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Synthesis, characterization and crystal structures of the first pentacoordinate nickel(II) complexes containing N,S-donor ligands †

M. Dolores Santana, Gabriel García,* Antonio Rufete, M. Carmen Ramírez de Arellano and Gregorio López

Departamento de Química Inorgánica, Universidad de Murcia, 30071 Murcia, Spain

Received 13th September 1999, Accepted 10th December 1999

By reaction of the hydroxo nickel complexes $[Ni([12]aneN_3)(\mu\text{-}OH)]_2^{2+}$ ($[12]aneN_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($[12]aneN_3$-mc1) and its 9-methyl derivative ($[12]aneN_3$-mc2)) with heterocyclic-2-thiones in acetone, the pentacoordinate nickel(II) complexes $[Ni([12]aneN_3)(LL')]^+$ (LL′ = py2S (pyridine-2-thionate) **1**, **5**; pym2S (pyrimidine-2-thionate) **2**, **6**; bzimSH (benzimidazole-2-thionate) **3**, **7**; bztzS (benzothiazole-2-thionate) **4**, **8**) have been prepared. The X-ray diffraction study on **5**, **6** and **7** shows that the thionate is bonded to nickel atom as chelating η^2-N,S ligand, the nickel atom being in a distorted square pyramidal geometry. Complex **7** is the first structurally characterized example of a 1,3-benzimidazole-2-thionate derivative acting as a chelating ligand. The 2-D NOE technique (NOESY) allowed us to assign the isotropically shifted resonances due to coordinated thionates. Elemental analysis as well as IR and UV-VIS spectroscopic studies have also been used to aid structural characterization.

The coordination of metal ions to heterocyclic thiones is of current interest because they can be used in the synthesis of clinically useful drugs.[1] Moreover, in the last few years the chemistry of nickel(II) complexes containing heterocyclic thione ligands has attracted considerable attention due to the significance of nickel–sulfur interactions in biological systems.[2,3]

These kind of ligands are characterized by thione–thiol tautomerism[4] and pyridine-2-thione exists predominantly as the thione form (Chart 1 a) in neutral solution[5] and in the solid state.[6] Heterocyclic thionates can act as monodentate ligands involving either the exocyclic sulfur (η^1-S) (Chart 1 b)[7] or the endocyclic nitrogen (η^1-N) atoms (Chart 1 c)[8] and they can also behave as bidentate (Chart 1 d)[9] or bridging ligands (Chart 1 e).[10] In the case of nickel(II), monochelate[11] and bischelate[12] diamagnetic square-planar complexes as well as homoleptic trischelate octahedral complexes[13] have been reported. However, to our knowledge, no mononuclear pentacoordinate nickel(II) complexes containing heterocyclic thionates have been described and only the binuclear complex $(Et_4N)[Ni_2(\mu\text{-}tz2S)_4Cl]$ (tz2S = 1,3-thiazoline-2-thionate) has been prepared. The crystal structure of this complex shows a nickel atom in a diamagnetic square-planar NiS_4 geometry and another nickel atom in a paramagnetic square-based pyramidal NiN_4Cl coordination.[14] Few complexes with benzothiadiazole have been reported and so metal thiadiazole chemistry is scarcely known.

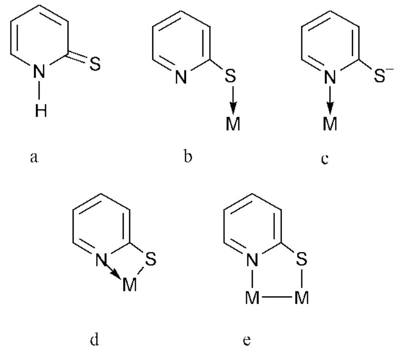

Chart 1 Coordination modes of heterocyclic-2-thionate.

We have reported the reactivity of the hydroxo nickel complexes $[Ni([12]aneN_3)(\mu\text{-}OH)]_2^{2+}$ ($[12]aneN_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($[12]aneN_3$-mc1) and its 9-methyl derivative ($[12]aneN_3$-mc2))[15,16] containing pentacoordinate nickel towards aryl-salicylaldimines,[17] β-ketoimines[18] and 2-pyridone.[19] As a further study on the synthesis, spectroscopic and structural characterization of pentacoordinate nickel(II) complexes, herein we report the synthesis, characterization and crystal structures of the first pentacoordinate nickel(II) complexes containing the N,S-donor ligands heterocyclic-2-thionates including the first chelating benzo-1,3-imidazoline-2-thionate derivative. The common method for incorporation of thiolate into transition metal complexes involves either the displacement of a halide by a thiolate anion from an alkali-metal thiolate or the generation of the thiolate in solution by addition of organic base to the reaction mixture containing the thiol. When a transition metal hydroxo complex is used, the direct reaction between the hydroxo complex and the thiol should lead to the formation of the thiolate complex. Thus we have prepared μ-thiolate complexes[20–23] by reaction between the binuclear complexes[23] $[Ni(C_6F_5)_2(\mu\text{-}OH)]_2^{2-}$, $\{[Pd(8\text{-}NC_9H_6CH_2)]_2(\mu\text{-}OH)(\mu\text{-carboxylate})\}$[21] and $\{Pd_2[2\text{-}Me_2NCH_2\text{-}C_6H_4]_2(\mu\text{-}OH)(\mu\text{-}Br)\}$[22] and thiols. This method has also been used for incorporation of heterocyclic thiones into transition metal complexes.[11,24]

Results and discussion

Synthetic and X-ray studies

The pentacoordinate thionate complexes of nickel(II) were isolated from reaction mixtures of $[Ni([12]aneN_3)(\mu\text{-}OH)]_2^{2+}$ and the corresponding heterocyclic-2-thione (1 : 2 molar ratio) in acetone. The isolated complexes are sketched in Scheme 1. The acidic proton of the thione is abstracted by the hydroxo complex providing the anion which is trapped by the metal substrate

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† Electronic supplementary data (ESI) available: selected IR spectroscopic data. See http://www.rsc.org/suppdata/dt/a9/a907367a/

DOI: 10.1039/a907367a

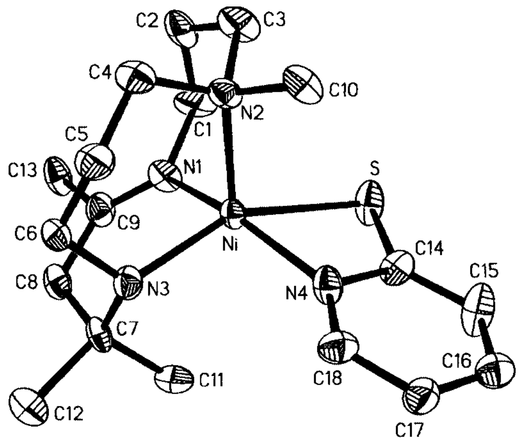


Fig. 1 View of the structure of the [Ni([12]aneN_3-mc2)(py2S)]$^+$ cation with the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.

