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# Correlation between crystal symmetry and the splitting of *d* orbital in the thiocyanate nickel(II) complexes

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# ABSTRACT

New [Ni(SCN)<sub>2</sub>(L)<sub>4/2</sub>] complexes, where L = py (1),  $\gamma$ -pic (2), pyCH<sub>2</sub>OH (3), py(CH<sub>2</sub>)<sub>3</sub>OH (4) were synthesized in simple reactions of NiCl<sub>2</sub>·6H<sub>2</sub>O with ammonia thiocyanate and pyridine type ligands in methanol solutions. Blue crystals of [Ni(SCN)<sub>2</sub>(py)<sub>4</sub>] (1), [Ni(SCN)<sub>2</sub>(pyCH<sub>2</sub>OH)<sub>2</sub>] (3) and [Ni(SCN)<sub>2</sub>(py(CH<sub>2</sub>)<sub>3</sub>OH)<sub>2</sub>] (4) crystallize in the monoclinic system, blue crystal of [Ni(SCN)<sub>2</sub>( $\gamma$ -pic)<sub>4</sub>] (2) – in the tetragonal one, and red crystal of [Ni(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5) – in the triclinic one. The ligands of complexes (1) and (3) were indicated as rather strong  $\pi$ -acceptors while that of complex (4) one has some  $\pi$ -donor properties. When the aliphatic chain (CH<sub>2</sub>) elongates in the sequence: (1), (3) and (4), an increase in the orbital contribution to the magnetic moment and a decrease in the 10Dq value of the d orbital splitting are related to the change of the point group symmetry from  $D_{2h}$ , via  $D_{2v}$  to  $C_{2h}$ .

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# 1. Introduction

Investigations on the syntheses, crystal, molecular, and electronic structures of metal complexes containing ambidentate ligands are of great interest in connection with the accumulation of metal complexes having ambidentate ligands and with regulation the reactivities of active sites in metal complexes. Many transition metal complexes containing ambidentate ligands have been synthesized, and their structures, physical properties, and linkage isomerisation reactions of the ambidentate units have been investigated. Thiocvanate complexes with the formula of  $[M(NCS)_2L_4]$ . where L is a N-donor ligand such as pyridine, are called Wernertype complexes and they are well known. Nickel(II) thiocyanate complexes with N-donor ligands are investigated due to their structural properties (ability to occur in *cis* and *trans* isomers) [1], formation of coordination polymers in which thiocyanate ligands are bridging ligands as linear anions [2], and examination of solvatochromic behavior of metal complexes [3]. The complexes of Ni(II) with thiocyanate ligands are interesting because of their architectures organized by non-covalent contacts as hydrogen bonds or  $\pi - \pi$  stacking interaction [4]. The crystal structures of isothiocyanate nickel(II) complexes with pyridine,  $\gamma$ -picoline and triphenylphosphine ligands are known but their electronic structure and/or spectroscopic and magnetic properties were not determined [5–9]. Their interesting structural properties and potential application are attractive in studies of magnetism or magnetic exchange ions.

# 2. Experimental

# 2.1. Synthesis

All reagents used for the synthesis of the complex are commercially available and were used without further purification. The [Ni(SCN)<sub>2</sub>(L)<sub>4/2</sub>] complexes, where L = py (1),  $\gamma$ -pic (2), pyCH<sub>2</sub>OH (3), py(CH<sub>2</sub>)<sub>3</sub>OH (4) were synthesized in the reaction between NiCl<sub>2</sub>·6H<sub>2</sub>O (0.24 g;  $1 \times 10^{-4}$  mol), NH<sub>4</sub>SCN (0.15 g;  $2 \times 10^{-4}$  mol) and stoichiometric volumes of pyridine,  $\gamma$ -picoline, 2-(hydroxymethyl)pyridine and 2-(hydroxypropyl)pyridine in methanolic solution (50 cm<sup>3</sup>). The mixtures of the compounds were refluxed for 1 h. After this time, the volume of the solvent was reduced to about 20 cm<sup>3</sup>, the solution was cooled and precipitated light blue crystals suitable to X-ray analysis were filtered off. Additionally, the reaction between pyridine, NH<sub>4</sub>SCN and triphenylphosphine has been carried out, and finally the complex with coordination number 4 – [Ni(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**5**) – has been obtained.

(1) [Ni(SCN)<sub>2</sub>(py)<sub>4</sub>]: Yield 74%. IR (KBr): 3059  $v_{CH}$ ; 2079  $v_{(CN from SCN)}$ ; 1600  $v_{CN}$ ,  $v_{C=C}$ ; 1486, 1356  $\delta_{(C-CH in the plane)}$ ; 1442  $v_{Ph}$ ; 1069  $\delta_{(C-CH in the plane)}$ ; 1008  $\delta_{(C-H out of the plane)}$ ; 800  $v_{(SC from SCN)}$ , 768  $\delta_{(C-C out of the plane)}$ ; 713, 700  $\delta_{(C-C in the plane)}$ ; 482  $\delta_{(NCS)}$ , 429  $v_{(Ni-Npy)}$ . UV–Vis (methanol; log $\varepsilon$ ) [calculated]: 953.1 (1.21), 746.4 (1.13), 581.2 (1.75), 380.5 (3.14), 214.2 (4.97).





