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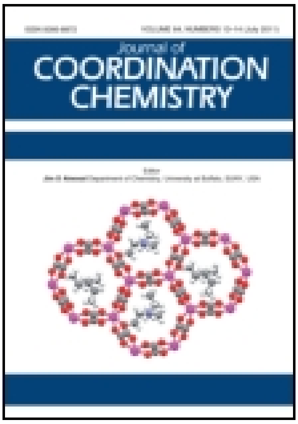

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Synthesis and characterization of new Ni(II) complexes with S,N-heterocycle ligands: influence of the steric strain of ligands on coordination

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Synthesis and characterization of new Ni(II) complexes with S,N-heterocycle ligands: influence of the steric strain of ligands on coordination

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The complexes $[NiCl_2(PyTn)_2]\cdot 2H_2O$ (**1**), $[Ni(H_2O)_2(PyTn)_2](NO_3)_2$ (**2**), $[Ni(H_2O)_2(PzTz)_2]Cl_2$ (**3**) and $[Ni(H_2O)_2(PzTz)_2](NO_3)_2$ (**4**) [PyTn = 2-(1-pyrazolyl)-2-thiazoline; PzTz = 2-(1-pyrazolyl)-1,3-thiazine] have been prepared and characterized by elemental analysis, electronic spectroscopy, IR spectroscopy and single crystal X-ray diffraction to determine if the size of the S,N-heterocycle influences coordination to Ni(II). The four complexes are six coordinate as a distorted octahedron. The disposition of chlorides and water is *trans* in **1** and **2**, whereas **3** and **4** are *cis*, as a consequence of the steric strain induced by the larger S,N-ring.

Keywords: Thiazoline; Thiazine; Pyrazole; Ni(II) complexes; Crystal structure

1. Introduction

Compounds containing N,N or S,N heterocycles have been extensively used in coordination chemistry as ligands towards transition metal ions, with special interest in biological systems [1].

Heterocycles with N and/or S are present in several natural and synthetic compounds with interesting biological properties. In this way, thiazolines constitute a building block in medicines like micacocidin and penicillin [2], and 1,3-thiazines are contained in β-lactam antibiotics like cephalosporin [3]. These heterocycles also have applications in food [4] and agricultural [5, 6] industry. For these reasons, our group has studied the coordination chemistry of ligands containing 2-thiazoline or 1,3-thiazine rings in their structure [7–11].

Many pyrazole derivatives possess pharmacologic applications, such as sulfaphenazole (antibacterial) [12] or celecoxib (anti-inflammatory) [13]. Moreover, pyrazole-based ligands have been investigated as model complexes that can mimic the active site of metalloenzymes which contain imidazole from histidine, bound to the metal centre in the active site [14]. This is the case of hydrotris(pyrazolyl)borates, that have been

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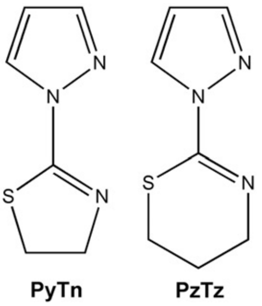

Scheme 1. Structure of PyTn and PzTz.

employed to model metalloproteins thanks to their ability to mimic the multiple coordination of histidine to metal ions [15].

Combination of these heterocycles in new compounds can provide coordination versatility, since they can act as N,N or S,N donors through nitrogen of pyrazole and N or S from thiazoline or thiazine, depending on the metal [16]. Different structural features in the ligands, for example heterocycle arrangement, can cause differences in the coordination environment of the metal [11, 17]. We have recently developed several new pyrazole/S,N-heterocycle ligands and started to study their coordination behavior towards d block metals [18, 19].

In this work, we prepare and characterize four Ni(II) complexes with 2-(1-pyrazolyl)-2-thiazoline (PyTn) and 2-(1-pyrazolyl)-1,3-thiazine (PzTz) (scheme 1), previously published [18, 19], and study the influence of the structural differences of ligands, i.e. the size of the S,N-heterocycle, on the coordination environment of the metal. Ni(II) is widely used in coordination chemistry due to its tendency to form stable and simple coordination compounds with low coordination numbers (four, five or six) [20].

Results are reported on isolation of $[NiCl_2(PyTn)_2] \cdot 2H_2O$ (**1**), $[Ni(H_2O)_2(PyTn)_2](NO_3)_2$ (**2**), $[Ni(H_2O)_2(PzTz)_2]Cl_2$ (**3**) and $[Ni(H_2O)_2(PzTz)_2](NO_3)_2$ (**4**) and characterization by elemental analyses, single-crystal X-ray diffraction, electronic spectroscopy and IR spectroscopy.