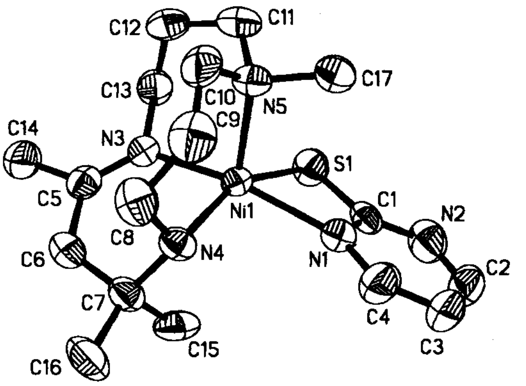


Fig. 2 View of the structure of the [Ni([12]aneN_3-mc2)(pym2S)]$^+$ cation with the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.

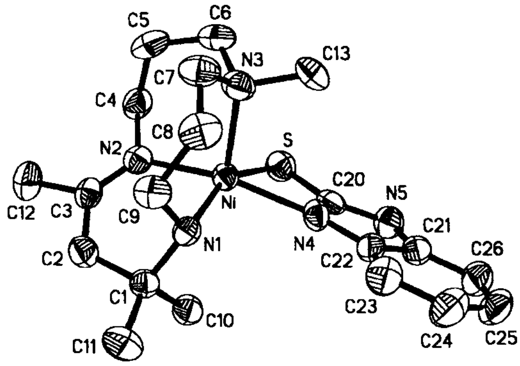
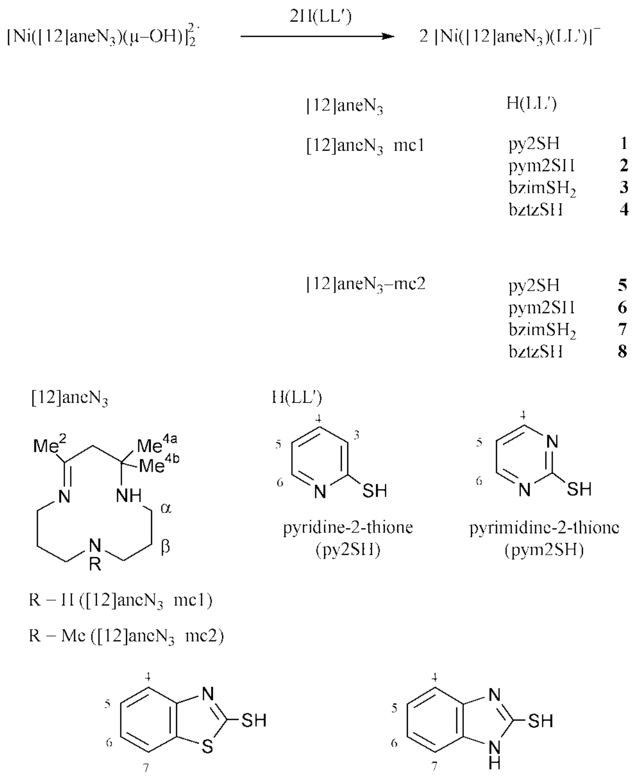


Fig. 3 View of the structure of the [Ni([12]aneN_3-mc2)(bzimSH)]$^+$ cation with the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.



Scheme 1 Reaction scheme and proton labelling.

(the Ni([12]aneN_3) moiety) to form the new nickel(II) complex with concomitant release of water. Complexes **1**–**8** all have in common the N–C–S structural group generated by deprotonation of the heterocyclic thione. These versatile N,S-donor ligands exhibit the four different coordination modes mentioned above. However, for first-row transition metals a four membered chelate ring (Chart 1 d) is generally formed in spite of its small bite. This coordination mode has been confirmed by X-ray diffraction for complexes **5**, **6** and **7**.

The crystal structure determination revealed that green crystals of **5** consist of [Ni([12]aneN_3-mc2)(py2S)]$^+$ cations and ClO_4^- anions. The structure of the cation with the labelling scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The coordination geometry around nickel is distorted square pyramidal with the basal plane formed by N1, N3, N4 and S (Table 1). The rmsd of the plane is 0.063 Å. The Ni atom is 0.363 Å out of this plane towards the apical N2 atom. The basal plane forms a dihedral angle of 14.3° with the plane defined by S, C14→C18 and N4. The Ni–[12]aneN_3-mc2 distances are not significantly different (2.022–2.081 Å) in contrast with [Ni([12]aneN_3-mc2)($OC_6H_5CH{=}NC_6H_4$-*o*)]$^+$ and [Ni([12]aneN_3-mc2)($C_6H_5COCHC(NC_6H_5)(CH_3)$)]$^+$ where there are two Ni–N distances (2.05 Å, mean) shorter than the other (2.12 Å, mean).[17,18] The Ni–N4 (thioamide) bond distance 2.095(11) Å is longer than those observed in square-planar, octahedral and mixed-ligand trischelated complexes.[9,11] However, both the Ni–S distance (2.427(4) Å) and N4–Ni–S angle (69.2(3)°) of the chelating ligand are somewhat shorter than the distances and angles reported for octahedral complexes[9] although the Ni–S distance is longer than that observed in the square-planar (NBu_4)[Ni(C_6F_5)$_2$(py2S)] complex.[11]