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(2) [Ni(SCN)<sub>2</sub>( $\gamma$ -pic)<sub>4</sub>]: Yield 70%. IR (KBr): 3087  $\nu_{ArH}$ ; 2865  $\nu_{CH}$ ; 2064  $\nu_{(CN from SCN)}$ ; 1618  $\nu_{CN}$ ,  $\nu_{C=C}$ ; 1503, 1211  $\delta_{(C-CH in the plane)}$ ; 1421  $\nu_{Ph}$ ; 1020  $\delta_{(C-CH in the plane)}$ ; 963  $\delta_{(C-H out of the plane)}$ ; 810  $\nu_{(SC from SCN)}$ , 725  $\delta_{(C-C in the plane)}$ ; 496  $\delta_{(NCS)}$ . UV–Vis (methanol; loge): 1039.2 (1.19), 751.4 (1.09), 617.7 (1.61), 375.4 (3.05), 214.7 (4.84).

(3) [Ni(SCN)<sub>2</sub>(pyCH<sub>2</sub>OH)<sub>2</sub>]: Yield 68%. IR (KBr): 3182  $v_{OH}$ ; 2937  $v_{CH}$ ; 2114  $v_{(CN \text{ from SCN})}$ ; 1610  $v_{CN}$ ,  $v_{C=C}$ ; 1489, 1274  $\delta_{(C-CH \text{ in the plane})}$ ; 1449  $v_{_{PR}}$ ; 1032  $\delta_{(C-CH \text{ in the plane})}$ ; 966  $\delta_{(C-H \text{ out of the plane})}$ ; 818  $v_{(SC \text{ from SCN})}$ , 765  $\delta_{(C-C \text{ out of the plane})}$ ; 727  $\delta_{(C-C \text{ in the plane})}$ ; 470  $\delta_{(NCS)}$ , 422  $v_{(Ni-Npy)}$ . UV–Vis (methanol; log $\varepsilon$ ): 994.5 (1.19), 750.4 (1.11), 599.2 (2.01), 399.6 (3.05), 217.9 (4.84).

(4) [Ni(SCN)<sub>2</sub>(py(CH<sub>2</sub>)<sub>3</sub>OH))<sub>2</sub>]: Yield 64%. IR (KBr): 3296  $\nu_{OH}$ ; 2992, 2961  $\nu_{CH}$ ; 2106, 2062  $\nu_{(CN from SCN)}$ ; 1605  $\nu_{CN}$ ,  $\nu_{C=C}$ ; 1483, 1270  $\delta_{(C-CH in the plane)}$ ; 1454  $\nu_{Ph}$ ; 1038  $\delta_{(C-CH in the plane)}$ ; 929  $\delta_{(C-H out of the plane)}$ ; 822  $\nu_{(SC from SCN)}$ , 777  $\delta_{(C-C out of the plane)}$ ; 755  $\delta_{(C-C in the plane)}$ ; 498  $\delta_{(NCS)}$ , 437  $\nu_{(Ni-Npy)}$ . UV–Vis (methanol; log $\varepsilon$ ): 1067.0 (1.19), 763.2 (1.12), 655.1 (1.99), 399.1 (3.05), 213.9 (4.84).

(5) [Ni(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]: IR (KBr): 3060  $v_{ArH}$ ; 2088  $v_{(CN \text{ from SCN})}$ ; 1479, 1308  $\delta_{(C-CH \text{ in the plane})}$ ; 1433  $v_{Ph(P-Ph)}$ ; 1096  $\delta_{(C-CH \text{ in the plane})}$ ; 998  $\delta_{(C-H \text{ out of the plane})}$ ; 867  $v_{(SC \text{ from SCN})}$ ; 750  $\delta_{(C-C \text{ out of the plane})}$ ; 692  $\delta_{(C-C \text{ in the plane})}$ ; 523, 512, 497  $\delta_{(NCS)}$ . UV–Vis (methanol; logɛ): 963.5 (1.17), 629.4 (1.30), 402.2 (1.86), 215.3 (5.12). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 7.284–7.692 (m, PPh<sub>3</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>): 30.213 (s, PPh<sub>3</sub>).

# 2.2. Measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range of 4000–400 cm<sup>-1</sup> with the sample in the form of KBr pellet. Electronic spectra were measured on a Lab Alliance UV–Vis 8500 spectrophotometer in the range of 1100–180 nm in methanol solution. The <sup>1</sup>H and <sup>31</sup>P NMR spectra of complex [10] were obtained at room temperature in CDCl<sub>3</sub> using a Bruker 400 spectrometer.

The static (dc) susceptibility and magnetization measurements were performed using a Lake Shore 7225 ac susceptometer/dc magnetometer in the external magnetic field of 1 kOe and in the temperature range of 4.2–250 K as well as in the external magnetic field up to 60 kOe and at 4.6 K, respectively. Both the magnetic susceptibility and magnetization were measured in the zero-field-cooled mode. The magnetic susceptibility has been corrected by the temperature independent contribution,  $\chi_0$ , using a Curie–Weiss law fitting procedure [10]. The Landé factor has been estimated from the magnetization isotherm  $\sigma(H)$  at 4.6 K using the Brillouin fitting procedure ( $g_{\sigma}$ ) and from the Curie constant *C* fitted from the temperature dependence of magnetic susceptibility  $\chi(T)$  and denoted as  $g_{\chi}$ . Because any of the (1), (3) and (4) complexes did not reach the saturation in the magnetic field up to 60 kOe, the  $g_{\sigma}$  values have only an estimated meaning.

# 2.3. Calculations

The density functional theory (DFT) calculations were carried out using GAUSSIAN 09 program [11]. The DFT/B3LYP [12,13] method was used for the geometry optimization and electronic structure determination. The calculations were performed using the polarization functions for all atoms: 6-311(d,p) - nickel, 6-31g(2d,p) sulfur, 6-31(d,p) - carbon, nitrogen and <math>6-31g(d,p) - hydrogen. The contribution of a group to a molecular orbital was calculated using Mulliken population analysis. The GaussSum 2.2 [14] was used to calculate group contributions to the molecular orbitals and to prepare the overlap population density-of-states (OPDOS) spectra. The OPDOS spectra were created by convoluting the molecular orbital information with GAUSSIAN curves of unit height and FWHM of 0.3 eV.

