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Synthesis, crystal structure and magnetic properties of a new ferromagnetic nickel(II) dimer derived from a hexadentate Schiff base ligand

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Abstract

A new end-on bis(μ-azido) nickel(II) complex of the formula $[Ni_2(L^1)(N_3)_4]$ (**1**) (L^1 = hexadentate Schiff base ligand made from the reaction of 2 moles of 2-benzoyl pyridine and 1 mole of triethylenetetramine) has been prepared and characterized by single crystal X-ray diffraction studies. Each nickel center is coordinated in a distorted octahedral (NiN_6) fashion consisting of three nitrogen atoms from the hexadentate ligand moiety, two nitrogen atoms from two end-on azido ligands and the last one from another terminal azido ion. The variable temperature magnetic susceptibility of compound **1** shows that the nickel centers are ferromagnetically coupled. The Ni–N–Ni bridge angles are very similar [98.36(8)° and 97.66(9)°] and the Ni···Ni separation is 3.155(1) Å. The magnetic exchange coupling constant $J = 21.8\ cm^{-1}$ is consistent with the structure and the value has been compared with some similar reported compounds.

Keywords: Binuclear nickel(II) complex; Crystal structure; Magnetic properties; End-on azido ligand complex; Terminal azido ion complex; Hexadentate ligand

1. Introduction

Studies on the coordination behavior of transition metal complexes along with their structures and magnetic properties have received considerable attention in recent years [1–10]. Common strategies to prepare such complexes using a polynucleating ligand and an unused arm or donor site of a mononuclear complex have been recognized [11,12]. Another way of their preparation is by utilization of flexidentate behavior of a multidentate ligand and judicial choice of bridging ligands. Among the bridging ligands pseudohalide ions especially the azido ion has long been known for its versatile bridging coordination modes that generate dimeric and polymeric compounds [1–10,13]. The azide ligand in such complexes can act as either end-on ($\mu_{1,1}$-N_3) [1–4] or end-to-end ($\mu_{1,3}$-N_3) [5,6] bridges (Chart 1). The most important aspect of these bridged complexes is the variety of their magnetic exchange interactions. The end-on bridging mode exerts ferromagnetic exchange interactions while that of end-to-end propagates anti-

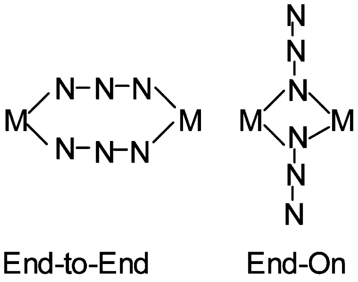

Chart 1. Possible coordination modes for azido ligands.

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ferromagnetic exchange between paramagnetic centers [14–18].

We describe here the synthesis of a new bis(μ-azido) nickel(II) complex of the formula $[Ni_2(L^1)(N_3)_4]$ (**1**) (L^1 = hexadentate ligand), where two azido ions act in an end-on bridging mode and other two act as terminal donors. The single crystal X-ray structure with its magnetic properties are also discussed.

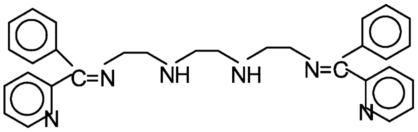
2. Experimental

2.1. Materials

Triethylenetetramine, 2-benzoyl pyridine and sodium azide were purchased from the Lancaster Chemical Company Inc. and were used as received. All other solvents and chemicals were of analytical grade.

2.2. Synthesis of ligand

The hexadentate ligand was made adopting a procedure modified from that for a similar type of ligand [19]. Triethylenetetramine (0.73 g, 5 mmol) and 2-benzoyl pyridine (1.83 g, 10 mmol) were refluxed in 15 cm^3 dehydrated alcohol for 4 h. The hexadentate ligand was isolated after evaporating the solvent and purified from alcohol. The product was isolated as a brown semisolid mass after drying in a vacuum over P_4O_{10}: yield 2.07 g (~87%). *Anal.* Found: C, 75.92; H, 6.91; N, 17.29. Calc. For $C_{30}H_{32}N_6$: C, 75.61; H, 6.77; N, 17.63%.