The crystal structure of the cation of [Ni([12]aneN_3-mc2)(pym2S)]PF_6 (**6**) is shown in Fig. 2 together with the atom-numbering scheme. Selected bond distances and angles are given in Table 1. The structure shows the presence of two independent molecules. In each one, the Ni atom is bound to a [12]aneN_3-mc2 molecule through the three N atoms and to pym2S$^-$ ligand through one of its N atoms and an S atom. The geometry around nickel is distorted square pyramidal. The rmsd of the basal planes N1, N3, N4 and S1 and N1A, N3A, N4A and S1A are 0.060 and 0.067 Å, respectively. The Ni1 and Ni1A atoms are 0.356 and 0.375 Å out of the corresponding basal plane. These planes form dihedral angles of 13.4 and 16.7°, respectively, with the corresponding plane S1, C1, N2, C2→C4 and N1 and S1A, C1A, N2A, C2A→C4A and N1A. The Ni–S bond distances being 2.413(3) and 2.403(3) Å and Ni–$N_{thionate}$ bond distances being 2.107(8) and 2.125(9) Å are quite normal. However, the Ni–S bond distances are shorter and the Ni–N bond distances are longer than that observed in homoleptic and mixed-ligand trischelate complexes.[9] The N–Ni–S "bite" angles (68.8(2)°) of the chelating ligand lie in the range that has previously been observed.[9]

Table 1 Selected bond lengths (Å) and angles (°) for complexes **5**, **6** and **7**

Complex **5**			
Ni–N(1)	2.022(9)	Ni–N(4)	2.095(11)
Ni–N(2)	2.081(10)	Ni–S	2.427(4)
Ni–N(3)	2.041(10)	S–C(14)	1.721(14)
N(1)–Ni–N(3)	91.0(4)	N(1)–Ni–N(2)	94.6(4)
N(3)–Ni–N(2)	102.1(4)	N(1)–Ni–N(4)	161.5(5)
N(3)–Ni–N(4)	93.1(4)	N(2)–Ni–N(4)	102.2(4)
N(1)–Ni–S	100.0(3)	N(3)–Ni–S	153.4(3)
N(2)–Ni–S	101.1(3)	N(4)–Ni–S	69.2(3)
Complex **6**			
Ni(1)–N(1)	2.107(8)	Ni(1)–N(5)	2.066(8)
Ni(1)–N(3)	2.024(8)	Ni(1)–S(1)	2.413(3)
Ni(1)–N(4)	2.048(8)	S(1)–C(1)	1.729(11)
Ni(1A)–N(1A)	2.125(9)	Ni(1A)–N(5A)	2.058(8)
Ni(1A)–N(3A)	2.026(8)	Ni(1A)–S(1A)	2.403(3)
Ni(1A)–N(4A)	2.056(8)	S(1A)–C(1A)	1.719(11)
N(1)–Ni(1)–N(3)	161.3(3)	N(1)–Ni(1)–N(4)	94.9(3)
N(3)–Ni(1)–N(4)	90.3(3)	N(1)–Ni(1)–N(5)	103.2(3)
N(3)–Ni(1)–N(5)	93.5(3)	N(4)–Ni(1)–N(5)	100.6(3)
N(1)–Ni(1)–S(1)	68.8(2)	N(3)–Ni(1)–S(1)	99.6(2)
N(4)–Ni(1)–S(1)	154.5(2)	N(5)–Ni(1)–S(1)	102.2(3)
N(1A)–Ni(1A)–N(3A)	161.0(3)	N(1A)–Ni(1A)–N(4A)	93.6(3)
N(3A)–Ni(1A)–N(4A)	91.0(3)	N(1A)–Ni(1A)–N(5A)	103.7(3)
N(3A)–Ni(1A)–N(5A)	93.4(3)	N(4A)–Ni(1A)–N(5A)	101.5(3)
N(1A)–Ni(1A)–S(1A)	68.8(2)	N(3A)–Ni(1A)–S(1A)	99.6(2)
N(4A)–Ni(1A)–S(1A)	152.7(2)	N(5A)–Ni(1A)–S(1A)	102.9(3)
Complex **7**			
Ni–N(1)	2.039(6)	Ni–N(4)	2.044(6)
Ni–N(2)	2.014(6)	Ni–S	2.587(2)
Ni–N(3)	2.061(6)	S–C(20)	1.714(8)
N(2)–Ni–N(1)	90.8(2)	N(2)–Ni–N(4)	158.7(2)
N(1)–Ni–N(4)	96.1(2)	N(2)–Ni–N(3)	95.1(2)
N(1)–Ni–N(3)	101.6(2)	N(4)–Ni–N(3)	103.2(2)
N(2)–Ni–S	97.6(2)	N(1)–Ni–S	153.2(2)
N(4)–Ni–S	67.8(2)	N(3)–Ni–S	102.9(2)

The structure and labelling of [Ni([12]aneN$_3$-mc2)(bzimSH)]PF$_6$ **7** are shown in Fig. 3. Selected bond distances and angles are given in Table 1. The nickel atom in **7** is coordinated in a distorted square pyramidal geometry to the sulfur and nitrogen atoms of the monodeprotonated bzimSH$^-$ ligand and three nitrogen atoms of the [12]aneN$_3$-mc2 molecule. The nickel atom is 0.392 Å out of the basal plane defined by N1, N2, N4 and S. The rmsd of this plane is 0.075 Å. The plane defined by S, C20, N5, C21→C26 and N4 forms a dihedral angle of 10.3° with the basal plane. The Ni–N (macrocycle) distances are a little shorter than that observed in **5**. The bzimSH$^-$ anion acts as chelating ligand through the exocyclic S and the heterocyclic N atoms. The Ni–S 2.587(2) Å and Ni–N(4) 2.044(6) Å bond distances are quite normal. The C(20)–N(4) and C(20)–N(5) bond distances 1.317(9) and 1.354(10) Å, respectively, are in agreement with a C–N double bond delocalization. The N(4)–Ni–S "bite" angle 67.8(2)° is smaller than that observed in **5** and **6**. However, neither similarity nor difference can be established with other metal complexes because the reported thiadiazole metal derivatives are limited to Cu(I),[25] Ag(I)[25] and Rh(I)[26] complexes. Thus in Cu(I) complexes the thiadiazole ligand acts by interconnecting six-membered rings of copper and in the Ag(I) derivatives the metal atoms are bonded to thiadiazole ligands to give a linear chain, only using the nitrogen atoms in both kind of complexes. The Rh(I) complexes showed two bridging N–C–S ligands in a μ-(η^{1,2}-S) coordination mode, which undergoes a change to the μ-(η^1-N : η^2-S) coordination mode by replacement of ancillary ligands. Therefore the structure of complex **7** shows the first mononuclear complex in which the bzimSH$^-$ acts as chelating ligand through the S and N atoms.

