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The comparison of structure and bond between $[Ni(pz^{ph})_4(NCS)_2]$ and $[Ni(pz^{But})_4(NCS)_2]$

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Abstract

Two nickel(II) complexes with thiocyanate and different substituted pyrazole ligands, $[Ni(pz^R)_4(SCN)_2]$ (R = ph for (1) and *n*-But for (2), $pz^R = 3$ -substituted pyrazole), have been synthesized and their crystal structures have been determined. The compound 1 crystallizes in the monoclinic system, space group $P2_1/n$, a = 8.591(5) Å, b = 17.936(10) Å, c = 12.861(7) Å, $\beta = 106.490(10)^\circ$, Z = 2, $R_1 = 0.0665$, $wR_2 = 0.1375$. The compound 2 crystallizes in the monoclinic system, space group $P2_1/c$, a = 12.805(3) Å, b = 22.718(5) Å, c = 13.396(3) Å, $\beta = 94.480(5)^\circ$, Z = 4, $R_1 = 0.0729$, $wR_2 = 0.1665$. The nickel(II) ion in each complex is coordinated by four pyrazole nitrogen atoms and two nitrogen atoms of NCS⁻ to form a distorted octahedron. The two nitrogen atoms of NCS⁻ are located at axial positions and the four nitrogen atoms of pyrazoles are located at equatorial positions. The average Ni–N(pz^R) and Ni–N(NCS) bond lengths are observed to be 2.111 and 2.068 Å for 1, 2.095 and 2.098 Å for 2, respectively. In 1, the intermolecular hydrogen bonds form quasi 1D structure. The intramolecular hydrogen bonds are found in 2. The spectroscopic and bond properties have also been discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nickel(II) complexes; Pyrazole; Thiocyanate; Crystal structure; 1D complex

1. Introduction

Pyrazole and its derivatives (pz^R) are strong twonitrogen donor ligands. They are widely used as terminal ligands [1–3], bridging ligands [4–10] and the precursors for synthesis of various multi-nitrogen donor ligands in the coordination chemistry, bioinorganic chemistry and organometallic chemistry. Recent interests in pyrazole ligands are focused on poly (pyrazolyl)borate ligands [11,12]. Poly(pyrazolyl)-

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borate ligands have been aroused by its resemblance to active sites in some metalloenzymes and metalloproteins such as carbonic anhydrase (CA) [13–20], nitrite reductases (NiR) [21–23], hemocyanin (Hc) [24–30] and blue copper proteins [31–33]. During our efforts to synthesize the model complexes of nickel-containing enzymes and nickel-iron hydrogenase by using hydrido-tris(pyrazolyl)borate ligands, two novel nickel(II) complexes [Ni(pz^R)₄(SCN)₂] (R = ph for (1) and *n*-But for (2), pz^R = 3-substituted pyrazole) were isolated. This paper presents the synthesis, crystal structure and properties of [Ni(pz^{ph})₄(SCN)₂] (1) and [Ni(pz^{But})₄(SCN)₂] (2).

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Table 1Data collection and processing parameters for 1 and 2

