds by metal ion co-ordination is well known.[45] For C–N single bonds, however, similar activation is quite uncommon, the only known example being the oxidative dealkylation of amines.[46–48] The metal-induced bond activation described here involves cleavage of C–N single bond(s) of the co-ordinated Hmmpcd ligand. While with phenol and aminoalcohols the dissociated bond(s) is directly associated with metal bound nitrogen N(2) atom, the corresponding bond C(12)–N(5) in the case of methanol as substrate is attached to a pyrazolyl nitrogen atom. Nickel presumably promotes these reactions because of the metal ion's preference for square planar geometry which renders one of the pyrazolyl arms of the ligand susceptible to nucleophilic attack, facilitated by the positive charge on the complex. With aminoalcohol there is perhaps a second nucleophilic attack at the methylene carbon which is then removed as some form of heterocyclic derivative, leaving the dimethylpyrazole. The product **1** obtained in methanol is a square planar compound in an acyclic ligand environment, that undergoes $Ni^{II} \longrightarrow Ni^{I}$ reversible electron transfer, as monitored by cyclic voltammetry. A five-co-ordination geometry that favours stabilisation of nickel(I) on the voltammetric timescale is probably completed by the binding of a methoxy group of the modified ligand structure.

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