Spectroscopic studies and magnetic measurements

Deprotonation of the ligands is accompanied by substantial modification of their IR spectra with ν(N–H) absent from the spectra of the metal derivatives **1**–**8** and significant perturbation of the "thioamide" spectra (1500–750 cm^{-1}).[1] In all cases, shifts to shorter wavelengths are observed for ν(C=N) and ν(C–S) relative to the free neutral ligand, whereas the 650 cm^{-1} band (ν(C=S)) is absent. Additional bands for ν(Ni–S) (≈470 cm^{-1}) as well as ν(Ni–N) (≈280 cm^{-1}) are observed. Such vibrational activity is clearly indicative of S,N-coordination.[11,27] The observed shifts in the ligand vibrations upon coordination with respect to the free N,S co-ligand are similar in all complexes. Therefore the S, N-coordination of the ligand can be predicted for the complexes for which the crystal structure is not available (supplementary data). Strong bands at 1100 and 620 cm^{-1} are assigned to the uncoordinated perchlorate.[18]

The electronic spectra of the complexes in acetone solution are all similar and show bands in the 600 and 390 nm regions which could be assigned to $^3B_1(F) \rightarrow {}^3E(F)$ and $^3B_1(F) \rightarrow {}^3A_2, {}^3E(P)$ transitions, respectively.[28] Both λ_{max} values and molar absorptivities are consistent with a pentacoordinate environment around nickel(II).[17,18] The spectra also show strong MLCT bands in the 320 nm region.

The ^{1}H-NMR data for complexes **1**–**8** are collected in Table 2. The spectra show the resonance line pattern observed for the macrocycle ligands that has been assigned on the basis of previous studies of nickel macrocyclic complexes.[17–19] The α-methylene protons shift downfield whereas the β-methylene protons shift upfield with regard to the diamagnetic position.

Table 2 ^{1}H NMR data (δ)[a]

Complex	H_α	H_β	2-Me	4-Me(a,b)	9-Me	H-thionate[b]
1	359.0	−5.7	−12.9	28.9		74.8(6) 68.5(4) 57.6(5) 47.9(3)
	343.5	−12.5		21.3		
	220.8 (2H)	−15.8				
	173.5 (2H)	−28.7				
	30.3	−30.2 (2H)				
	27.3					
2	373.9	−5.8	−16.2	29.8		75.7(6) 69.9(4) 46.3(5)
	357.8	−12.6		22.7		
	224.9 (2H)	−16.2				
	181.3 (2H)	−29.5				
	50.6 (2H)	−31.8 (2H)				
3	339.0	−7.4	−13.7	48.7		32.0(4) 23.7(5) 7.8(7) 7.5(6)
	304.8	−12.7		22.1		11.3(NH)
	244.1	−15.2				
	196.9	−29.4				
	79.8	−29.9				
	36.7	−32.6				
	34.8					
	21.2					
4	400.7	−6.9	−15.0	56.1		36.1(4) 17.5(5) 10.3(7) 8.1(6)
	364.4	−7.7		22.7		
	240.6	−12.7				
	217.7	−29.1				
	77.2	−32.4				
	38.9	−33.9				
	33.4					
	18.3					
5	290.4	−3.9	−13.6	31.8	107.5	76.7(6) 67.8(4) 56.2(5) 54.2(3)
	285.1	−11.7 (2H)		22.2		
	239.1 (2H)	−28.3				
	160.2 (2H)	−29.9				
	59.8	−33.1				
	15.6					
6	296.5	−3.8	−14.2	31.9	112.2	73.1(6) 59.2(4) 44.1(5)
	290.8	−11.7 (2H)		22.7		
	238.4 (2H)	−28.5				
	165.7 (2H)	−30.9				
	55.8	−34.4				
	16.7					
7	312.1	−5.7	−14.2	52.1	111.7	33.7(4) 24.1(5) 8.4(7) 7.5(6)
	278.3	−12.2 (2H)		22.6		17.6(NH)
	268.8	−28.8				
	174.1	−31.9 (2H)				
	64.5					
	38.8					
	36.4					
	21.7					
8	321.5	−5.0	−15.4	63.1	124.5	35.6(4) 17.5(5) 10.2(7) 8.5(6)
	292.2	−12.2 (2H)		23.4		
	257.0	−28.1				
	195.3	−32.9				
	40.1	−34.3				
	31.9					
	18.1					

[a] In $(CD_3)_2CO$ solution. [b] The value in parentheses indicates which thionate proton the resonance has been assigned to, see Scheme 1 for the numbering of the thionate protons.

Equatorial protons are expected to experience larger contact shifts than axial protons and therefore the most downfield resonances are due to α-CH_{eq} and the most upfield ones to β-CH_{eq}.[29] The isotropically shifted ^{1}H-NMR signals observed for methyl groups (2-Me, 4-Me(a, b) and 9-Me-N) can be initially assigned by inspection of their peak areas. The assignment of individual thionate resonances could be accomplished by NOESY measurements, because the narrow resonances of the complexes facilitated these experiments. Fig. 4 shows the NOESY spectrum of complex **5**, only in the region relevant to assign thionate resonances. Firstly the assignment of the broad signal from the thionate 3-H proton of complexes **1** and **5** was clear from its absence in the spectra of complexes **2** and **6** in which it is substituted by nitrogen. The resonance at 67.8 ppm is connected through NOESY cross peaks with the signals at 76.7, 56.2 and 22.2 ppm. The NOESY spectrum also shows connectivity between signals at 76.7 and 67.8 and 22.2 ppm, and between signals at 56.2 and 67.8 and 31.8 ppm. Since the resonances at 22.2 and 31.8 ppm have been assigned to 4-Me(a, b) groups of the macrocycle, the resonances at 76.7, 67.8 and 56.2 must correspond to thionate protons and can be assigned to 6-H, 4-H and 5-H protons respectively. This specific assignment can be deduced from the inspection of the X-ray structure, the C(11) atom being nearer to the hydrogen atoms H(18) and H(16) than the H(17) (Fig. 1). The NOESY spectrum of complex **7** (Fig. 5) shows cross signals between resonances at 24.1 and 33.7 and 7.5 ppm. These signals can be assigned to the thionate 5-H, 4-H and 6-H protons and the only remaining unassigned protons in **7** are 7-H and NH. The signal to the NH proton can be assigned to the resonance at 17.6 ppm since this resonance is solvent exchangeable and the 7-H proton can therefore be assigned to the signal at 8.4 ppm. This last assignment is