L

2.3. Preparation of $[Ni_2(L^1)(N_3)_4]$ (**1**)

To an acetonitrile solution (5 cm^3) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.146 g, 0.5 mmol) was added 0.119 g (0.25 mmol) of ligand (L) in 15 cm^3 acetonitrile over a period of 15 min. To the resulting greenish–red solution, an aqueous solution (0.065 g, 1.0 mmol, 2 cm^3 H_2O) of sodium azide was added slowly. The solution was then filtered, insoluble precipitate was discarded and the filtrate was left for slow evaporation and after 3–4 days deep red needle crystals of **1** were obtained (0.023 g, ~12%). *Anal.* Found: C, 48.86; H, 4.16; N, 31.76; Ni, 14.62. Calc. For $C_{32}H_{34}N_{18}Ni_2$: C, 48.77; H, 4.35; N, 31.99; Ni, 14.89%.

Caution: Azido complexes are potentially explosive especially in the presence of organic ligands. Therefore, preparation and handling of these compounds deserve special attention.

2.4. Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen were performed using a Perkin Elmer 2400II elemental analyzer. The nickel content was determined gravimetrically as the nickel dimethyl glyoximate complex. Variable temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID spectrophotometer. Pascal's constants were utilized to estimate diamagnetic correction, this value was subtracted from the experimental susceptibility data to give the molar magnetic susceptibility (χ_M). IR spectra (4000–400 cm^{-1}) were taken at 298 K using a JASCO FT/IR-420 spectrometer.

2.5. Crystal structure determination and refinement

A suitable crystal of **1** was mounted on a Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα radiation. The unit cell parameters were determined by least-squares refinement of setting angles of 25 reflections. Intensity data were collected in the ω–2θ scan mode. The data were corrected for Lorentz and polarization effects [20]. The structure was solved by direct methods and expanded by Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using teXsan [21] crystallographic software package of Molecular Structure Corporation. The crystal data and data collection details are shown in Table 1.

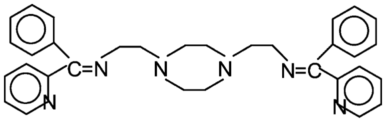
3. Results and discussion

3.1. Synthesis

The ligand (L) was synthesized by refluxing triethylenetetramine and 2-benzoyl pyridine in a 1:2 mole ratio in dehydrated alcohol. It reacted with nickel(II) nitrate/perchlorate hexahydrate and sodium azide in the ratio $Ni^{II}:L:N_3^- = 2:1:4$ in aqueous acetonitrile medium affording red crystalline products suitable for X-ray crystallographic work and having composition $[Ni_2L^1(N_3)_4]$ (**1**), where L^1 = changed hexadentate ligand L in the transformation process. It is also interesting to note that the reaction of L and nickel(II) perchlorate hexahydrate using a mole ratio of 1:1 in aqueous acetonitrile produced a dark colored crystalline complex of composition $[NiL](ClO_4)_2$ (**2**) [22].

Table 1
The crystal data and data collection summary for **1**

Empirical formula	$C_{32}H_{34}N_{18}Ni_2$
Formula weight	788.14
Space group	$P2_1/c$ (no. 14)
a (Å)	15.724(1)
b (Å)	8.9170(7)
c (Å)	25.497(1)
α (°)	90
β (°)	104.28(1)
γ (°)	90
V (Å^3)	3464.5(4)
Z	4
D_{calc} (g cm^{-3})	1.511
F(000)	1632
Crystal size (mm)	0.22 × 0.20 × 0.12
μ (Mo Kα) (mm^{-1})	1.141
λ (Å)	0.71069
Temperature (K)	273
$2\theta_{max}$ (°)	55.1
Reflections collected	21 470
Independent reflections	8309 ($R_{int} = 0.022$)
Reflections observed [$I > 1.5\sigma(I)$]	5336
Goodness-of-fit	0.95
R; R_w	0.037; 0.036
Largest difference peak and hole (e Å^{-3})	0.40 and −0.22



L1

The rearrangement of L to L^1 occurred in the presence of both nickel salt and azido ion. The poor yield of **1** coupled with other experimental evidences have indicated that most probably the origin of the extra $\cdots CH_2{-}CH_2\cdots$ fragment present in L^1 compared to L was the ligand itself. The azido ion in the presence of nickel undergoes nucleophilic attack on one $\cdots CH_2{-}CH_2\cdots$ part of L followed by hydrolysis and breakdown of the ligand to generate some diketone [23] like derivatives ($O{=}\overset{|}{C}{-}\overset{|}{C}{=}O$). This diketone can again react with the $\cdots NH{-}CH_2{-}CH_2{-}NH\cdots$ part of L to produce the dimminium ion [24], which is further reduced by an azido ion and subsequently forms L^1.