	$[Ni(pz^{ph})_4(SCN)_2]$ (1)	$[Ni(pz^{But})_4(SCN)_2]$ (2)
Empirical formula	C ₃₈ H ₃₂ N ₁₀ NiS ₂	C ₃₀ H ₄₈ N ₁₀ NiS ₂
Formula weight	751.57	671.61
Temperature (K)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c
a (Å)	8.591(5)	12.805(3)
<i>b</i> (Å)	17.936(10)	22.718(5)
<i>c</i> (Å)	12.861(7)	13.396(3)
α (°)	90	90
β(°)	106.490(10)	94.480(5)
γ (°)	90	90
Volume, Z	1900.2(18) Å ³ , 2	3884.8(15) Å ³ , 4
Density (calculated) (g/cm ³)	1.314	1.148
Absorption coefficient	0.662 mm^{-1}	0.639 mm^{-1}
F(000)	780	1432
Crystal size (mm ³)	$0.30 \times 0.25 \times 0.20$	$0.40 \times 0.30 \times 0.20$
θ range for data collection (°)	2.00-25.03	1.77-25.03
Limiting indices	$-7 \le h \le 10$	$-15 \le h \le 14$
-	$-21 \le k \le 20$	$-27 \le k \le 25$
	$-15 \le l \le 14$	$-15 \le l \le 8$
Reflections collected	6449	15 555
Independent reflections	2775 [$R_{\rm int} = 0.0658$]	6699 $[R_{int} = 0.0719]$
Absorption correction	Sadabs	Sadabs
Max. and min. transmission	0.8790 and 0.8262	0.8829 and 0.7842
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2775/0/220	6699/0/388
Goodness-of-fit on F^2	0.952	1.021
<i>R</i> 1, <i>wR</i> 2 [$I > 2\sigma(I)$]	0.0665, 0.1375	0.0729, 0.1665
R1, $wR2$ (all data)	0.1476, 0.1644	0.1533, 0.2058
Largest diff. peak and hole	0.304 and $-0.212 \text{ e}\text{\AA}^{-3}$	1.477 and -0.300 eÅ^{-3}

 $R1 = \Sigma ||F_{o}| - |F_{C}|| / \sum |F_{o}|, \ wR2 = (\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum (F_{o}^{2})^{2})^{1/2}, \ w = 1 / [\sigma^{2}(Fo^{2}) + (0.0728P)^{2} + 0.0000P], \ P = (Fo^{2} + 2Fc^{2})/3 \text{ for } 1 \text{ and } w = 1 / [\sigma^{2}(Fo^{2}) + (0.1000P)^{2} + 0.0000P], \ P = (Fo^{2} + 2Fc^{2})/3 \text{ for } 2.$

2. Experimental

2.1. General

Potassium hydridotris(3-phethylpyrazolyl) borate (KTp^{ph}) and potassium tetrakis(3-butylpyrazolyl)borate $(KB(pz^{But})_4)$ were prepared by a literature procedure [34]. The purities were confirmed by IR, MS-FAB and elemental analysis. The other chemicals were reagent grade and used as received.

Elemental analyses for C, H and N were obtained at the Institute of Elemental Organic Chemistry, Nankai University. IR spectra were recorded in KBr disks on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm⁻¹ region. UV–Vis spectra in MeOH were recorded on a Shimadzu UV-2401 PC UV–VIS scanning spectrophotometer. Mass spectra were performed at the Central Laboratory of Nankai University on VG ZAB-HS spectrometer.

2.2. Preparation of $[Ni(pz^{ph})_4(SCN)_2]$ (1)

A methanolic solution (10 ml) of KTp^{ph} (0.2 mmol, 96.0 mg) was added to a solution of Ni(ClO₄)₂·6H₂O (0.2 mmol, 73.1 mg) in methanol (5 ml). The mixture was stirred for 10 h at room temperature. An aqueous solution (1 ml) of KSCN (0.6 mmol, 58.3 mg) was added to the mixture. Then the reaction was stirred for another 10 h. The resultant was filtered to get rid of any solid particles and left to

Table 2	
Bond lengths (Å) and angles (°)	