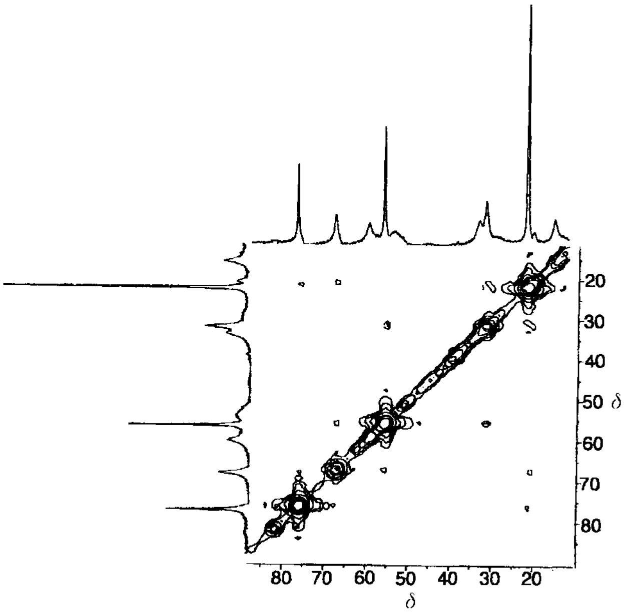


Fig. 4 ^{1}H NOESY spectrum of **5** obtained at 200 MHz at 22 °C in $(CD_3)_2CO$ solution. This map was collected with a 3 ms mixing time, 256 t1 values (4096 scans each) using 2K data points in F2 dimension, only the region relevant to assign resonances is shown in the top trace.

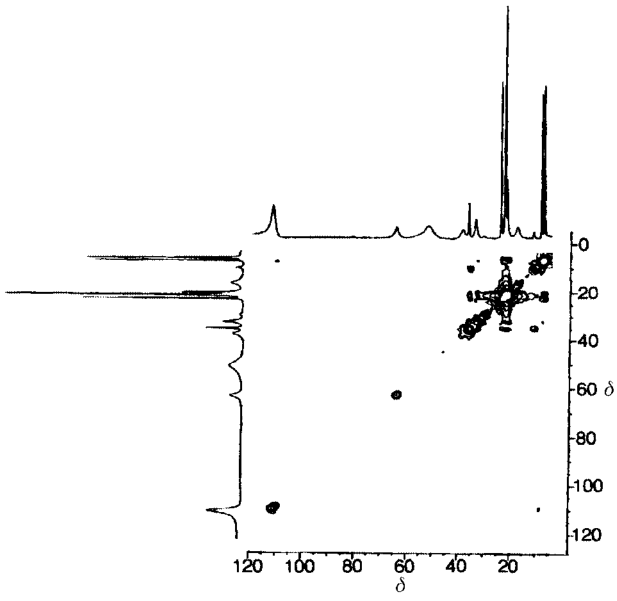


Fig. 5 ^{1}H NOESY spectrum of **7** obtained at 200 MHz at 22 °C in $(CD_3)_2CO$ solution. This map was collected with a 3 ms mixing time, 256 t1 values (4096 scans each) using 2K data points in F2 dimension, only the region relevant to assign resonances is shown in the top trace.

supported by the connectivity through the NOESY cross peak of the signal due to 9-Me–N (111.7 ppm) with the 7-H signal at 8.4 ppm. From the inspection of the X-ray structure (Fig. 3) the methyl group (9-Me–N) is nearer to the thionate 7-H proton than the 6-H proton. Fig. 6 shows the NOESY spectrum of complex **8** in the region 7–45 ppm. The resonance at 35.6 ppm is connected through NOESY cross peaks with the signals at 17.5 and 8.5 ppm. These signals, as for **3** and **7**, can be assigned to the thionate 4-H, 5-H and 6-H protons and the remaining resonance at 10.2 ppm can therefore be assigned to the thionate 7-H proton. All the resonances of the thionate protons are downfield to TMS; this is in accordance with a dominant σ-delocalization pattern of spin density and is consistent with the ground state of Ni(II) which has two unpaired electrons in σ-symmetry orbitals ($d_{x^2-y^2}$, d_{z^2}). However, the net spin density in the d_π orbitals could be polarized by the unpaired electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals *via* spin–orbit coupling and this mechanism can distribute spin density into the thionate rings.

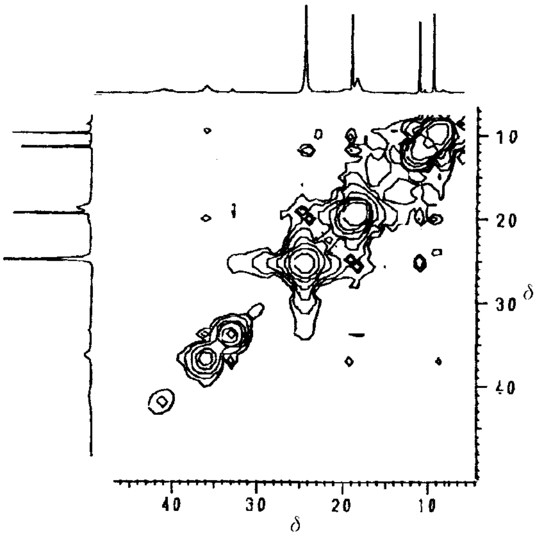


Fig. 6 ^{1}H NOESY spectrum of **8** obtained at 200 MHz at 22 °C in $(CD_3)_2CO$ solution. This map was collected with a 5 ms mixing time, 256 t1 values (4096 scans each) using 2K data points in F2 dimension, only the region relevant to assign resonances is shown in the top trace.

The effective magnetic moment values at 290 K for all these compounds are in the range 2.93–2.99 μ_B. These values are those expected for a triplet spin ground state ($S = 1$) and they clearly show that all these compounds are high spin Ni(II) complexes.

Experimental

Materials

The complexes $[Ni([12]aneN_3)(\mu\text{-}OH)]_2(A)_2$ ($A = ClO_4$, PF_6) were synthesized by procedures previously described.[15,16] All commercial reagents were used without further purification. Solvents were dried and distilled by general methods before use. **CAUTION**: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts should be prepared and handled with great care.