3.2. IR spectroscopy

The IR spectrum of **1** exhibits two broad bands corresponding to the asymmetric stretching vibrations of N_3 [$\nu_{as}(N_3)$] at 2061 and 2022 cm^{-1}, which are similar to those reported [1a,3b]. The stretching vibrations of the C=N bond of the Schiff base are at 1629 and 1581 cm^{-1} and 1637 and 1592 cm^{-1} for L and compound **1** respectively [25].

3.3. Crystal structure of [$Ni_2(L^1)(N_3)_4$] (1)

The ORTEP drawing of **1** is shown in Fig. 1 and the selected bond distances and angles are listed in Table 2. Each nickel atom is located in a distorted octahedral coordination environment surrounded by six nitrogen atoms, three from the hexadentate ligand moiety, two from end-on μ_2-bridges azido groups and the last one from the one terminal azido ion. The Ni(1)···Ni(2) distance is 3.155(1) Å. The Ni–N(bridging) distances range from 2.061(2) to 2.130(2) Å; Ni–N(terminal) distances are the same [Ni(1)–N(13), 2.070(3) and Ni(2)–N(16), 2.070(3) Å] and other Ni–N distances (from six nitrogen atoms of the hexadentate ligand moiety) vary between 2.005(2) and 2.271(2) Å. The Ni–N bond distances mostly match those observed in analogous NiN_6 chromophores [1–6], but there are two slightly longer distances [Ni(1)–N(1), 2.2420(18) and Ni(2)–N(4), 2.271(2) Å] possibly due to structural constraints imposed by the diazacyclohexane ring of the ligand. The bridging angles are very similar [Ni(1)–N(7)–Ni(2), 98.36(8)° and Ni(1)–N(10)–Ni(2), 97.66(9)°]. The azido ligands (terminal and end-on) are very close to linear with an average $N_\alpha{-}N_\beta{-}N_\gamma$ angle of 178.6(5)°. The $N_\alpha{-}N_\beta$ bond lengths [1.172(4)–1.201(4) Å] are a little longer than those of $N_\beta{-}N_\gamma$ bonds [1.141(5)–1.166(4) Å], where N_α indicates the nitrogen atom coordinated to nickel(II) centers. These variations in bond distances have also been observed for azido ions bonded in a terminal or μ_2-1,1-bridging fashion [1–6].

3.4. Magnetic properties

A variable-temperature magnetic susceptibility study was performed on polycrystalline samples of **1**. The magnetic susceptibility (χ_M) of this compound was examined in a 10.0 kG field in the 2.0–300.0 K range. The μ_{eff} per Ni_2 molecule slowly increases from $5.00\mu_B$ at 300 K to $5.49\mu_B$ at 30 K and then decreases to $4.35\mu_B$ at 2 K. These correspond to $\chi_M T$ values of 3.11, 3.74 and 2.37 cm^3 K mol^{-1} at these three temperatures (Fig. 2). The $\chi_M T$ vs. T plot is indicative of ferromagnetic coupling. The decrease of the magnetic moment at low temperature is attributed to a combination of zero field splitting of the ground state and intermolecular exchange interactions. Ginsberg [26] pointed out that these two parameters are very strongly dependent on each other. It is thus difficult to calculate these values with reasonable accuracy. These two parameters are also important at low temperature where experimental uncertainties are high [2a]. That is why neglecting D as a fitting parameter, the data were fit using the theoretical χ_M vs. T expression for a dimer of two $S = 1$ nickel(II) ions. Least-squares fitting of the experimental data to this expression gave $J = 21.8$ cm^{-1}, $g = 2.28$ and $\theta = -1.10$, where θ is the Curie–Weiss constant. The fit is