2. Experimental

2.1. *General procedures*

All reagents were commercial grade material and used without purification. 2-(1-pyrazolyl)-2-thiazoline (PyTn) and 2-(1-pyrazolyl)-1,3-thiazine (PzTz) were synthesized as previously reported [18, 19]. Chemical analyses of carbon, hydrogen, nitrogen and sulfur were performed by microanalytical methods using a Leco CHNS-932 microanalyser. IR spectra were recorded on a Thermo IR-300 spectrophotometer from KBr pellets in the 4000–370 cm^{-1} range and on a Perkin-Elmer FT-IR 1700X spectrophotometer from Nujol mull at 500–150 cm^{-1}. The UV-Vis-NIR reflectance spectra in the 200–1500 nm range were registered from a pellet of the sample using a Shimadzu UV-3101 PC spectrophotometer and $BaSO_4$ as a reference.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of [$NiCl_2(PyTn)_2$]·$2H_2O$ (1). A solution containing $NiCl_2 \cdot 6H_2O$ (75.0 mg, 0.316 mmol) in 1 mL ethanol 96% was added to a solution (5 mL) of PyTn (92.0 mg, 0.6 mmol) in ethanol 96%. The resulting solution was allowed to evaporate slowly at room temperature. After a few hours, X-ray quality crystals as blue prisms were isolated from the solution. Crystals were filtered, washed with cold ether and air-dried. Yield: 112.0 mg, 79.1%. Anal. Calcd for $C_{12}H_{18}Cl_2N_6NiO_2S_2$ (%): C, 30.53; H, 3.84; N, 17.80; S, 13.58. Found: C, 30.43; H, 3.76; N, 17.53; S, 13.23. IR (KBr): (sh = shoulder, w = weak, m = medium, s = strong, vs = very strong) thiazoline ring vibrations 1625(vs) [ν(C=N)], 1006(s), 904(m), 784(s), 726(w), 651(m), 609(s), 575(m), 447(m) cm^{-1}; pyrazole ring vibrations: 1537(s), 1404(vs), 1364(vs), 949(sh) cm^{-1}.

2.2.2. Synthesis of [$Ni(H_2O)_2(PyTn)_2$](NO_3)$_2$ (2). This complex was prepared by reacting a methanol solution (1 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (90.0 mg, 0.3 mmol) with a solution (5 mL) of PyTn (92.0 mg, 0.6 mmol) in the same solvent. Blue crystals were isolated after slow evaporation of the solution at room temperature. The crystals were filtered, washed with cold ether and finally air-dried. Yield: 139.2 mg, 88.4%. Anal. Calcd for $C_{12}H_{18}N_8NiO_8S_2$ (%): C, 27.44; H, 3.45; N, 21.34; S, 12.21. Found: C, 27.44; H, 3.30; N, 21.27; S, 12.11. IR (KBr): thiazoline ring vibrations 1626(vs) [ν(C=N)], 1005(s), 902(m), 774(m), 650(m), 610(s), 573(m), 446(w) cm^{-1}; pyrazole ring vibrations: 1537(s), 1404(s), 1363(s), 948(sh) cm^{-1}.

2.2.3. Synthesis of [$Ni(H_2O)_2(PzTz)_2$]Cl_2 (3). $NiCl_2 \cdot 6H_2O$ (75.0 mg, 0.316 mmol) dissolved in methanol (1 mL) was added to a methanol solution (5 mL) of PzTz (100.0 mg, 0.6 mmol). By liquid-vapor diffusion of ether over this solution, blue crystals were isolated. Crystals were separated by filtration, washed with cold ether and air-dried. Yield: 75.8 mg, 50.5%. Anal. Calcd for $C_{14}H_{22}Cl_2N_6NiS_2O_2 \cdot 1.5\ H_2O$ (%): C, 31.95; H, 4.53; N, 15.86; S, 11.93. Found: C, 31.90; H, 4.59; N, 15.94; S, 12.16. IR (KBr): thiazine ring vibrations 1621(vs) [ν(C=N)], 954(m), 917(w), 891(m), 810(s), 737(m), 618(m), 587(w), 533(w), 443(w) cm^{-1}; pyrazole ring vibrations: 1521(s), 1406(s), 1340(m), 1003(s) cm^{-1}.

2.2.4. Synthesis of [$Ni(H_2O)_2(PzTz)_2$](NO_3)$_2$ (4). This complex was isolated from a methanol solution (1 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (90.0 mg, 0.3 mmol) that was added to a methanol solution (5 mL) of PzTz (100.0 mg, 0.6 mmol). After several days, X-ray quality crystals as blue prisms were isolated from the solution at room temperature. Crystals were filtered, washed with cold ether and air-dried. Yield: 103.4 mg, 62.3%. Anal. Calcd for $C_{14}H_{22}N_8NiS_2O_8$ (%): C, 30.40; H, 3.98; N, 20.26; S, 11.58. Found: C, 30.07; H, 4.19; N, 20.18; S, 11.54. IR (KBr): thiazine ring vibrations 1619(vs) [ν(C=N)], 954(w), 917(w), 889(w), 802(m), 784(m), 613(m), 584(w), 532(w), 441(w) cm^{-1}; pyrazole ring vibrations: 1521(m), 1403(vs), 1384(vs), 1336(s), 1004(s) cm^{-1}.