Physical measurements

C, H, N and S analyses were carried out with a microanalyzer Carlo Erba model EA 1108. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The NMR spectra of $(CD_3)_2CO$ solutions were recorded on a Bruker model AC 200E (standard $SiMe_4$) or a Varian Unity 300 spectrometer. NOESY spectra were recorded on the Bruker spectrometer at 22 °C in $(CD_3)_2CO$ solutions using 256 individual FID's with 4096 scans each. The UV/VIS spectra (in acetone) were recorded on a Hitachi 2000V spectrophotometer for the 350–800 nm range. Fast atom bombardment (FAB) mass spectra were run on a Fisons VG Autospec spectrometer operating in the FAB$^+$ mode. Magnetic susceptibilities of polycrystalline samples were measured at room temperature (290 K) with a fully automatized AZTEC DMS8 pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Bruker BE15 electromagnet. The applied field was 1.8 T. The magnetometer was calibrated with $Hg[Co(NCS)_4]$. Corrections for diamagnetism were estimated from Pascal's constants. Magnetic susceptibility data were also corrected for the temperature independent paramagnetism (100×10^{-6} cm^3 mol^{-1} per Ni) and magnetization of the sample.

Table 3 Crystallographic data for complexes **5**, **6** and **7**

	5	**6**	**7**
Formula	$C_{18}H_{31}ClN_4NiO_4S$	$C_{17}H_{30}F_6N_5NiPS$	$C_{20}H_{32}F_6N_5NiPS$
M	493.69	540.20	578.25
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
μ(Mo-Kα)/mm^{-1}	1.138	1.068	0.990
R_{int}	0.1053	0.0906	0.0378
$R1[I > 2\sigma(I)]$	0.0865	0.0768	0.0673
$wR2$(all data)	0.2278	0.2213	0.2004
a/Å	11.030(2)	11.202(3)	10.938(2)
b/Å	12.477(2)	24.771(7)	14.318(2)
c/Å	15.874(3)	16.585(5)	15.938(2)
β/°		93.10(2)	92.73(1)
U/Å^3	2184.5(6)	4595(2)	2493.2(6)
T/K	173(2)	291(2)	291(2)
Z	4	8	4
Measured reflections	3498	11314	4797
Independent reflections	3220	8055	4373

Synthesis

[Ni([12]aneN$_3$-mc1)(py2S)]ClO$_4$ 1. The compound py2SH (52 mg, 0.46 mmol) was added to a suspension of [Ni([12]aneN$_3$-mc1)(μ-OH)]$_2$(ClO$_4$)$_2$ (178 mg, 0.23 mmol) in acetone (25 cm^3). The reaction mixture was stirred for 1 h and a bright green solution was obtained. Acetone was then removed under reduced pressure until *ca.* 10 cm^3 remained, and the addition of diethyl ether (25 cm^3) resulted in the formation of a green solid which was filtered off, washed with diethyl ether and air-dried. Yield: 181 mg, 82% (Found: C, 42.4; H, 6.2; N, 11.6; S, 7.1%. $C_{17}H_{29}N_4SClO_4Ni$ requires C, 42.6; H, 6.1; N, 11.7; S, 6.7%); *m*/*z* 379 (M$^+$, 100%), 269 (M − py2S); λ_{max}/nm (Me$_2$CO) 617 and 388 (ε/dm^3 mol^{-1} cm^{-1} 80 and 112); IR: ν(N–H) 3248, 3240, ν(C=N) 1658, ν(C=N) + ν(N–C=S) 1588, 1550, ν(C–S) 1300, ν(Ni–S) 488, ν(Ni–N) 282 cm^{-1}; $\mu_{eff} = 2.95\ \mu_B$.

[Ni([12]aneN$_3$-mc1)(pym2S)]ClO$_4$ 2. The compound was prepared in a similar way to that for **1** using pym2SH (25 mg, 0.22 mmol) and [Ni([12]aneN$_3$-mc1)(μ-OH)]$_2$(ClO$_4$)$_2$ (85 mg, 0.11 mmol). A green solid was obtained. Yield: 92 mg, 86% (Found: C, 39.9; H, 6.1; N, 13.9; S, 6.3%. $C_{16}H_{28}N_5SClO_4Ni$ requires C, 39.9; H, 5.9; N, 14.6; S, 6.7%); *m*/*z* 380 (M$^+$, 100%), 269 (M − pym2S); λ_{max}/nm (Me$_2$CO) 618 and 389 (ε/dm^3 mol^{-1} cm^{-1} 49 and 106); IR: ν(N–H) 3245, 3230, ν(C=N) 1658, ν(C=N) + ν(N–C=S) 1575, 1545, ν(C–S) 1288, ν(Ni–S) 482, ν(Ni–N) 282 cm^{-1}; $\mu_{eff} = 2.97\ \mu_B$.

[Ni([12]aneN$_3$-mc1)(bzimSH)]PF$_6$ 3. To a suspension of [Ni([12]aneN$_3$-mc1)(μ-OH)]$_2$(PF$_6$)$_2$ (303 mg, 0.35 mmol) in acetone (35 cm^3) bzimSH$_2$ (105 mg, 0.70 mmol) was added. The mixture was stirred for 30 min. The solvent was removed under reduced pressure until *ca.* 15 cm^3 remained and diethyl ether (20 cm^3) was added to the solution. Cooling to −20 °C afforded a green solid which was filtered off, washed with diethyl ether and dried at 100 °C in the oven. Yield: 386 mg, 98% (Found: C, 40.5; H, 5.8; N, 12.2; S, 5.2%. $C_{19}H_{30}N_5SPF_6Ni$ requires C, 40.4; H, 5.4; N, 12.4; S, 5.7%); *m*/*z* 418 (M$^+$, 100%), 268 (M − bzimSH); λ_{max}/nm (Me$_2$CO) 612 and 394 (ε/dm^3 mol^{-1} cm^{-1} 69 and 298); IR: ν(N–H) 3408, ν(N–H) 3258, 3240, ν(C=N) 1662, ν(C=N) + ν(N–C=S) 1490, 1462, ν(C–S) 1296, ν(Ni–S) 452, ν(Ni–N) 278 cm^{-1}; $\mu_{eff} = 2.97\ \mu_B$.