## 2.4. Crystal structures determination and refinement

Crystals of  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(\gamma-pic)_4]$  (2),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3),  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) and red crystal of  $[Ni(SCN)_2(PPh_3)_2]$  (5) were mounted in turn on a Xcalibur, Atlas,

#### Table 1

Crystal data and structure refinement details of  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(\gamma-pic)_4]$  (2),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3),  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) and  $[Ni(SCN)_2(PPh_3)_2]$  (5) complexes.

Complex	1	2	3	4	5
Empirical formula	C <sub>22</sub> H <sub>20</sub> N <sub>6</sub> NiS <sub>2</sub>	C <sub>26</sub> H <sub>28</sub> N <sub>6</sub> NiS <sub>2</sub>	C14H14N4NiO2S2	C <sub>18</sub> H <sub>22</sub> N <sub>4</sub> NiO <sub>2</sub> S <sub>2</sub>	C38H30N2NiP2S2
Formula weight	491.27	547.37	393.12	449.23	699.45
Т (К)	298.0(2)	298.0(2)	298.0(2)	298.0(2)	298.0(2)
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic	triclinic
Space group	C2/c	I41/a	C2/c	$P2_1/c$	ΡĪ
Unit cell dimensions					
a (Å)	12.4046(5)	16.681(2)	14.8446(4)	9.5985(3)	7.9451(4)
b (Å)	12.9341(4)	16.681(2)	8.3106(2)	10.1797(4)	10.4777(5)
c (Å)	15.1196(7)	22.632(5)	14.1261(4)	10.9082(3)	11.4926(5)
α	90	90	90	90	68.924(4)
β	107.241(5)	90	103.403(3)	107.451(3)	74.572(2)
γ γ	90	90	90	90	87.769(3)
V (Å <sup>3</sup> )	2316.83(16)	6297.2(18)	1695.24(8)	1016.78(5)	858.84(7)
Z	4	8	4	2	1
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.408	1.155	1.540	1.467	1.352
Absorption coefficient (mm <sup>-1</sup> )	1.039	0.771	1.415	1.180	0.809
$F(0\ 0\ 0)$	1016	2288	808	468	362
Crystal dimensions (mm)	$0.42 \times 0.10 \times 0.07$	$0.24 \times 0.23 \times 0.19$	$0.22\times0.10\times0.07$	$0.39 \times 0.21 \times 0.14$	$0.44 \times 0.09 \times 0.07$
$\theta$ Range for data collection (°)	3.43-25.05	3.45-25.05	3.59-25.05	3.88-25.05	3.48-25.05
Index ranges	$-14 \leqslant h \leqslant 14$	$-19\leqslant h\leqslant 19$	$-17 \leqslant h \leqslant 17$	$-11\leqslant h\leqslant 11$	$-9\leqslant h\leqslant 9$
	$-15 \leqslant k \leqslant 15$	$-19 \leqslant k \leqslant 16$	$-9 \leqslant k \leqslant 9$	$-12 \leqslant k \leqslant 12$	$-12\leqslant k\leqslant 12$
	$-18\leqslant l\leqslant 18$	$-26 \leqslant l \leqslant 26$	$-16 \leqslant l \leqslant 16$	$-12 \leqslant l \leqslant 12$	$-13 \leqslant l \leqslant 13$
Reflections collected	10 853	14 915	8153	9448	15 751
Independent reflections	$2025 [R(_{int}) = 0.0273]$	$2787 [R(_{int}) = 0.0271]$	$1497 [R(_{int}) = 0.0216]$	$1799 [R(_{int}) = 0.0247]$	3371 [R( <sub>int</sub> ) = 0.0288]
Data/restraints/parameters	2025/0/142	2787/0/161	1497/0/105	1799/0/128	3371/0/205
Goodness-of-fit (GOF) on F <sup>2</sup>	1.053	1.041	1.102	1.085	0.912
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0232$	$R_1 = 0.0308$	$R_1 = 0.0474$	$R_1 = 0.0218$	$R_1 = 0.0324$
	$wR_2 = 0.0582$	$wR_2 = 0.0900$	$wR_2 = 0.1047$	$wR_2 = 0.0574$	$wR_2 = 0.0557$
R indices (all data)	$R_1 = 0.0314$	$R_1 = 0.0467$	$R_1 = 0.0509$	$R_1 = 0.0267$	$R_1 = 0.0614$
	$wR_2 = 0.0592$	$wR_2 = 0.0936$	$wR_2 = 0.1064$	$wR_2 = 0.0585$	$wR_2 = 0.0649$
Largest difference in peak and hole	0.189 and -0.244	0.238 and -0.211	1.108 and -1.132	0.248 and -0.282	0.277 and -0.171



(1)





Fig. 1. The ORTEP drawing of  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(\gamma-pic)_4]$  (2),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3),  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) and  $[Ni(SCN)_2(PPh_3)_2]$  (5) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 1 (continued)

### Table 2

Selected bond lengths (Å) and angles (°) for  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(\gamma-pic)_4]$  (2),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3),  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) and  $[Ni(SCN)_2(PPh_3)_2]$  (5) complexes with optimized geometries in gas phases.