2.3. *Crystal structure determination*

X-ray diffraction measurements were performed using a Bruker APEX or a Bruker SMART CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Absorption corrections were applied using SADABS [21]. The structures were solved by direct methods and subsequent Fourier differences using the SHELXS-97 [22] program and refined by full-matrix least-squares on F^2 with SHELXL-97 [23], included in the WINGX package [24], assuming anisotropic displacement parameters for non-hydrogen atoms, except for disordered atoms with isotropic displacement parameters. The crystal structure of **2** presented a disorder affecting C(6) as a consequence of exchange in positions for the thiazoline and pyrazole rings. Due to the impossibility of modeling this disorder, C(6) was refined assuming an isotropic displacement parameter, leaving three Fourier peaks with high electron density, Q1 = 2.48 eÅ^3 (*0.0579*, *−0.4187*, *−0.1346*), Q2 = 2.46 eÅ^3 (*0.1084*, *−0.3702*, *−0.0818*) and Q3 = 2.07 eÅ^3 (*0.0467*, *−0.4349*, *−0.0836*), located at 0.4–0.5 Å of C(6). Despite this disorder, the structure of **2** was determined without ambiguity, however, data involving bond distances and angles should be handled with caution. The crystal structure of **3** presented a dynamic disorder affecting C(3) and C(4) corresponding to the thiazine ring in PzTz. This dynamic disorder was modeled using two sets of positions with total occupancy constrained to unity. The refined occupancy was 54% for C(3A) and C(4A) and 46% for C(3B) and C(4B). All hydrogens were positioned geometrically, with U_{iso} values derived from U_{eq} values of the corresponding carbons. However, hydrogens of water were detected by Fourier differences and were refined with fixed O–H and H–H distances (0.957(3) and 1.513(3) Å, respectively). Graphical representations of the molecular structures were generated using ORTEP3 [25] and Mercury [26] for Windows. Experimental details of the crystal structure determinations are listed in table 1.

3. Results and discussion

3.1. *Crystal structures*

The molecular structures together with the atom numbering schemes are shown in figures 1–4. Selected bond lengths and angles are listed in table 2. Due to the disorder present in **2**, only the main features of the formal structural model are discussed in the text, with bond lengths and angles reported as "Supplementary material" online, as well as the hydrogen bonds parameters and structure.

The X-ray data indicate that in **1** the nickel(II) coordinates to two chlorides, two thiazoline nitrogens and two pyrazole nitrogens from two PyTn, which are bidentate in such a way that a five-membered chelate ring is formed (figure 1). The chlorides are *trans* and the coordination polyhedron can be described as a distorted octahedron with the ligand-metal-ligand angles varying from 78.9(1)° to 101.1(1)°.

For **2**, the monoclinic unit cell contains four nitrates and two $[Ni(H_2O)_2(PyTn)]^{2+}$ cations; therefore the salt can be formulated as *trans*-$[Ni(H_2O)_2(PyTn)](NO_3)_2$ (figure 2). Nickel coordinates to two bidentate PyTn molecules with the other two coordination positions occupied by two waters in a *trans* disposition. Thus, the coordination polyhedron around nickel(II) is a distorted octahedron.

Table 1. Crystal data and structure refinement details for **1**–**4**.

	1	**2**	**3**	**4**
Crystal shape	Prism	Prism	Prism	Prism
Color	Blue	Blue	Blue	Blue
Size (mm^3)	$0.33 \times 0.29 \times 0.20$	$0.28 \times 0.22 \times 0.12$	$0.25 \times 0.19 \times 0.16$	$0.64 \times 0.55 \times 0.19$
Chemical formula	$C_{12}H_{18}Cl_2N_6NiO_2S_2$	$C_{12}H_{18}N_8NiO_8S_2$	$C_{14}H_{22}Cl_2N_6NiS_2O_2$	$C_{14}H_{22}N_8NiS_2O_8$
Formula weight	472.05	525.17	500.11	553.23
Crystal system	Triclinic	Monoclinic	Trigonal	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P3_121$	$P2_12_12_1$
Unit cell dimensions (Å, °)				
a	7.146(1)	8.229(5)	9.115(1)	7.944(2)
b	7.781(1)	10.306(5)		16.483(4)
c	8.485(1)	11.580(5)	21.484(1)	16.634(4)
α	99.33(1)			
β	94.20(1)	91.069(5)		
γ	92.09(1)			
Cell volume (Å^3), Z	463.8(1), 1	981.9(9), 2	1545.95(3), 3	2178.2(9), 4
T (K)	293(2)	100(2)	100(2)	110(2)
D_{calc} (g cm^{-3})	1.69	1.776	1.612	1.687
μ (mm^{-1})	1.579	1.263	1.426	1.143
$F(000)$	242	540	774	1144
θ range	2.4–28.3	2.7–26.4	2.6–30.5	1.7–26.3
Index range	$-9 \le h \le 9$; $-10 \le k \le 10$; $0 \le l \le 11$	$-10 \le h \le 10$; $0 \le k \le 12$; $0 \le l \le 14$	$-13 \le h \le 6$; $0 \le k \le 13$; $0 \le l \le 30$	$-9 \le h \le 9$; $0 \le k \le 20$; $0 \le l \le 20$
Independent reflections	2278	2020	3142	4447
Observed reflections $[F > 4.0\sigma(F)]$	2004 $[F > 4.0\sigma(F)]$	1816 $[F > 4.0\sigma(F)]$	3059 $[F > 4.0\sigma(F)]$	4255 $[F > 4.0\sigma(F)]$
Max./Min. transmission	0.743/0.624	0.863/0.719	0.804/0.717	0.812/0.528
No. of ref. parameters	123	145	131	314
R $[F > 4.0\sigma(F)]$[a]	0.034	0.092	0.020	0.022
wR $[F > 4.0\sigma(F)]$[b]	0.100	0.235	0.048	0.052
Goodness-of-fit (GOF)[c]	1.074	1.147	1.056	1.063
ρ_{max}; ρ_{min} (eÅ^{-3})	0.509; −0.646	2.482; −1.425	0.266; −0.343	0.475; −0.236

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[c] The goodness-of-fit (GOF) equals $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{rf\ln s} - N_{params})\}^{1/2}$.