[Ni([12]aneN$_3$-mc1)(bztzS)]PF$_6$ 4. Complex **4** was prepared in a fashion analogous to that for **3**, starting from [Ni([12]aneN$_3$-mc1)(μ-OH)]$_2$(PF$_6$)$_2$ (200 mg, 0.23 mmol) and bztzSH (77 mg, 0.46 mmol). Yield: 209 mg, 78% (Found: C, 39.2; H, 5.1; N, 10.0; S, 11.1%. $C_{19}H_{29}N_4S_2PF_6Ni$ requires C, 39.2; H, 5.0; N, 9.6; S, 11.0%); *m*/*z* 435 (M$^+$, 100%), 269 (M − bztzS); λ_{max}/nm (Me$_2$CO) 620 and 387 (ε/dm^3 mol^{-1} cm^{-1} 86 and 708); IR: ν(N–H) 3240, 3230, ν(C=N) 1658, ν(C=N) + ν(N–C=S) 1585, 1470, ν(C–S) 1260, ν(Ni–S) 450, ν(Ni–N) 278 cm^{-1}; $\mu_{eff} = 2.94\ \mu_B$.

[Ni([12]aneN$_3$-mc2)(py2S)]ClO$_4$ 5. The compound was prepared in a similar way to that for **1** using py2SH (27 mg, 0.24 mmol) and [Ni([12]aneN$_3$-mc2)(μ-OH)]$_2$(ClO$_4$)$_2$ (96 mg, 0.12 mmol). A green solid was obtained. Yield: 101 mg, 85% (Found: C, 43.1; H, 6.5; N, 11.7; S, 6.1%. $C_{18}H_{31}N_4SClO_4Ni$ requires C, 43.8; H, 6.3; N, 11.4; S, 6.5%); *m*/*z* 393 (M$^+$, 100%), 282 (M − py2S); λ_{max}/nm (Me$_2$CO) 617 and 389 (ε/dm^3 mol^{-1} cm^{-1} 95 and 107); IR: ν(N–H) 3265, ν(C=N) 1655, ν(C=N) + ν(N–C=S) 1580, 1550, ν(C–S) 1300, ν(Ni–S) 490, ν(Ni–N) 282 cm^{-1}; $\mu_{eff} = 2.93\ \mu_B$.

[Ni([12]aneN$_3$-mc2)(pym2S)]PF$_6$ 6. To a suspension of [Ni([12]aneN$_3$-mc2)(μ-OH)]$_2$(PF$_6$)$_2$ (100 mg, 0.11 mmol) in acetone (20 cm^3) pymSH (25 mg, 0.22 mmol) was added. The mixture was heated under reflux with stirring for 2 h. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether (20 cm^3). The product was obtained as a green solid which was filtered off, washed with diethyl ether and air-dried. Yield: 89 mg, 75% (Found: C, 37.6; H, 5.5; N, 13.1; S, 6.0%. $C_{17}H_{30}N_5SPF_6Ni$ requires C, 37.8; H, 5.6; N, 13.0; S, 5.9%); *m*/*z* 394 (M$^+$, 100%), 282 (M − pymS); λ_{max}/nm (Me$_2$CO) 618 and 391 (ε/dm^3 mol^{-1} cm^{-1} 46 and 117); IR: ν(N–H) 3280, ν(C=N) 1655, ν(C=N) + ν(N–C=S) 1575, 1534, ν(C–S) 1304, ν(Ni–S) 468, ν(Ni–N) 294 cm^{-1}; $\mu_{eff} = 2.96\ \mu_B$.

[Ni([12]aneN$_3$-mc2)(bzimSH)]PF$_6$ 7. Complex **7** was prepared in a fashion analogous to that for **3**, starting from [Ni([12]aneN$_3$-mc2)(μ-OH)]$_2$(PF$_6$)$_2$ (312 mg, 0.35 mmol) and bzimSH$_2$ (105 mg, 0.70 mmol). Yield: 275 mg, 68% (Found: C, 40.5; H, 5.4; N, 12.0; S, 5.1%. $C_{20}H_{32}N_5SPF_6Ni$ requires C, 41.5; H, 5.6; N, 12.1; S, 5.5%); *m*/*z* 432 (M$^+$, 100%), 283 (M − bzimSH); λ_{max}/nm (Me$_2$CO) 625 and 399 (ε/dm^3 mol^{-1} cm^{-1} 76 and 244); IR: ν(N–H) 3392, ν(N–H) 3264, ν(C=N) 1650, ν(C=N) + ν(N–C=S) 1492, 1462, ν(C–S) 1300, ν(Ni–S) 422, ν(Ni–N) 294 cm^{-1}; $\mu_{eff} = 2.99\ \mu_B$.

[Ni([12]aneN$_3$-mc2)(bztzS)]PF$_6$ 8. Complex **8** was prepared in a fashion analogous to that for **3**, starting from [Ni([12]aneN$_3$-mc2)(μ-OH)]$_2$(PF$_6$)$_2$ (303 mg, 0.34 mmol) and bztzSH (114 mg, 0.68 mmol). Yield: 260 mg, 64% (Found: C, 39.4; H, 5.1; N, 9.4; S, 10.8%. $C_{20}H_{31}N_4S_2PF_6Ni$ requires C, 40.3; H, 5.2; N, 9.4; S, 10.8%); *m*/*z* 449 (M$^+$, 100%), 283 (M − bztzS); λ_{max}/nm (Me$_2$CO) 631 and 395 (ε/dm^3 mol^{-1} cm^{-1} 73 and 426); IR: ν(N–H) 3254, ν(C=N) 1660, ν(C=N) + ν(N–C=S) 1558, 1472, ν(C–S) 1256, ν(Ni–S) 490, ν(Ni–N) 282 cm^{-1}; $\mu_{eff} = 2.97\ \mu_B$.

Crystal structure determination of compounds 5, 6 and 7

Crystals of [Ni([12]aneN_3-mc2)(py2S)]ClO_4 **5** were obtained by slow ether diffusion onto an acetone solution and crystals of [Ni([12]aneN_3-mc2)(pym2S)]PF_6 **6** and [Ni([12]aneN_3-mc2)-(bzimSH)]PF_6 **7** were obtained by slow evaporation of an acetone solution. In all cases, crystals were mounted on glass fibres and transferred to the diffractometer (Siemens P4) as summarised in Table 3. Cell constants were refined from *ca.* 60 reflections in the 2θ range 10–25°. The structures were solved by the heavy atom method and refined anisotropically on F^2 (program SHELXL-93 (**5** and **7**), SHELXL-97 (**6**)).[30,31] Hydrogen atoms were included using a riding model. The structure of compound **5** was refined as an enantiomeric twin with components 44(6)% and 56(6)%.[32] For compound **6** both hexafluorophosphate anions are disordered over two sites.