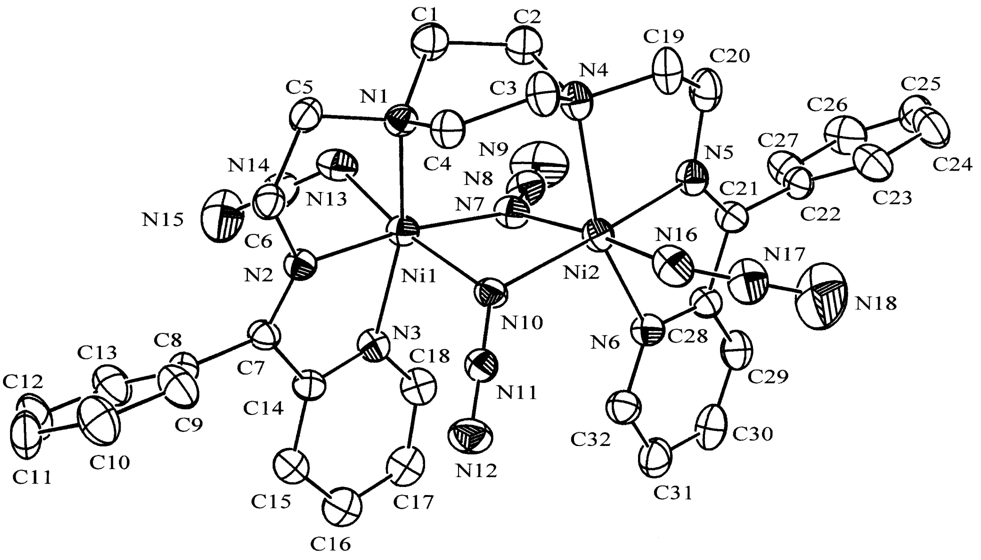


Fig. 1. ORTEP drawing of $[Ni_2(L^1)(N_3)_4]$ (**1**) with atom labelling scheme. For clarity the hydrogen atoms are not shown.

Table 2
Selected bond distances (Å) and bond angles (°) for complex **1**

Bond distances			
Ni(1)–N(1)	2.2420(18)	Ni(1)–N(2)	2.0126(19)
Ni(1)–N(3)	2.099(2)	Ni(1)–N(7)	2.061(2)
Ni(1)–N(10)	2.130(2)	Ni(1)–N(13)	2.070(3)
Ni(2)–N(4)	2.271(2)	Ni(2)–N(5)	2.005(2)
Ni(2)–N(6)	2.102(2)	Ni(2)–N(7)	2.108(2)
Ni(2)–N(10)	2.061(2)	Ni(2)–N(16)	2.070(3)
N(7)–N(8)	1.189(4)	N(8)–N(9)	1.143(5)
N(10)–N(11)	1.201(4)	N(11)–N(12)	1.155(4)
N(13)–N(14)	1.181(4)	N(14)–N(15)	1.166(4)
N(16)–N(17)	1.172(4)	N(17)–N(18)	1.141(5)
Bond angles			
N(1)–Ni(1)–N(2)	81.02(7)	N(1)–Ni(1)–N(3)	158.51(7)
N(1)–Ni(1)–N(7)	101.86(8)	N(1)–Ni(1)–N(10)	88.34(7)
N(1)–Ni(1)–N(13)	91.17(9)	N(2)–Ni(1)–N(3)	78.07(8)
N(2)–Ni(1)–N(7)	171.25(9)	N(2)–Ni(1)–N(10)	93.28(7)
N(2)–Ni(1)–N(13)	95.37(9)	N(3)–Ni(1)–N(7)	98.13(9)
N(3)–Ni(1)–N(10)	87.94(9)	N(3)–Ni(1)–N(13)	95.65(10)
N(7)–Ni(1)–N(10)	78.63(8)	N(7)–Ni(1)–N(13)	91.84(10)
N(10)–Ni(1)–N(13)	171.15(9)	N(4)–Ni(2)–N(5)	80.90(9)
N(4)–Ni(2)–N(6)	158.81(8)	N(4)–Ni(2)–N(7)	88.87(9)
N(4)–Ni(2)–N(10)	98.96(9)	N(4)–Ni(2)–N(16)	91.14(10)
N(5)–Ni(2)–N(6)	78.22(9)	N(5)–Ni(2)–N(7)	95.00(9)
N(5)–Ni(2)–N(10)	174.15(9)	N(5)–Ni(2)–N(16)	93.93(10)
N(6)–Ni(2)–N(7)	89.36(9)	N(6)–Ni(2)–N(10)	101.43(9)
N(6)–Ni(2)–N(16)	93.86(10)	N(7)–Ni(2)–N(10)	79.14(8)
Ni(1)–N(7)–Ni(2)	98.36(8)	Ni(1)–N(10)–Ni(2)	97.66(9)
N(7)–N(8)–N(9)	178.2(4)	N(10)–N(11)–N(12)	178.9(3)
N(13)–N(14)–N(15)	178.5(3)	N(16)–N(17)–N(18)	178.5(4)