Complex	1		2		3		4		5	
Bond lengths (Å)										
	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
Ni(1)-N(1)	2.053(14)	2.041	2.072(2)	2.029	2.034(14)	1.993	2.038(13)	1.982	1.826(16)	1.835
Ni(1)-N(2)	2.157(12)	2.234	2.127(17)	2.169	2.058(12)	2.121	2.167(12)	2.274		
Ni(1)-N(3)	2.169(13)	2.243	2.131(16)	2.171						
Ni(1)-O(1)					2.125(12)	2.172	2.115(11)	2.127		
Ni(1)-P(1)									2.247(4)	2.308
N(1)-C(1)	1.154(2)	1.186	1.155(3)	1.186	1.148(2)	1.191	1.156(2)	1.189	1.157(3)	1.186
S(1)-C(1)	1.624(18)	1.626	1.617(3)	1.631	1.631(18)	1.626	1.636(16)	1.623	1.612(2)	1.616
Angles (°)										
N(1) - Ni(1) - N(2)	90.97(5)	90.10	90.28(7)	90.06	95 46(5)	04 87	86 30(5)	86 58		
N(1) - Ni(1) - N(2) N(1) - Ni(1) - N(3)	90.57(5)	80.08	90.23(7)	90.12	33.40(3)	54.67	00.00(0)	80.56		
N(2) - Ni(1) - N(3)	90.33(3)	01.12	90.33(7)	90.12						
N(2) - Ni(1) - N(3) N(1) - Ni(1) - O(1)	52.77(5)	51.12	30.70(0)	50.15	172 01(5)	163.87	85 81(5)	86.27		
N(1) - Ni(1) - O(1) N(2) - Ni(1) - O(1)					77 43(5)	75.68	90.36(5)	00.27		
N(2) = NI(1) = O(1) N(1) = NI(1) = D(1)					77.45(5)	75.00	50.50(5)	50.50	02 12(5)	02.25
$N_{1}(1) - N_{1}(1) - F_{1}(1)$ $N_{2}(1) - N_{1}(1) - C_{1}(1)$	156 59(12)	150 47	152 01(16)	150.02	174 01(12)	164 55	162 (11(12)	162 59	52.13(J) 172.27(15)	92.2J 174.97
N(1) = C(1) = C(1) N(1) = C(1) = C(1)	170.06(15)	170.01	170.80(2)	170.04	179.20(15)	177.05	103.41(12) 170.21(15)	179.90	173.27(13) 170.46(19)	174.07
IN(1) - C(1) - S(1)	170.00(15)	179.91	179.60(2)	179.94	176.29(15)	177.05	179.51(15)	176.89	179.40(18)	179.44

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Hydrogen bonds for (1-4) complexes (Å and  $^\circ)\!.$ 

$D - H \cdots A$	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)			
[Ni(SCN) <sub>2</sub> (py) <sub>4</sub> ] (1)							
$C(11)-H(11)\cdots N(1)$	0.93	2.59	3.119(2)	116.7			
$[Ni(SCN)_2(\gamma-pic)_4]$ (2)							
$C(2)-H(2)\cdots N(1)$	0.93	2.61	3.112(3)	114.1			
$[Ni(SCN)_2(pyCH_2OH)_2]$ (3)							
$O(1)-H(1)\cdots S(2) #1$	0.74(2)	2.43(2)	3.1579(14)	167(2)			
$O(2)-H(2)\cdot\cdot S(1) #2$	0.75(2)	2.49(2)	3.2088(14)	164(2)			
$[Ni(SCN)_2(py(CH_2)_3OH)_2]$ (4)							
$O(1)-H(1) \cdot \cdot \cdot S(1) #3$	0.78(2)	2.51(2)	3.2640(14)	163(2)			
$C(7)-H(7A) \cdot \cdot \cdot N(1) #4$	0.97	2.45	3.304(2)	146.1			

Symmetry transformations used to generate equivalent atoms: #1 1/2 + x, -y, -1/2 + z; #2 -x, 1 - y, 2 - z; #3 1 - x, 1/2 + y, -1/2 - z; #4 1 - x, -y, -z.

Gemini ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at temperature of 298.0(2) K, with  $\omega$  scan mode. Ewald sphere reflections were collected up to  $2\theta = 50.10^{\circ}$ . The unit cell parameters were determined from least-squares refinement of the setting angles of 6500, 7620, 9298, 6738 and 7167 strongest reflections for complexes (1–5), respectively. During the data reduction, the decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption corrections were applied. The structures were solved by direct method. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on  $F^2$ . All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic temperature factor equal to 1.2 times the value of equivalent temperature factor of the parent atom, with geometry idealization after each cycle. The oLEX2 program [15] was used for all calculations. Atomic scattering factors were those incorporated in the computer programs.

# 3. Results and discussion

Infrared spectra of the complexes present characteristic bands due to ligands vibrations. The stretching modes of the aryl C-H bond display maxima at 3059, 3061, 2937, 2992, and 3060 cm<sup>-1</sup> for complexes (1–5), respectively. In the spectra of complexes (3) and (4), bands with maxima at 3182 and 3296 cm<sup>-1</sup>, characteristic to OH groups, are visible. The  $v_{C=N}$  band of pyridine ring appears at about 1600 cm $^{-1}$ . In the case of complex (**5**), the stretching modes of the phosphine phenyl C-H have maximum at 1433 cm<sup>-1</sup>, which is characteristic for triphenylphosphine complexes. The  $v_{CN}$ ,  $v_{CS}$  and  $\delta_{NCS}$  frequencies of isothiocyanato ligands present maxima at 2079 cm<sup>-1</sup> (1), 2064 (2), 2114 (3), 2114 cm<sup>-1</sup> (4), 2088 cm<sup>-1</sup> (5), 800, 810, 818, 822, 867 cm<sup>-1</sup>, and 482, 496, 470, 498, 497 cm<sup>-1</sup>, respectively, and it is in good agreement with the end-on NCS coordination. In complex (**3**), two NCS ligands are in *cis* position and in the IR spectrum two v<sub>CN</sub> stretches are expected, but only one broadening band has been recorded. The singlet at 30.213 ppm in the <sup>31</sup>P NMR spectrum of complex (5) indicated that both triphenylphosphine ligands in the complex are equivalent and they are mutually *trans* disposed. The <sup>1</sup>H NMR spectrum of the complex displayed sets of signals in the range of 7.284-7.692 ppm, characteristic to triphenylphosphine ligands.