$[Ni(pz^{ph})_4(NCS)_2] (1)$		$[Ni(pz^{But})_4(NCS)_2]$ (2)	
Ni(1)-N(5)	2.067(5)	Ni(1)-N(2)	2.084(5)
Ni(1)-N(1)	2.106(5)	Ni(1)-N(5)	2.088(4)
Ni(1)-N(3)	2.114(5)	Ni(1)-N(9)	2.100(5)
N(1)-C(1)	1.147(7)	Ni(1)-N(3)	2.094(5)
N(2)-C(2)	1.123(6)	Ni(1)-N(7)	2.096(4)
		N(5)-C(10)	1.152(7)
N(5)-Ni(1)-N(1)#1	89.3(2)	N(2)-Ni(1)-N(5)	91.16(19)
N(5)-Ni(1)-N(1)	90.7(2)	N(2)-Ni(1)-N(9)	88.84(19)
N(5)-Ni(1)-N(3)	88.84(18)	N(5)-Ni(1)-N(9)	93.75(17)
N(5)#1-Ni(1)-N(3)	91.16(18)	N(2)-Ni(1)-N(3)	88.45(19)
N(1) - Ni(1) - N(3)	92.75(19)	N(5)-Ni(1)-N(3)	85.69(17)
N(1)-Ni(1)-N(3)#1	87.25(19)	N(9)-Ni(1)-N(3)	177.22(19)
N(1)-C(1)-S(1)	176.4(6)	N(2)-Ni(1)-N(7)	90.88(19)
N(2)-C(2)-S(2)	177.5(5)	N(5)-Ni(1)-N(7)	177.9(2)
		N(9) - Ni(1) - N(7)	86.79(18)
		N(3)-Ni(1)-N(7)	93.86(17)
		N(2)-Ni(1)-N(1)	179.3(2)
		N(5) - Ni(1) - N(1)	89.54(19)
		N(9) - Ni(1) - N(1)	91.1(2)
		N(3)-Ni(1)-N(1)	91.64(19)
		N(7) - Ni(1) - N(1)	88.4(2)
		N(5)-C(10)-S(1)	178.2(6)

#1 = -x + 2, -y, -z + 1.

evaporate slowly at room temperature. Blue crystals suitable for X-ray analysis were obtained after several days. Yield: 67%. Anal. Calcd for $C_{38}H_{32}N_{10}NiS_2$ (1): C, 60.71; H, 4.29; N, 18.64. Found: C, 60.91; H, 4.22; N, 18.43%.

2.3. Preparation of $[Ni(pz^{But})_4(SCN)_2]$ (2)

The synthetic method of **2** is similar to that of **1** except that KTp^{ph} was replaced by $KB(pz^{But})_4$. After several days, blue crystals suitable for X-ray analysis were obtained. Yield: 61%. Anal. Calcd for $C_{30}H_{48}N_{10}NiS_2$ (**2**): C, 53.66; H, 7.20; N, 20.86. Found: C, 53.79; H, 7.11; N, 20.71%.

3. Structure determination

X-ray diffractions were collected on a BRU-KER SMART 1000 CCD detector with graphitemonochromatized Mo K α radiation ($\lambda =$ 0.71073 Å). The structures were solved by direct method using the program SHELXS 97 [35] and Fourier difference techniques, and refined by fullmatrix least-squares method on F^2 using SHELXL 97 [36]. Crystal data and structure refinements are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

4. Result and discussion

4.1. Preparation of the complexes

The complexes were determined to be $[Ni(pz^{ph})_4 (NCS)_2]$ (1) and $[Ni(pz^{But})_4(NCS)_2]$ (2) by singlecrystal X-ray diffraction. During the reaction, the ligands KTp^{ph} and $KB(pz^{But})_4$ were decomposed to pyrazoles. Owing to strong Lewis acidity of the Ni(II) ion, small amount of water, excess reactant of KSCN and the stereoscopic force of pz^{ph} or pz^{But} , the B–N bond broke up completely,. Similar phenomena has been observed in other hydridotris(pyrazolyl)borate and hydridotris(pyrazolyl)methane complexes [2,3, 37–39].

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Fig. 1. ORTEP drawing of [Ni(pz^{ph})₄(NCS)₂] (1).

4.2. Crystal structure of the complexes

The structures of the two complexes are very similar. The ORTEP drawings of **1** and **2** are shown in Figs. 1 and 2, respectively. The nickel(II) ion in each complex is coordinated by four substituted pyrazole nitrogen atoms and two nitrogen atoms of NCS⁻ to form a distorted octahedron. The two nitrogen atoms of NCS⁻ are located at axial positions and the four nitrogen atoms of pyrazole are located at equatorial positions. The average Ni–N(pz^R) and Ni–N(NCS) bond lengths are observed to be 2.111 and 2.068 Å for 1, 2.095 and 2.098 Å for **2**, respectively. The Ni–N_{pz} bond lengths are similar to other values described in the literature. For example, in [Ni(HL)₃][PF₆]·2H₂O (HL = 3-(2-pyridyl)pyrazole) the Ni–N_{pz} distance is