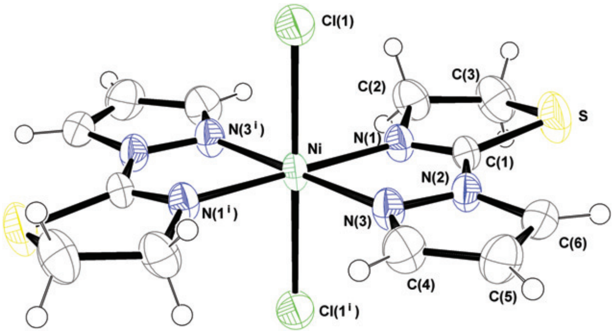

Figure 1. Molecular structure of [NiCl$_2$(PyTn)$_2$] in **1**. The thermal ellipsoids are plotted at the 50% probability level and hydrogens are included as spheres of arbitrary radii.

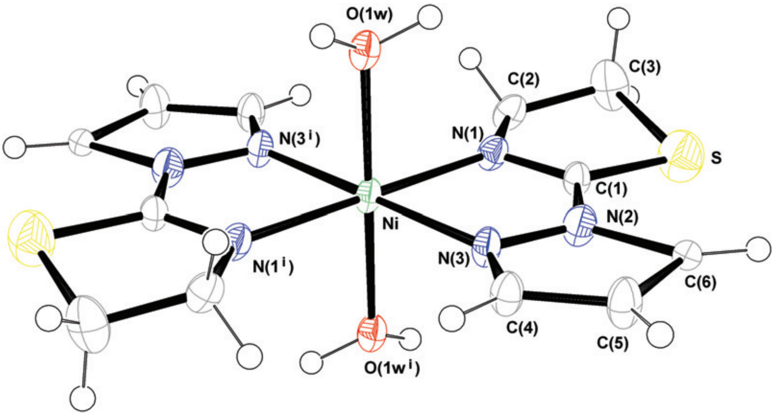

Figure 2. Crystal structure of $[Ni(H_2O)_2(PyTn)_2]^{2+}$ in **2**. The thermal ellipsoids are plotted at the 50% probability level and hydrogens are included as spheres of arbitrary radii.

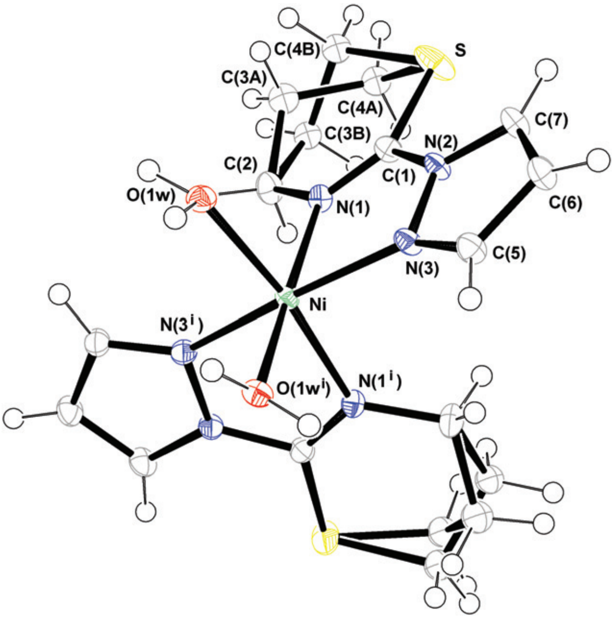

Figure 3. Crystal structure of $[Ni(H_2O)_2(PzTz)_2]^{2+}$ in **3**. The thermal ellipsoids are plotted at the 50% probability level and hydrogens are included as spheres of arbitrary radii.

Compounds **3** and **4** correspond with the salts *cis*-$[Ni(H_2O)_2(PzTz)_2]Cl_2$ and *cis*-$[Ni(H_2O)_2(PzTz)_2](NO_3)_2$, respectively, according to the X-ray diffraction results. The coordination chemistry around Ni(II) in both cases can be considered as a distorted octahedron with nickel bonded to two bidentate PzTz molecules and two waters. In **3** and **4** waters are *cis* (figures 3 and 4).

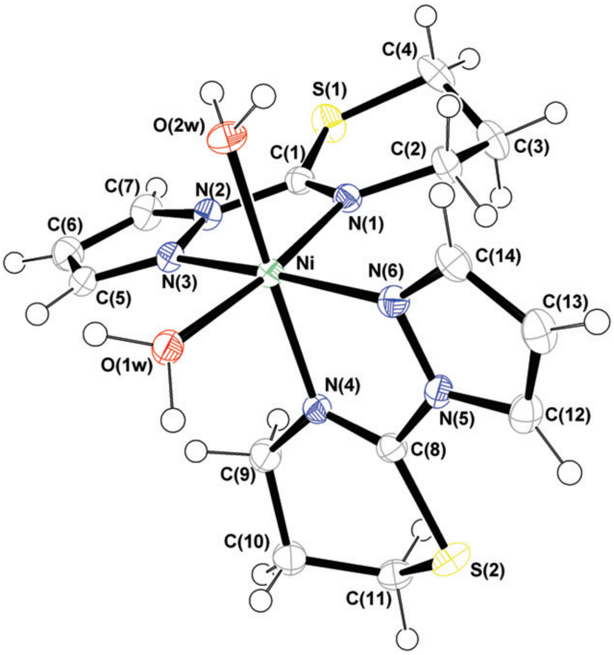

Figure 4. Crystal structure of $[Ni(H_2O)_2(PzTz)_2]^{2+}$ in **4**. The thermal ellipsoids are plotted at the 50% probability level and hydrogens are included as spheres of arbitrary radii.