**Fig. 2.** The crystal packing of complexes (3) and (4) viewing down the *c* axis with hydrogen bonds indicated by dotted lines.

The complexes (1–4) crystallise in the monoclinic space group C2/c and  $P2_1/c$  respectively and the plane square complex (5) in triclinic P1 space group. Details concerning crystal data and refinement are gathered in Table 1. The molecular structures with the structural drawings of the compounds are shown in Fig. 1. The selected bond lengths and angles (experimental and calculated) are listed in Table 2. In the complexes (1-4), nickel atoms have octahedral environment with the thiocyanate ligands bonded to metal center through nitrogen atom. In the complexes under study, the nickel(II) ion is located in the crystallographic center of inversion (1, 4, and 5) or on two-fold axis (2 and 3) and its coordination environment consists of two thiocyanato ligands and four pyridine,  $\gamma$ -picoline ligands (**1** and **2**) or two 2-(hydroxymethyl/hydroxypropyl)pyridine (**3** and **4**) molecules. In the case of complexes with pyridine and  $\gamma$ -picoline ligands, the coordination polyhedron is an almost perfect octahedron with angular deviations smaller than  $3^{\circ}$ . In the case of complexes (3) and (4), the distortions from



**Fig. 3.** The experimental (black) and calculated (red) IR transitions of  $[Ni(SCN)_2(py)_4]$  (1) and  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

octahedron are visible in the angles N(1)-Ni(1)-O(1) with value  $\sim$ 8° for complex (**3**) and 4.2° for (**4**). The C–N and C–S bond length values fall in the 1.148(2)-1.157(3) Å and 1.612(2) Å, 1.636(16) Å ranges for the studied complexes, similar to those observed for thiocyanate complexes. The Ni-N<sub>(heterocyclic ligand)</sub> and Ni-O distances are normal and comparable with distances in other nickel(II) complexes containing the heterocyclic ligands. The distances between Ni-y-picoline are shorter about 0.03 Å that those observed for Ni-pyridine in complexes (2) and (1) respectively; indicating  $\gamma$ -picoline is a stronger  $\pi$ -acceptor than pyridine, which was confirmed by the calculations described below. Ni-N-C angles range from 152.91(16)° (2) to 174.91(13)° (3) in the studied complexes. In all complexes, the values of Ni-N-C angles are in a good agreement with those found for Ni<sup>2+</sup> having bent terminally bonded NCS ligand (141-174°) [16]. The conformations of molecules (1 and 2) are stabilized by intramolecular hydrogen bonds. and in crystal packing of complexes (3 and 4) intermolecular



(4)

**Fig. 4.** The electrostatic potential (ESP) surfaces of  $[Ni(SCN)_2(py)_4]$  (1) and  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) complexes. The ESP surface is shown both in space (with positive and negative regions shown in blue and red, respectively) and mapped on electron densities (in the range of 0.05 a.u. – deepest red – to –0.005 a.u. – deepest blue) of the molecule (ESP colour scale is such that  $\delta^+ \rightarrow \delta^-$  in the direction red  $\rightarrow$  blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hydrogen bonds are observed and collected in Table 3. In Fig. 2, the two dimensional networks formed by the hydrogen bonds in the complexes (**3**) and (**4**) are shown.



**Fig. 5.** The overlap partial density-of-states (OPDOS) diagrams for interactions between nickel and A – isothiocyanate ligands, and B – pyridine type ligands.



Fig. 6. The UV-Vis spectrum of complex (1).



**Fig. 7.** The *E*/*B* vs. *Dq*/*B* dependence of Tanabe–Sugano diagram for octahedrally coordinated Ni<sup>+2</sup> ion. The vertical lines represent the case of  $[Ni(SCN)_2(py)_4](1)$  and  $[Ni(SCN)_2(py(CH_2)_3OH)_2](4)$  chromophore.

# 3.1. Electronic structure

To form an insight in the electronic structures and bonding properties of the studied complexes, calculations using the density functional theory (DFT) method were carried out. Before the calculations their geometries were optimized in singlet states using the DFT method with the B3LYP functional. In general, the predicted bond lengths and angles are in a good agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations. As an example, the IR experimental and calculated spectra of  $[Ni(SCN)_2(py)_4]$  (1) and  $[Ni(SCN)_2(py(CH_2)_3OH))_2]$  (4) are presented in Fig. 3. Maximum differences between the optimized and experimental geometries of the studied compounds are visible in Ni(1)–N(2) distance ( $\sim$ 0.100 Å) for complex (3) and in N(2)– Ni(1)-N(3) angle  $(2.9^{\circ})$  for (1). Additionally from Fig. 3 is visible that the hydrogen bonds are poorly interpreted by the calculations in GAUSSIAN. The stabilization energies calculated in NBO [17] analyses have shown that the lone pairs localized on the N atom of NCS<sup>-</sup> ligands in complex (1) donate the charge to nickel, and the stabilization energy is 127.95 kcal/mol, and 68.69, 151.87 and 72.18 kcal/mol in the complexes (2-4), respectively. The stabilization energies connected to interaction between N-heteroaromatic ligands and nickel central ion are 170.53, 65.11, 157.74 and 59.17 kcal/mol in compounds (1-4), respectively. The back donations from nickel to N-heteroaromatic ligands have values 31.17 kcal/mol to pyridine ligand, 62.59 kcal/mol to  $\gamma$ -picoline and 21.39, 25.42 kcal/mol to 2-(hydroxymethyl)pyridine and 2-(hydroxypropyl)pyridine ligands, respectively. The back donations

#### Table 4

Calculated UV–Vis transitions for the [Ni(SCN)<sub>2</sub>(py)<sub>4</sub>] (1) and [Ni(SCN)<sub>2</sub>(pyCH<sub>2</sub>OH)<sub>2</sub>] (3) complexes. The experimental values are given for comparison.