in the range 2.056-2.080 Å [40]. The coordination geometry of **1** is a central symmetrical constringing octahedron. The average bond length of $Ni-N(pz^R)$ of 1 is longer than that of 2, while the average bond length of Ni-N(NCS) of 1 is shorter than that of 2. The bonds of four Ni-N_{pz} at equatorial positions are elongated while the bonds of two Ni-N(SCN) at axial positions are compressed. It is because the steric effect of ph is larger than that of But. The comparison of structural parameters of 1 and 2 are listed in Table 3. There are two complex molecules of 1 in the cell. The hydrogen atoms of N2-H2B and N4-H4A are connected by weak intermolecular hydrogen bonds with N5(pz) and S1 atoms of adjacent complex molecule to form quasi one-dimensional (1D) chain structure. The nearest Ni···Ni distance is 8.591 Å.

Table 3									
Hydrogen	bond	lengths	(Å)	and	angles	(°) f	or 1	and	2

$[Ni(Hpz^{ph})_4(NCS)_2] (1)$		$[Ni(Hpz^{But})_4(NCS)_2] (2)$		
$N(2)-H(2B)\cdots N(5)$	2.431(117.9)	$N(4)-H(4B)\cdots N(2)$	2.407(117.44)	
$N(4)-H(4A)\cdots N(5)$	2.491(116.6)	$N(10) - H(10B) \cdot \cdot \cdot N(2)$	2.685(110.57)	
$N(2)-H(2B)\cdots S(1)$	3.019(122.7)	$N(8)-H(8D)\cdots N(1)$	2.405(118.2)	
$N(4)-H(4A)\cdots S(1)$	2.933(136.9)	$N(6)-H(6A)\cdots N(1)$	2.717(109.1)	





Fig. 2. ORTEP drawing of $[Ni(pz^{But})_4(NCS)_2]$ (2).

The hydrogen bond lengths of N2-H2B···N5, N4-H4A...N5, N2-H2B...S1 and N4-H4A...S1 are 2.431, 2.491, 3.019 and 2.933 Å; the hydrogen bond angles are 117.9, 116.6, 122.7 and 136.9°, respectively. The molecular packing of 1 is shown in Fig. 3. There are four complex molecules of 2 in the cell. The hydrogen atoms in N4-H4B and N10-H10B are connected by intramolecular hydrogen bonds with N2(NCS), and those in N6-H6A and N8-H8A are connected by intramolecular hydrogen bonds with N1(NCS). The hydrogen bond lengths of N4-H4B····N2, N10-H10B····N2 and N8-H8D····N1 are 2.407, 2.685 and 2.405 Å, respectively. The hydrogen bond angles are 117.44, 110.57 and 118.2°, respectively. The distance of N6···N is 3.145 Å. All hydrogen bond lengths and angles are also listed in Table 3.

4.3. Spectroscopic properties

The IR spectra of the two complexes are very similar and the data are listed in Table 4. The typical

stretch frequency of ν_{B-H} at 2400 cm⁻¹ of KTp^{ph} disappears. The stretch frequencies of $\nu_{C=N}$ of SCN⁻ are observed at 2010 cm⁻¹ for **1** and 1988 cm⁻¹ for **2**, respectively. The $\nu_{C=N}$ of **1** is red shifted than **2**, which is consistent with the shorter bond length of C=N. The other absorption peaks appeared at 1700–650 cm⁻¹ are consistent with pz^{ph} or pz^{But} but not with KTp^{ph} or KB(pz^{But})₄.