The Ni–Cl bond distance in **1** is comparable to the value 2.440(1) Å found for $[NiCl_2(ATH)_2]$ (ATH = 2-acetyl-2-thiazoline hydrazone) [27]. Likewise, the Ni-OH_2 and Ni-$N_{pyrazole}$ bond lengths in **3** and **4** are of same order as values reported for $[Ni(HL^1)_2(H_2O)_2]Br_2 \cdot 2.5DMF$ [average Ni–O = 2.094 Å, average Ni–N = 2.042 Å; HL^1 = 3-phenyl-5-(6-methyl-(2-pyridyl))pyrazole] [28] and $[Ni(L3)(H_2O)_2]Br_2 \cdot 3H_2O$ [Ni–O = 2.076(3) Å, Ni–N = 2.091(4) Å; L3 = 1-(α-(phenylimino)benzyl)3,5-dimethyl-pyrazole] [29]. The Ni–$N_{pyrazole}$ bond lengths in **1** are comparable to values found in **3** and **4**. The Ni–$N_{thiazoline}$ bond length may be compared with the value 2.075(2) Å found in $[NiCl_2(ATH)_2]$. It is remarkable that only one compound with a Ni–$N_{thiazine}$ distance, $[Ni(H_2O)_2(PyTz)_2]Cl_2 \cdot 6H_2O$ (PyTz = 2-(2-piridyl)iminotetrahydro-1,3-thiazine), has been found. The distance for this bond in this complex [2.075(2) Å] [30] is slightly shorter than found in **3** and **4**.

Since both hydrogen bond donors and hydrogen bond acceptors are present in the crystal structures, the possibility of forming hydrogen bonds in the crystal exists (see figures 5–7). Thus, **1** is stabilized by a hydrogen bond network in which chlorides are hydrogen acceptors and crystallization waters are hydrogen donors. For **3**, the intermolecular hydrogen bonds lead to zigzag chains parallel to the *c* axis. In **4** the hydrogen bond network forms sheets perpendicular to the crystallographic *c* axis. The hydrogen donors are coordination waters whereas chlorides in **3** and oxygens of the nitrates in **4** are hydrogen acceptors. The geometrical parameters for the hydrogen bonds in **1**, **3** and **4** are listed in table 3.

The dispositions of the ligands in the coordination spheres are a consequence of the size of the ligand. Thus, in complexes containing PyTn, the ligands are *trans* with the

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **3** and **4**.

	1	**3**	**4**
Ni–N(1)	2.056(2)	2.094(1)	2.088(2)
Ni–N(4)			2.104(2)
Ni–N(3)	2.109(2)	2.045(1)	2.052(2)
Ni–N(6)			2.044(2)
Ni–Cl	2.458(1)		
Ni–O(1w)		2.084(1)	2.060(1)
Ni–O(2w)			2.067(1)
Cl–Ni–N(1)	87.3(1)		
Cl–Ni–N(1$^{\mathrm{i}}$)	92.7(1)		
Cl–Ni–N(3)	90.8(1)		
Cl–Ni–N(3$^{\mathrm{i}}$)	89.2(1)		
O(1w)–Ni–O(2w)			88.1(1)
O(1w)–Ni–O(1w$^{\mathrm{i}}$)		86.4(1)	
O(1w)–Ni–N(1)		89.3(1)	174.1(1)
O(1w)–Ni–N(1$^{\mathrm{i}}$)		172.4(1)	
O(1w)–Ni–N(3)		91.4(1)	96.5(1)
O(1w)–Ni–N(3$^{\mathrm{i}}$)		95.2(1)	
O(1w)–Ni–N(4)			90.3(1)
O(1w)–Ni–N(6)			91.3(1)
N(1)–Ni–N(1$^{\mathrm{i}}$)		95.6(1)	
N(1)–Ni–N(3)	78.9(1)	78.3(1)	78.4(1)
N(1)–Ni–N(3$^{\mathrm{i}}$)	101.1(1)	95.2(1)	
N(1)–Ni–N(4)			93.2(1)
N(1)–Ni–N(6)			94.1(1)
N(3)–Ni–N(3$^{\mathrm{i}}$)		170.5(1)	
N(3)–Ni–N(6)			170.4(1)
N(4)–Ni–N(6)			78.1(1)
N(3)–Ni–O(2w)			92.8(1)
N(4)–Ni–O(2w)			170.9(1)
N(6)–Ni–O(2w)			93.0(1)

Symmetry codes: $^{\mathrm{i}}1-x, -y, 1-z$ for **1**; $-x, -x+y, 1/3-z$ for **3**.

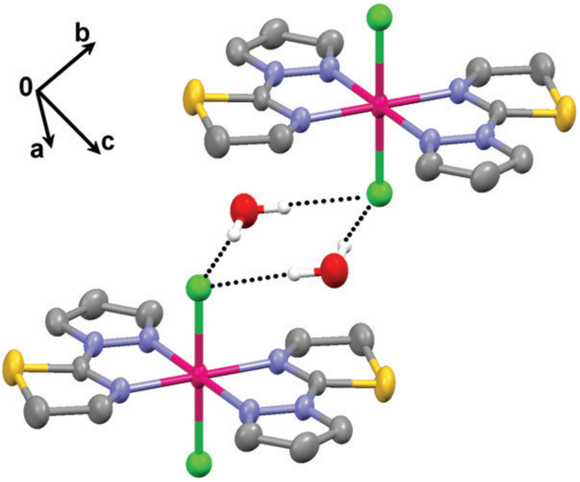

Figure 5. Hydrogen bonds in the crystal of **1**.