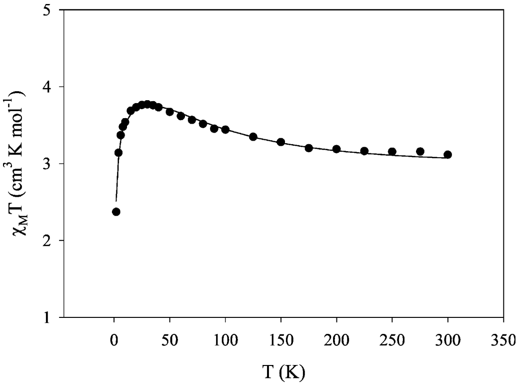


Fig. 2. Plot of $\chi_M T$ vs. T for **1**. Solid line shows the best fit as indicated in the text.

shown as a solid line in Fig. 2. The fit confirms a $S = 2$ ground state for **1**. The azido ligands generally propagate ferromagnetic coupling interaction between nickel(II) centers bound in a μ_2-1,1 end-on mode and antiferromagnetic coupling when bridging in a μ_2-1,3 end-to-end fashion. In order to study the influence of structural parameters on the magnetic exchange coupling of end-on azido-bridged binuclear complexes of Cu(II), Ni(II) and Mn(II), Ruiz et al. [15] applied hybrid density functional methods on some model complexes. They have found a correlation between J and the M–N–M bridging angle. For bis(μ-azido) end-on nickel(II) complexes the interactions are ferromagnetic for all the ranges of angles of θ with increasing values of θ to a maximum around $\theta = 104°$. The bond distances between metal and bridging atoms also strongly influence the value of ferromagnetic coupling which decreases with increasing Ni···Ni separation and Ni–N(bridging) distances. Table 3 compares the structural and magnetic parameters with other reported bis(μ_2-1,1-azido)nickel(II) complexes. Compound **1** has the slightly shorter Ni...Ni separation as well as the lowest bridge angle [average Ni–N–Ni angle is 98.01(10)°] among this type of end-on dibridged azido complexes. So, $J = 21.8$ cm^{-1} for complex **1** is consistent with its structural parameters.

Table 3
Structural and magnetic properties of **1** and selected di-μ_2-1,1-azido bridged nickel(II) complexes

Compound	Ni–N–Ni (°)	Ni···Ni (Å)	Ni–N(bridging) (Å)	J (cm^{-1})	Ref.
$[Ni(terpy)(N_3)_2]_2\cdot 2H_2O$	101.3	3.276	2.038, 2.198	+20.1	[1b]
$[\{Ni(pepci)(N_3)_2\}_2]$	102.2, 101.0	3.297	2.107, 2.163, 2.109, 2.128	+36.3	[3b]
$(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$	103.8	3.273	2.092, 2.067	+43.9	[4a]
$(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$	104.9	3.434	2.166, 2.167	+33.8	[4a]
$[\{Ni_2(Medpt)_2(N_3)_2\}(\mu\text{-}(1,1\text{-}N_3)_2]$	103.7	3.448	2.217, 2.169	+46.7	[2]
$(\mu\text{-}N_3)_2[Ni(232\text{-}tet)]_2(PF_6)_2$	104.6	3.449	2.177, 2.183	+34.3	[3a]
$[\{Ni(terpy)(N_3)\}_2]\cdot H_2O$	101.6	3.274	2.039, 2.184	+22.8	[1a]
$[Ni_2(terpy)_2(N_3)_3(H_2O)](ClO_4)\cdot H_2O$	102.46, 100.60	3.265	2.068, 2.119, 2.069, 2.175	+13.6	[1a]
$[\{Ni(en)_2\}_2(\mu\text{-}N_3)_2](ClO_4)_2$	104.3	3.369	2.144, 2.123	+20.9	[4b]
$[Ni_2(L^1)(N_3)_4]$	98.36, 97.66	3.155	2.061, 2.108, 2.130, 2.061	+21.8	Present work