CCDC reference number 186/1768.

See http://www.rsc.org/suppdata/dt/a9/a907367a/ for crystallographic files in .cif format.

Acknowledgements

We thank the DGES (project PB97-1036), Spain, for financial support and the Ministerio de Educación y Ciencia, Spain, for a grant (to A. R.). Dr F. Lloret of the University of Valencia, Spain, is thanked for measuring magnetic susceptibilities.

References

1 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
2 *Metal Atoms in Biological Systems, Vol. 23: Nickel and its Role in Biology*, eds. H. Siegel and A. Siegel, Marcel Dekker, New York, 1988.
3 M. A. Halcrow and G. Christou, *Chem. Rev.*, 1994, **94**, 2421.
4 E. S. Raper, A. R. W. Jackson and D. J. Gardiner, *Inorg. Chim. Acta*, 1984, **84**, L1.
5 E. Spinner, *J. Org. Chem.*, 1958, **23**, 2037; *J. Chem. Soc.*, 1960, 1237.
6 B. P. Penfold, *Acta Crystallogr.*, 1953, **6**, 707.
7 J. Bravo, J. S. Casas, M. V. Casteno, M. Gayoso, Y. P. Mascarenhas, A. Sánchez, C. de O. P. Santos and J. Sordo, *Inorg. Chem.*, 1985, **24**, 3435; E. Block, M. Brito, M. Gernon, D. McGowthy, H. Kang and J. Zubieta, *Inorg. Chem.*, 1990, **29**, 3172; P. D. Cookson and E. R. T. Tiekink, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 259; K. L. Brandenburg, M. J. Heeg and H. B. Abrahamson, *Inorg. Chem.*, 1987, **26**, 1064.
8 C. C. Ashworth, N. A. Bailey, M. Johnson, J. A. McCleverty, N. Morrison and B. Tabbiner, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 743; J. A. McCleverty, N. J. Morrison, N. Spencer, C. A. Ashworth, N. A. Bailey, M. R. Johnson, J. M. A. Smith, B. A. Tabbiner and R. C. Taylor, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 1945.
9 E. S. Raper, *Coord. Chem. Rev.*, 1996, **153**, 199.
10 E. S. Raper, *Coord. Chem. Rev.*, 1997, **165**, 475.
11 G. López, G. Sánchez, G. García, J. García, A. Martínez, J. A. Hermoso and M. Martínez-Ripoll, *J. Organomet. Chem.*, 1992, **435**, 193.
12 E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *Inorg. Chim. Acta*, 1991, **188**, 7.
13 E. S. Raper, A. M. Britton and W. Clegg, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3341; S. G. Rosenfield, S. A. Swedborg, L. Gelmini, D. W. Stephens and P. D. Mascharak, *Inorg. Chem.*, 1987, **26**, 2792.
14 E. S. Raper, A. M. Britton and W. Clegg, *Inorg. Chim. Acta*, 1989, **166**, 171.
15 J. W. L. Martin, J. H. Johnston and N. F. Curtis, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 68.
16 A. Escuer, R. Vicente and J. Ribas, *Polyhedron*, 1992, **11**, 453.
17 M. D. Santana, A. Rufete, G. Sánchez, G. García, G. López, J. Casabó, E. Molins and C. Miravitlles, *Inorg. Chim. Acta*, 1997, **255**, 21.
18 M. D. Santana, A. Rufete, G. García, G. López, J. Casabó, A. Cabrero, E. Molins and C. Miravitlles, *Polyhedron*, 1997, **16**, 3713.
19 M. D. Santana, G. García, A. Rufete, G. Sánchez, M. C. Ramírez de Arellano and G. López, *Inorg. Chem. Commun.*, 1998, **1**, 267.
20 G. Sánchez, F. Ruiz, M. D. Santana, G. García, G. López, A. Martínez, J. A. Hermoso and M. Martínez-Ripoll, *J. Chem.Soc.*, *Dalton Trans.*, 1994, 19.
21 J. Ruiz, N. Cutillas, J. Torregrosa, G. García, G. López, P. A. Chaloner, P. B. Hitchchock and R. M. Harrison, *J. Chem.Soc.*, *Dalton Trans.*, 1994, 2353.
22 J. Ruiz, N. Cutillas, J. Sampedro, G. López, A. Martínez, J. A. Hermoso and M. Martínez-Ripoll, *J. Organomet. Chem.*, 1996, **526**, 67.
23 G. López, G. García, G. Sánchez, J. García, J. Ruiz, J. A. Hermoso, A. Vegas and M. Martínez-Ripoll, *Inorg. Chem.*, 1992, **31**, 1518.
24 J. Ruiz, F. Florenciano, G. López, P. A. Chaloner and P. B. Hitchchock, *Inorg. Chim.Acta*, 1998, **281**, 165.
25 M. Munakata, T. Kuroda-Sowa, M. Maekawa, M. Nakamura, S. Akiyama and S. Kitagawa, *Inorg. Chem.*, 1994, **33**, 1284.
26 C. Tejel, B. E. Villarroya, M. A. Ciriano, A. J. Edwards, F. J. Lahoz, L. A. Oro, M. Lanfranchi, A. Tiripicchio and M. Tiripicchio-Camellini, *Inorg. Chem.*, 1998, **37**, 3954.
27 L. Ballester, A. Gutierrez, M. F. Perpiñán, T. Rico, E. Gutierrez-Puebla and A. Monge, *Polyhedron*, 1994, **13**, 2277.
28 A. B. P. Lever, *Inorganic electronic spectroscopy*, Elsevier, Amsterdam, 1984, p. 513–520.
29 G. N. La Mar, W. Horrocks, Jr. and R. H. Holm (eds.), *NMR of Paramagnetic Molecules*, Academic Press, New York, 1973, p. 243.
30 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.
31 G. M. Sheldrick, *SHELXL-93*, University of Göttingen, Göttingen, Germany, 1993.
32 H. D. Flack, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 876.

Paper a907367a