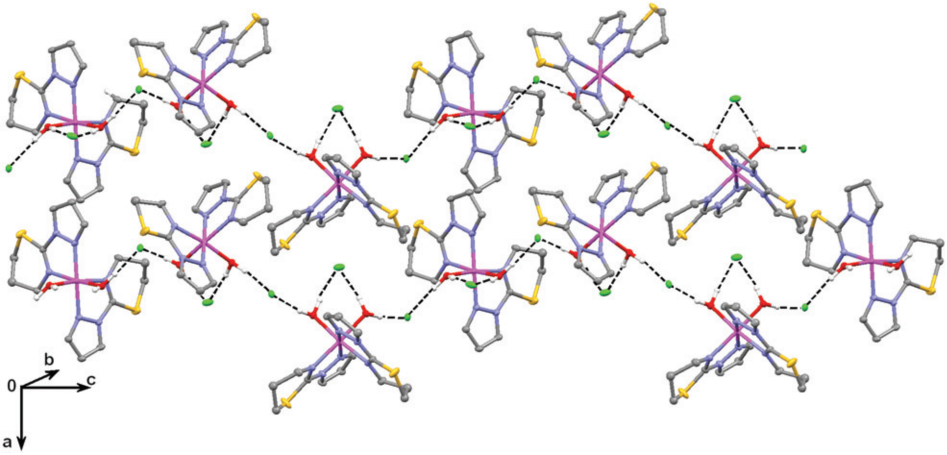

Figure 6. Hydrogen bonds in the crystal of **3**.

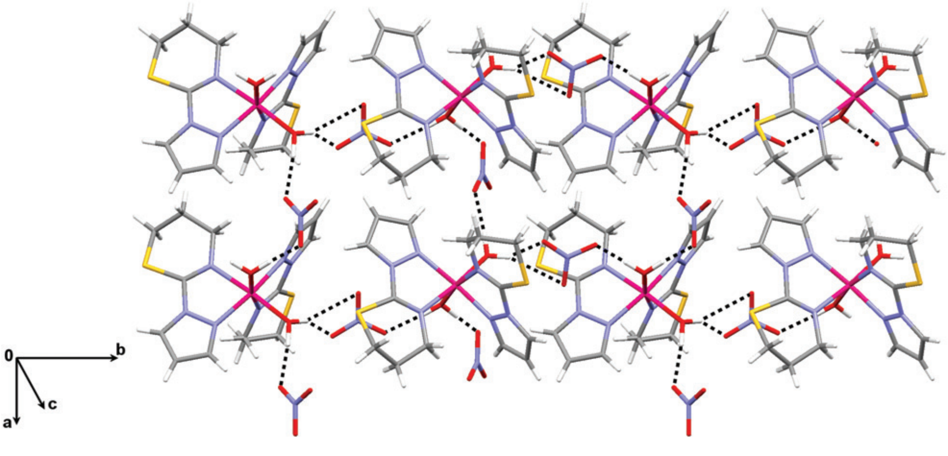

Figure 7. Hydrogen bonds in the crystal of **4**.

pyrazole ring of one PyTn faced with the thiazoline ring of the other PyTn molecule. However, in **3** and **4** steric hindrance induced by increase in size of the six-membered S,N-heterocycle does not permit the thiazine and pyrazole rings being close and ligands must be *cis* in order to minimize steric effects. This has been observed in other Ni(II) complexes, e.g. $[Ni(en)_2(H_2O)_2]^{2+}$ and $[Ni(bpy)_2(H_2O)_2]^{2+}$. In the Cambridge Structural Database (CSD, Version v5.32, August 2011) [31] 22 compounds containing $[Ni(en)_2(H_2O)_2]^{2+}$ have been found; 15 of them with *trans* waters. However, when ethylenediamine is replaced by larger ligands like bipyridine the waters are *cis* in order to decrease the steric hindrance, as can be observed in the five complexes containing the $[Ni(bpy)_2(H_2O)_2]^{2+}$ cation obtained in the CSD.

Table 3. Hydrogen bond parameters for **1**, **3** and **4**.

D–H···A	Position of A	A···D (Å)	A···H–D (°)
1			
O(1w)–H(1w)···Cl	x, y, z	3.227(3)	172(2)
O(1w)–H(2w)···Cl	$-x+1, -y+1, -z+1$	3.290(2)	172(2)
3			
O(1w)–H(2w)···Cl(1)	x, y, z	3.074(1)	170(1)
O(1w)–H(1w)···Cl(2)	$x+1, y, z$	3.065(1)	170(1)
O(1w)–H(1w)···Cl(2)	$x+1, y, -z$	3.065(1)	170(1)
4			
O(1w)–H(1w)···O(2)	x, y, z	2.799(2)	172(1)
O(1w)–H(2w)···O(5)	$-x+1, y+1/2, -z+1/2$	2.805(2)	155(2)
O(2w)–H(3w)···O(1)	$x-1, y, z$	2.792(2)	166(2)
O(2w)–H(4w)···O(6)	$x-1, y, z$	2.735(2)	164(1)

Table 4. Position (cm^{-1}) of the bands and spectral parameters calculated for **1**–**4**.