(	Wavelength [nm]	Contributions	Exp. (nm)
(	1)		
8	381.1	$H-8(\beta) \rightarrow LUMO(\beta)$ (97%)	953.1
5	795.8	$\text{H-12}(\beta) \rightarrow \text{L+2}(\beta) \text{ (55\%), } \text{H-1}(\beta) \rightarrow \text{LUMO}(\beta) \text{ (11\%)}$	
5	785.5	$\text{H-13}(\beta) \rightarrow \text{LUMO}(\beta) \text{ (12\%), H-13}(\beta) \rightarrow \text{L+2}(\beta) \text{ (30\%),}$	746.4
		$H-10(\beta) \rightarrow L+2(\beta)$ (20%)	
5	528.5	$HOMO(\beta) \rightarrow LUMO(\beta)$ (20%)	581.2
5	522.1	$\text{H-12}(\beta) \rightarrow \text{LUMO}(\beta) \text{ (35\%), H-12}(\beta) \rightarrow \text{L+2}(\beta) \text{ (25\%)}$	
4	490.5	H-17(β) → L+2(β) (15%), $H$ -8(β) → L+2(β) (77%)	
(	3)		
-	1052.4	$H-8(\beta) \rightarrow LUMO(\beta)$ (87%), $HOMO(\beta) \rightarrow LUMO(\beta)$	994.5
		(22%)	
8	354.8	$H-13(\beta) \rightarrow L+1(\beta) (11\%), H-7(\beta) \rightarrow LUMO(\beta) (21\%), H-$	750.4
		$6(\beta) \rightarrow L+1(\beta) (48\%)$	
8	329.9	$H-7(\beta) \rightarrow L+1(\beta)$ (27%), $H-6(\beta) \rightarrow LUMO(\beta)$ (39%)	
5	540.6	$\text{H-7}(\beta) \rightarrow \text{LUMO}(\beta) \ (25\%), \ \text{H-1}(\beta) \rightarrow \text{LUMO}(\beta) \ (11\%)$	599.2
5	518.4	H-8( $\beta$ ) $\rightarrow$ L+1( $\beta$ ) (49%), HOMO( $\beta$ ) $\rightarrow$ L+1( $\beta$ ) (24%)	
	795.8 785.5 528.5 522.1 490.5 <b>3</b> ) 1052.4 354.8 329.9 540.6 518.4	$\begin{split} &H{-}12(\beta) \to L{+}2(\beta)~(55\%),~H{-}1(\beta) \to LUMO(\beta)~(11\%) \\ &H{-}13(\beta) \to LUMO(\beta)~(12\%),~H{-}13(\beta) \to L{+}2(\beta)~(30\%), \\ &H{-}10(\beta) \to L{+}2(\beta)~(20\%) \\ &HOMO(\beta) \to LUMO(\beta)~(20\%) \\ &H{-}12(\beta) \to LUMO(\beta)~(35\%),~H{-}12(\beta) \to L{+}2(\beta)~(25\%) \\ &H{-}17(\beta) \to L{+}2(\beta)~(15\%),~H{-}8(\beta) \to L{+}2(\beta)~(77\%) \\ \\ &H{-}8(\beta) \to LUMO(\beta)~(87\%),~HOMO(\beta) \to LUMO(\beta) \\ &(22\%) \\ &H{-}13(\beta) \to L{+}1(\beta)~(11\%),~H{-}7(\beta) \to LUMO(\beta)~(21\%),~H{-}6(\beta) \to L{+}1(\beta)~(48\%) \\ \\ &H{-}7(\beta) \to L{+}1(\beta)~(25\%),~H{-}6(\beta) \to LUMO(\beta)~(39\%) \\ &H{-}7(\beta) \to L{+}1(\beta)~(25\%),~H{-}1(\beta) \to LUMO(\beta)~(11\%) \\ \\ &H{-}8(\beta) \to L{+}1(\beta)~(49\%),~HOMO(\beta) \to L{+}1(\beta)~(24\%) \\ \end{split}$	746. 581. 994. 750. 599.

to thiocyanate ligands are equal to 20.54, 31.16, 33.53 and 25.00 kcal/mol for (1-4), respectively. The atomic charge calculations may describe the relocation of electron density of the compounds. The plots of the electrostatic potentials for the studied compounds (1) and (4) are shown in Fig. 4. The isoelectronic contours are plotted at 0.005 a.u. (3.1 kcal/mol). The color code of these maps is in the range of 0.05 a.u. (deepest red) to -0.005 a.u. (deepest blue), where blue indicates the strongest attraction and red indicates the strongest repulsion. Regions of negative V(r) are usually associated with the lone pair of electronegative atoms. The negative potential in the studied compounds wrap thiocyanate ligands and oxygen atoms in the compounds with 2-(hydroxymethyl) or 2-(hydroxypropyl)pyridine ligands. As one can see in the Fig. 4, negative potentials on sulfur atoms in the studied compounds are smaller than the ones on nitrogen atoms (not to mention oxygen donor atoms). The natural charges obtained from NBO analysis are close to each other:  $N_{(NCS)}$  -0.8, N(py) = -0.6 and  $S_{(NCS)}$  about -0.2. That is why, and additionally because of steric hindrance exerted by pyridine rings in compounds (1) and (2), the studied complexes do not form polymeric systems with NCS<sup>-</sup> connector.