4. Conclusion

The present study describes the preparation of a ferromagnetically coupled nickel(II) dinuclear complex from a flexible hexadentate Schiff base ligand and judical choice of bridging as well as terminal azido ion coordination. Complex **1** has a slightly shorter Ni···Ni separation as well as the lowest Ni–N–Ni bridging angle among the end-on bis(μ-azido) nickel(II) complexes. This type of ligand therefore provides an avenue to get a binuclear compound having interesting magnetic properties. Presently, in order to rationalize the process and to understand the mechanism of the ligand transformation, further experiments by changing the flexibility of the ligand and by using various transition metals are in progress.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 172396 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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References

[1] (a) M.G. Barandika, R. Cortes, L. Lezama, M.K. Urtiaga, M.I. Arriortua, T. Rojo, J. Chem. Soc., Dalton Trans. (1999) 2971;
(b) M.I. Arriortua, R. Cortes, L. Lezama, T. Rojo, X. Solans, M. Font-Bardia, Inorg. Chim. Acta 174 (1990) 263.
[2] (a) A. Escuer, R. Vicente, J. Ribas, J. Magn. Magn. Mater. 110 (1992) 181;
(b) A. Escuer, R. Vicente, J. Ribas, X. Solans, Inorg. Chem. 34 (1995) 1793.
[3] (a) A. Escuer, R. Vicente, M.S. El Fallah, X. Solans, M. Font-Bardia, Inorg. Chim. Acta 247 (1996) 85;
(b) R. Cortes, J.I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M.I. Arriortua, J. Chem. Soc., Dalton Trans. (1992) 2723.
[4] (a) R. Vicente, A. Escuer, J. Ribas, M.S. El Fallah, X. Solans, M. Font-Bardia, Inorg. Chem. 32 (1993) 1920;
(b) J. Ribas, M. Monfort, C. Diaz, C. Bartos, X. Solans, Inorg. Chem. 33 (1994) 484.
[5] (a) J. Ribas, M. Monfort, C. Diaz, C. Bartos, X. Solans, Inorg. Chem. 32 (1993) 3557;
(b) C.G. Pierpont, D.N. Hendrickson, D.M. Duggana, F. Wagner, E.K. Barefield, Inorg. Chem. 14 (1975) 604;
(c) P. Chaudhuri, M. Guttman, D. Ventur, K. Weighardt, B. Nuber, J. Weiss, J. Chem. Soc., Chem. Commun. 1 (1985) 1618.
[6] (a) A. Escuer, I. Castro, F. Mautner, M.S. El Fallah, R. Vicente, Inorg. Chem. 36 (1997) 4633;
(b) J. Ribas, M. Monfort, B.K. Ghosh, R. Cortes, X. Solans, M. Font-Bardia, Inorg. Chem. 35 (1996) 864;
(c) A. Escuer, R. Vicente, M.S. El Fallah, X. Solans, M. Font-Bardia, Inorg. Chim. Acta 278 (1998) 43.
[7] (a) M. Monfort, I. Resino, J. Ribas, H. Stoeckli-Evans, Angew. Chem., Int. Ed. Engl. 39 (2000) 191;
(b) B. Kersting, G. Steinfeld, D. Siebert, Chem. Eur. J. 7 (2001) 4253;
(c) M. Monfort, I. Resino, M.S. El Fallah, J. Ribas, X. Solans, M. Font-Bardia, H. Stoeckli-Evans, Chem. Eur. J. 7 (2001) 280;
(d) K.R. Reddy, M.V. Rajasekharan, J.-P. Tuchagues, Inorg. Chem. 37 (1998) 5978;
(e) R.J. Butcher, C.J. O'Connor, E. Sinn, Inorg. Chem. 18 (1979) 492;
(f) R.J. Butcher, C.J. O'Connor, E. Sinn, Inorg. Chem. 20 (1980) 3486;
(g) R.J. Butcher, C.J. O'Connor, E. Sinn, Inorg. Chem. 21 (1982) 616;
(h) A.B. Blake, E. Sinn, A. Yavari, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 229 (1995) 281.
[8] (a) S. Martin, M.G. Barandika, L. Lezama, J.L. Pizarro, Z.E. Serna, J.I.R. de Larramendi, M.I. Arriortua, T. Rojo, R. Cortes, Inorg. Chem. 40 (2001) 4109;
(b) A. Escuer, R. Vicente, M.A.S. Goher, F.A. Mautner, Inorg. Chem. 36 (1997) 3440;
(c) A. Escuer, R. Vicente, F.A. Mautner, M.A.S. Goher, M.A.M. Abu-Youssef, J. Chem. Soc., Chem. Commun. 1 (2002) 64.