	1	**2**	**3**	**4**
$\nu_1[^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)]$	8690	9890	10,630	10,480
$\nu_2[^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)]$	16,260	17,060	17,210	16780
$\nu_3[^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)]$	27,550	27,250	27,780 (sh)	27,780 (sh)
$10Dq$ (cm^{-1})	8690	9890	10,720	10,420
B (cm^{-1})	940	980	876	873

sh = shoulder.

3.2. *Spectroscopic studies*

The reflectance spectra of **1**–**4** are very similar and show the characteristic profile of octahedral Ni(II) complexes. The bands in each spectrum and their assignments to the transitions expected in an idealized O_h symmetry are indicated in table 4. The ligand field parameters, $10Dq$ and B, have been calculated from the positions of the d–d transitions using the following relationships [32]:

$$\nu_1 = 10Dq \tag{1}$$

$$\nu_2 = (1/2)(15B + 30Dq) - (1/2)[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{1/2} \tag{2}$$

$$\nu_3 = (1/2)(15B + 30Dq) - (1/2)[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{1/2} \tag{3}$$

The values listed in table 4 are similar to those found in other octahedral nickel(II) complexes [30, 33, 34].

Tentative assignments of significant bands in IR spectra of **1**–**4**, PyTn and PzTz [18, 19] are presented in table 5. Signals corresponding to S,N-heterocycle vibrations and to pyrazole ring vibrations shift in the complexes with respect to the free ligands, indicative of coordination *via* nitrogen of these cycles [35–37].

Table 5. IR spectral assignments (cm^{-1}) of PyTn, PzTz, **1**–**4**.

	PyTn	**1**	**2**	PzTz	**3**	**4**
ν(C=N)	1641(s)	1625(vs)	1626(vs)	1635(vs)	1621(vs)	1619(vs)
νn pyrazole	1514(m)	1537(s)	1537(s)	1510(m)	1521(s)	1521(m)
	1392(s)	1404(vs)	1404(s)	1419(s)	1406(s)	1403(vs)
	1350(s)	1364(vs)	1363(s)	1386(vs)		1384(vs)
Ni–$N_{pyrazole}$		292(w)	290(w)		289(w)	289(w)
Ni–$N_{thiazoline}$		268(w)	227(w)			
Ni–$N_{thiazine}$					269(w)	263(w)
Ni–Cl		210(w)				
Ni–O_{water}			354(w)		336(w)	337(w)

w = weak, m = medium, s = strong, vs = very strong.

In the low-frequency region, several bands corresponding to metal-ligand stretching vibrations are detected and tentative assignments are listed in table 5. ν(Ni–$N_{pyrazole}$) vibrations in nickel(II) complexes are in the range 264–292 cm^{-1} [38, 39]. Likewise, ν(Ni–$N_{thiazoline}$) is between 245 and 300 cm^{-1} [33, 34, 40, 41], whereas ν(Ni–$N_{thiazine}$) is reported at 270 cm^{-1} for $[Ni(btz)_3][ClO_4]_2$ (btz = 2,2′-bi-4,5-dihydro-thiazine) [42] and at 280 cm^{-1} for $[Ni(H_2O)_2(PyTz)_2]Cl_2$ [30]. Signals of Ni–Cl bond have been detected at 195–245 cm^{-1} [27, 33, 34]; ν(Ni-O_{water}) is reported over 330 cm^{-1} [33, 43, 44].

4. Conclusions

We have synthesized and structurally characterized four new Ni(II) complexes with 2-(1-pyrazolyl)-2-thiazoline (PyTn) and 2-(1-pyrazolyl)-1,3-thiazine (PzTz). Both ligands are bidentate towards Ni(II) forming monomeric octahedral complexes. The disposition of ligands in the coordination environment is conditioned by the size of the S,N-heterocycle; thus, complexes containing a 2-thiazoline ring (smaller S–C–N angle) are *trans* isomers, whereas complexes containing a 1,3-thiazine ring as ligand (larger S–C–N angle) are forced to adopt a *cis* disposition as a consequence of the steric hindrance introduced by the ligand.