In the frontier region, neighboring orbitals may show quasidegeneracy of the energetic levels. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. For this reason, the overlap population density-of-states (OPDOS) in terms of Mulliken population analysis was calculated using the GaussSum program. The results provide a pictorial representation of MOs compositions and their contributions to chemical bonding. The OPDOS diagrams are shown in Fig. 5, and they may enable us to ascertain the bonding, non-bonding and antibonding characteristics with respect to the particular fragments. A positive value in OPDOS plots means a bonding interaction, while a negative value represents antibonding interaction,

Table 5

Magnetic parameters of the  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3) and  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) complexes.

Complex	M (g/mol)	C (emu K/mol)	$\theta_{CW}(K)$	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$	gσ	$g_{\chi}$
(1) [Ni(SCN) <sub>2</sub> (py) <sub>4</sub> ]	491.27	1.04	0.3	2.88	2	2.04
(3) [Ni(SCN) <sub>2</sub> (pyCH <sub>2</sub> OH) <sub>2</sub> ]	393.12	1.23	-0.4	3.14	2.07	2.22
(4) [Ni(SCN) <sub>2</sub> (py(CH <sub>2</sub> ) <sub>3</sub> OH) <sub>2</sub> ]	449.23	1.38	-1.6	3.32	2.03	2.30

*M* is the molar mass, *C* is the Curie constant,  $\theta_{CW}$  is the paramagnetic Curie–Weiss temperature,  $\mu_{eff}$  is the effective magnetic moment, and  $g_{\sigma}$  and  $g_{\chi}$  are the Landé factors estimated from the magnetization isotherm  $\sigma(H)$  at 4.6 K using the Brillouin fitting procedure and from the Curie constant *C* fitted from the temperature dependence of magnetic susceptibility  $\chi(T)$ , respectively.

and a near zero value indicates a non-bonding interaction. As one can see from the OPDOS plots, the interaction between thiocyanate ligands and nickel ion in the complex with pyridine ligand is very small in HOMO and LUMO molecular orbitals. Similar interactions in the complexes (2) and (4) have antibonding character and the one in complex (3) - non-bonding character. In the lower HOMO orbitals (H-1, H-2), the interactions of N-donor ligands with nickel d-orbitals have negative values likewise in lowest virtual molecular orbitals in complexes (1) and (2). In the case of complex (3), LUMO has non-bonding character of Ni-L interaction, and in complex (4) a significant bonding effect is observed which is connected with the oxygen donor atoms in 2-(hydroxymethyl) - and 2-(hydroxypropyl)pyridine ligands. In the frontier occupied and virtual molecular orbitals, values of the interaction between nickel ions and pyridine type ligands indicate the ligands as rather strong  $\pi$ -acceptors, and in the case of 2-(hydroxypropyl)pyridine ligand.  $\pi$ -donor properties are pointed out. This conclusion is confirmed additionally by stabilization energy mentioned earlier.

# 3.2. Electronic spectra

The lowest state of the nickel(II) ion is <sup>3</sup>F term, which splits into  ${}^{3}A_{2g}$ ,  ${}^{3}T_{2g}$  and  ${}^{3}T_{1g}$  terms in the field with  $O_h$  symmetry. The studied complexes have  $D_2/C_2$  ( $D_{2h}/C_{2h}$ ) point group symmetry, and in this symmetry  ${}^{3}T_2$  and  ${}^{3}T_1$  terms split into singlet  ${}^{3}A_2$  and  ${}^{3}B_2$  and doublet  ${}^{3}E$  levels each. As a consequence, the first and second spin-allowed transition bands observed on the UV–Vis spectra of the complexes are assigned to  ${}^{3}T_2({}^{3}F) \rightarrow {}^{3}A_2({}^{3}F)$  and  ${}^{3}T_1({}^{3}F) \rightarrow {}^{3}A_2({}^{3}F)$ , respectively. The third absorption band results from a spin-allowed transition  ${}^{3}T_1({}^{3}P) \rightarrow {}^{3}A_2({}^{3}F)$ . In Fig. 6, the absorption spectrum of complex (1) is presented with three spin-allowed crystal field bands and one spin-forbidden transition. The values of the ligand

field parameter 10Dq, calculated on the basis of electronic bands positions for the investigated complexes (given in experimental part), are equal to 10Dq = 10 492 (1), 9623 (2), 10 055 (3), 9372 (**4**), and 10 379 cm<sup>-1</sup> (**5**). Racah parameter *B* is equal to 896, 822, 891, 882 and 886  $\text{cm}^{-1}$  for complexes (1–5), respectively. The Racah parameter *B* for a metal ion varies as a function of the ligand bound to the ion. The value of this parameter will be always lower for the complexed ion than that for the free ion. The reduction of the value of *B* is related to the extent of metal-ligand bond covalency. The metal-ligand bond becomes partially covalent when the *d*-orbitals overlap with the ligand orbitals. As a result, the interelectronic repulsion within the d-orbitals decreases and Bvalue is lowered. The ratio  $B/B_0 = \beta$  gives a measure of covalency in the metal-ligand bond. The nepheloauxetic parameters calculated for the studied complexes are  $\beta = 0.86$  for complexes (1) and (3), 0.79 for compound (2) and 0.85 for (4) and (5). It is noteworthy that the 10Da value decreases in the sequence (1), (3) and (4) for that the point group symmetry lowers. The bands recorded in the electronic spectra of complexes (1-4) have small molar extinction coefficients, and maxima about 750 nm. They are ascribed to  ${}^{1}E_{g}({}^{1}D)$  term in  $O_{h}$  symmetry, which separates in the  $D_{2}$ symmetry into  ${}^{1}A_{1}$  and  ${}^{1}B_{1}$  levels. This indicates that these bands correspond to spin-forbidden  ${}^{1}A_{1}/{}^{1}B_{1}({}^{1}D) \rightarrow {}^{3}A_{2}({}^{3}F)$  transitions. In Fig. 7, the Tanabe–Sugano diagram for d<sup>8</sup> ions in octahedral coordination is shown with the crystal field strength of the Ni<sup>2+</sup> ions in complexes (1) and (4) indicated by vertical lines. For the calculated Dq/B ratios (1.06–1.17) in the Tanabe–Sugano diagram for d<sup>8</sup> ions in octahedral coordination one can see that the  ${}^{1}E_{g}({}^{1}D)$  singlet state is lower than the  ${}^{3}T_{1g}({}^{3}F)$  term which confirms the bands positions in the spectra.