The UV–Vis spectra of complexes 1 and 2 are also similar and the data are listed in Table 4. In the UV range, one strong absorption appears at ca. 40 161 cm⁻¹ for **1** and 35 971 cm⁻¹ for **2**, respectively, which are assigned to ligand transition. The ligand transition of 1 is blue shifted than that of 2. In the visible region two relative strong absorptions can be observed at ca. 25 349, 13 793 cm^{-1} for 1 and 25 806, 15 875 cm^{-1} for **2**, respectively. They can be assigned to spin-allowed d-d transition of Ni(II), $\nu_3({}^3T_{1g}(P) \leftarrow {}^3A_{2g}), \ \nu_2({}^3T_{1g}(F) \leftarrow {}^3A_{2g}), \ respect$ ively. The weak peak appearing near ν_2 (ca. 13 300 cm⁻¹) can be assigned to spin-forbidden d-d transition of Ni(II)(d⁸), $v_4({}^{1}E_g \leftarrow {}^{3}A_{2g})$. The $\nu_1({}^{3}T_2 \leftarrow {}^{3}A_{2g})$ is not observed completely in the experimental region (200-1000 nm). The d-d transition of 1 is red shifted than that of 2. The ligand-field constants Dq, B', β and ν_1 were calculated by observed ν_3 and ν_2 [41], the results are also listed in Table 4. The Dq value of 1 is smaller than that of 2, indicating that the pz^{ph} is a weaker ligand than pz^{But}. The B' values of both complexes are less than that of free Ni(II) ion (1041 cm^{-1}) , indicative of some covalent bonding of Ni(II) in these complexes.

In conclusion, the structures of two nickel(II) complexes with thiocyanate and different substituted pyrazole ligands, $[Ni(pz^{ph})_4(SCN)_2]$ (1) and $[Ni(pz^{But})_4(SCN)_2]$ (2) are similar but the average equatorial Ni–N bond length of 1 is longer than that of 2. The average axial Ni–N bond length of 1 is shorter than that of 2. Intermolecular hydrogen bonds between adjacent complex molecules form quasi 1D structure in 1. The IR and UV–Vis spectroscopic results are consistent with the crystallographic results and perfectly related to each other.

5. Supplementary material

Additional materials, consisting of atomic

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Fig. 3. Molecular packing of [Ni(pz^{ph})₄(NCS)₂] (1).

Table 4 Summary of average bond lengths (Å), IR and UV–Vis spectra data for 1 and 2

		$[Ni(pz^{ph})_4(NCS)_2]$ (1)	$[Ni(pz^{But})_4(NCS)_2]$ (2)
$Ni-N(pz^R)$		2.111	2.095
Ni-N(NCS ⁻)		2.068	2.098
IR	$\nu_{\rm N}{\rm H}$	3250	3225
	$\nu_{\rm s(C\equiv N)}$	2010	1988
	CT(L)	40 161 (3776)	35 971 (3914)
$\nu (\mathrm{cm}^{-1}) (\epsilon (\mathrm{M}^{-1}\mathrm{cm}^{-1}))$	$\nu_1({}^3T_2 \leftarrow {}^3A_{2g})$	8236	9862
$\nu \left(\mathrm{cm}^{-1} \left(\boldsymbol{\epsilon} \left(\mathrm{M}^{-1} \mathrm{cm}^{-1} \right) \right) \right)$	$\nu_2({}^3T_{1\rho}(F) \leftarrow A_{2\rho})$	13 793 (18)	15 875 (19)
	$\nu_3({}^3T_{1g}(P) \leftarrow {}^3A_{2g})$	25 349 (88)	25 806 (62)
	$\nu_4({}^1\mathrm{E}_{\mathrm{o}} \leftarrow {}^3\mathrm{A}_{2\mathrm{o}})$	11 331 (2)	13 803 (1.2)
$Dq (cm^{-1})$		824	986
$B'(cm^{-1})$		962	806
β		0.92	0.77
$1 - \beta$		0.08	0.23

Note: The values in bracket are the molar extinction constant ϵ , the unit of ϵ is $M^{-1} cm^{-1}$.

coordinates and equivalent isotropic displacement parameters, are available from CCDC. Deposite numbers are 181790 for **1** and 181789 for **2**, respectively. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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