Supplementary material

CCDC 835821 to 835824 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M.A. Monge, C. Ruiz-Valero, N. Snejko. *Inorg. Chem.*, **41**, 2429 (2002).
[2] A. Ino, A. Murabayashi. *Tetrahedron*, **55**, 10271 (1999).
[3] A. Korolkovas, J.H. Burckhalter. *Compendio Esencial de Química Farmacéutica*, Reverté, Barcelona (1983).
[4] G. MacLeod, J.M. Ames. *J. Food Sci.*, **52**, 42 (1987).
[5] H. Du, J. Wang, Z. Hu, X. Yao, X. Zhang. *J. Agric. Food Chem.*, **56**, 10785 (2008).
[6] R. Caujolle, H. Amarouche, M. Payard, P.R. Loiseau, C. Bories, P.M. Loiseau, P. Gayral. *Eur. J. Med. Chem.*, **24**, 287 (1989).
[7] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, A.B. Rodríguez, A. Bernalte-García. *Inorg. Chim. Acta*, **366**, 373 (2011).
[8] A.M. Lozano-Vila, F. Luna-Giles, E. Viñuelas-Zahínos, F.L. Cumbrera, A.L. Ortiz, F.J. Barros-García, A.B. Rodríguez. *Inorg. Chim. Acta*, **365**, 282 (2011).
[9] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, M.C. Fernández-Calderón. *Eur. J. Med. Chem.*, **46**, 150 (2011).
[10] F.J. Barros-García, A. Bernalte-García, A.M. Lozano-Vila, F. Luna-Giles, J.A. Pariente, R. Pedrero-Marín, A.B. Rodríguez. *J. Inorg. Biochem.*, **100**, 1861 (2006).
[11] F.J. Barros-García, F. Luna-Giles, M.A. Maldonado-Rogado, E. Viñuelas-Zahínos. *Polyhedron*, **25**, 43 (2006).
[12] D.J. Abraham (Ed.). *Burger's Medicinal Chemistry and Drug Discovery*, 6th Edn, John Wiley & Sons (2003).
[13] T.D. Pennig, J.J. Talley, S.R. Bertenshaw, J.S. Carter, P.W. Collins, S. Docter, M.J. Graneto, L.F. Lee, J.W. Malecha, J.M. Miyashiro, R.S. Rogers, D.J. Rogier, S.S. Yu, G.D. Anderson, E.G. Burton, J.N. Cogburn, S.A. Gregory, C.M. Koboldt, W.E. Perkins, K. Seibert, A.W. Veenhuizen, Y.Y. Zhang, P.C. Isakson. *J. Med. Chem.*, **40**, 1347 (1997).
[14] F. Mani. *Coord. Chem. Rev.*, **120**, 325 (1992).
[15] N. Kitajima, W.B. Tolman. *Prog. Inorg. Chem.*, **43**, 419 (1995).
[16] A.M. Lozano-Vila, F. Luna-Giles, E. Viñuelas-Zahínos, F.L. Cumbrera, A.L. Ortiz, F.J. Barros-García. *Polyhedron*, **30**, 1157 (2011).
[17] M.A. Maldonado-Rogado, E. Viñuelas-Zahínos, F. Luna-Giles, A. Bernalte-García. *Polyhedron*, **26**, 3112 (2007).
[18] A. Bernalte-García, A.M. Lozano-Vila, F. Luna-Giles, R. Pedrero-Marín. *Polyhedron*, **25**, 1399 (2006).
[19] P. Torres-García, E. Viñuelas-Zahínos, F. Luna-Giles, J. Espino, F.J. Barros-García. *Polyhedron*, **30**, 2627 (2011).
[20] L. Sacconi, F. Mani. In *Comprehensive Coordination Chemistry*, G. Wilkinson (Ed.), Vol. 6, Pergamon Press, New York (1987).
[21] Bruker AXS Inc. *SADABS, version 2.03*, Bruker AXS Inc., Madison, Wisconsin, USA (2001).
[22] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structures Solution*, University of Göttingen, Germany (1997).
[23] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structures Refinement*, University of Göttingen, Germany (1997).
[24] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).
[25] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[26] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood. *J. Appl. Crystallogr.*, **41**, 466 (2008).
[27] E. Viñuelas-Zahínos, M.A. Maldonado-Rogado, F. Luna-Giles, F.J. Barros-García. *Polyhedron*, **27**, 879 (2008).
[28] J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J.F. Piniella, X. Solans, M. Font-Bardia, J. Ros. *Polyhedron*, **20**, 1029 (2001).
[29] Y.Y. Wang, S.A. Lin, F.M. Zhu, H.Y. Gao, Q. Wu. *Inorg. Chim. Acta*, **362**, 166 (2009).
[30] F.J. Barros-García, A. Bernalte-García, F.J. Higes-Rolando, F. Luna-Giles, R. Pedrero-Marín. *Polyhedron*, **23**, 1453 (2004).
[31] I.J. Bruno, J.C. Cole, P.R. Eddington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor. *Acta Crystallogr.*, **B58**, 389 (2002).
[32] D.K. Rastogi, K.C. Sharma, S.K. Dua, M.P. Teotia. *J. Inorg. Nucl. Chem.*, **37**, 685 (1975).
[33] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, A. Bernalte-García. *Polyhedron*, **28**, 4056 (2009).
[34] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, A. Bernalte-García. *Polyhedron*, **28**, 1173 (2009).
[35] M. Shakir, S.P. Vakey, F. Firdaus, P.S. Hameed. *Polyhedron*, **13**, 2319 (1994).
[36] B. Singh, R.N. Singh, R.C. Aggarwal. *Polyhedron*, **4**, 401 (1985).
[37] M.G. Abd El-Wahed, M.S. Refat, S.M. El-Megharbel. *J. Mol. Struct.*, **888**, 416 (2008).
[38] J. Reedijk. *Inorg. Chim. Acta*, **3**, 517 (1969).

[39] N.C. Saha, R.J. Butcher, S. Chaudhuri, N. Saha. *Polyhedron*, **24**, 1015 (2005).

[40] A. Bernalte-García, F.J. García-Barros, F.J. Higes-Rolando, F. Luna-Giles. *Polyhedron*, **18**, 2907 (1999).

[41] A. Bernalte-García, F.J. García-Barros, F.J. Higes-Rolando, A.M. Pizarro-Galán, C. Valenzuela-Calahorro. *Thermochim. Acta*, **339**, 95 (1999).

[42] J. Nelson, S. Martin-Nelson, W.D. Perry. *J. Chem. Soc., Dalton Trans.*, 1282 (1976).

[43] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Wiley, New York (1997).

[44] J.R. Ferraro. *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York (1971).