[9] (a) C.L. Sheppard, S.S. Tandon, L.K. Thompson, J.N. Bridson, D.O. Miller, M. Handa, F. Lloret, Inorg. Chim. Acta 250 (1996) 227;
(b) B. Graham, M.T.W. Hearn, P.C. Junk, C.M. Kepert, F.E. Mabbs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chem. 40 (2001) 1536.

[10] (a) L.K. Thompson, S.S. Tandon, F. Lloret, J. Cano, M. Julve, Inorg. Chem. 36 (1997) 3301;
(b) S. Sikorav, I. Bkouche-Wasksman, O. Kahn, Inorg. Chem. 23 (1984) 490;
(c) S.S. Tandon, L.K. Thompson, M.E. Manuel, J.N. Bridson, Inorg. Chem. 33 (1994) 5555;
(d) I.V. Seggern, F. Tuczek, W. Bensch, Inorg. Chem. 34 (1995) 5530.

[11] P. Dapporto, M. Formica, V. Fusi, M. Mivchaloni, P. Paoli, R. Pontellini, P. Rossi, Inorg. Chem. 39 (2000) 4663.

[12] (a) J. Sanmartin, M.R. Bermejo, A.M. Garcia-Deibe, O. Piro, E.E. Castellano, Chem. Commun. (1999) 1953;
(b) M.I. Fernandez-Garcia, B. Fernandez-Fernandez, M. Fondo, A.M. Garcia-Deibe, E. Gomez-Forneas, M.R. Bermejo, J. Sanmartin, A.M. Gonzalez, Inorg. Chim. Acta 304 (2000) 144.

[13] K. Vrieze, G. van Koten, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2 (references therein), Pergamon Press, Oxford, England, 1987, p. 225.

[14] M.-F. Charlot, O. Kahn, M. Chaillet, C. Larrieu, J. Am. Chem. Soc. 108 (1986) 2574.

[15] E. Ruiz, J. Cano, S. Alvarej, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.

[16] F.F. de Biani, E. Ruiz, J. Cano, J.J. Novoa, S. Alvarej, Inorg. Chem. 39 (2000) 3221.

[17] L.K. Thompson, S.S. Tandon, M.E. Manuel, Inorg. Chem. 34 (1995) 2356.

[18] M.A. Aebersold, B. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. Von Seggern, F. Tuczek, L. Ohrstrom, A. Grand, E. Lelievre-Berna, J. Am. Chem. Soc. 120 (1998) 5238.

[19] C. Jubert, A. Mahamadou, J. Marrot, J.-P. Barbier, J. Chem. Soc., Dalton Trans. (2001) 1230.

[20] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351.

[21] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

[22] We have also determined the crystal structure of **2**. The structure of **2** is as usual a monomeric hexacoordinated (NiN_6) nickel(II) compound and no ligand transformation has taken place (see supplementary materials for detailed structural drawing and data): S. Deoghoria, S.K. Chandra, Unpublished results.

[23] P.A. Manis, M.W. Rathke, J. Org. Chem. 45 (1980) 4952.

[24] S.J. Benkovic, P.A. Benkovic, D.R. Comfort, J. Am. Chem. Soc. 91 (1969) 1860.

[25] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1997.

[26] A.P. Ginsberg, R.L. Martin, R.W. Brookes, R.C. Sherwood, Inorg. Chem. 11 (1972) 2884.