Additionally the electronic spectra of these complexes were calculated in the GAUSSIAN program with PCM model (Table 4). Because



**Fig. 8.** Magnetic susceptibility  $\chi_{dc}$  vs. temperature *T* recorded at *H* = 1 kOe. Inset: magnetization  $\sigma$  vs. *H*/*T* at 4.6 K. The solid (red) line is for an estimation of the Landé factor. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the  $d \rightarrow d$  transitions are forbidden their oscillator strange are very small (close to 0.0) and the experimental spectra in the energy region of 1100–700 nm are widening that the calculated transitions are adequate to theses ones. The calculated UV–Vis spectra of these complexes (1) and (3) are collected in the Table 5. On the other hand these complexes are Werner-type except the complex (3) in which the donor properties of 2-(hydroxmethyl)pyridine pyridine ligand play role (on the UV–Vis spectrum the calculated  $d \rightarrow d$  transitions have values below 0.0009).

# 3.3. Magnetic properties

The magnetic properties for blue crystals of  $[Ni(SCN)_2(py)_4]$  (1),  $[Ni(SCN)_2(pyCH_2OH)_2]$  (3),  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$  (4) were studied. The  $\chi_{dc}(T)$  curves in Fig. 8a–c show paramagnetic behavior. The insets of Fig. 8a–c reveal a lack of saturation of magnetization up to 60 kOe. For the Ni<sup>2+</sup> ion (S = 1) with 3d<sup>8</sup> electronic configuration, the Landé factor g = 2, theoretical Curie constant C = 1 emu K/mol and the effective magneton spin-only value of  $p_{eff} =$  $2\sqrt{S(S+1)}$  = 2.83. The effective magnetic moment  $\mu_{\text{eff}}$  = 2.88  $\mu_{\text{B}}$ for complex (1) is close to  $p_{\text{eff}}$  indicating the spin-only contribution to the total magnetic moment. When the aliphatic chain  $(CH_2)$ elongates in the sequence: (1), (3) and (4), the Curie constant, effective magnetic moment and Landé factor increase while the paramagnetic Curie-Weiss temperature decreases (Table 5), suggesting an increase of the orbital contribution to the magnetic moment. The small values of the paramagnetic Curie-Weiss temperature,  $\theta_{CW}$ , also confirm the paramagnetic behavior for the (1), (3) and (4) complexes. A slight decrease of  $\theta_{CW}$  from 0.3 K for (1) via -0.4 for (2) to -1.6 K for (3) and a change of its sign with elongating of the aliphatic chain show that the orbital contribution favors a weak antiferromagnetic superexchange interaction. The  $\chi_{dc}(T)$  dependences for the (**2**) and (**5**) complexes are similar and show typical paramagnetic behavior.

# 4. Conclusions

In the simple one-pot syntheses isothiocyanate complexes of nickel(II) with pyridine,  $\gamma$ -picoline, 2-(hydroxymethyl)pyridine and 2-(hydroxypropyl)pyridine ligands were obtained. Additionally, an attempt to synthesize nickel(II) thiocyanate complex with pyridine and triphenylphosphine in coordination sphere was undertaken and square planar [Ni(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] complex was obtained. The studied complexes were characterized by IR, NMR (complex 5) spectroscopy, and their crystal structures were determined by X-ray diffraction. Electronic structures of the studied complexes were calculated using DFT method, and apart from the descriptions of frontier molecular orbitals and the relocation of the electron density of the compounds, the bonding properties in the complexes were determined. Based on calculated stabilizations energies, the values of the interaction between nickel ions and pyridine type ligands and the energy decomposition analysis indicated the ligands were rather strong  $\pi$ -acceptors. In the case of 2-(hydroxypropyl)pyridine ligand,  $\pi$ -donor properties were pointed out. The differences in acceptor properties of the ligands were shown in the values of ligand field parameters determined from electronic spectra of the complexes. Additionally, in the series of complexes (1), (3), and (4) in which the N-donor ligands differ from each other by  $CH_2$  group, point group symmetry lowering  $(D_{2h} \rightarrow D_{2v} \rightarrow C_{2h})$  had an impact on the 10Dq value. Similar behavior from the Landé factor calculations was also observed. It means that the increase of the orbital contribution to the total magnetic moment strongly influences the electronic structure and the chemical bonds.

# 5. Supplementary data

CCDC 763538, 767567, 763407, 765806, and 763986 contains the supplementary crystallographic data for  $[Ni(SCN)_2(py)_4]$ ,  $[Ni(SCN)_2(-pic)_4]$ ,  $[Ni(SCN)_2(pyCH2OH)_2]$ ,  $[Ni(SCN)_2(py(CH_2)_3OH)_2]$ and  $[Ni(SCN)_2(PPh_3)_2]$ . These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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