First examples of co(ii), ni(ii) and cu(ii) coordination compounds with 1-(pyr-id-2-yl)-1*h*-tetrazole: synthesis, structure and properties

Alina D. Ivanova, Yury V. Grigoriev, Vladislav Yu. Komarov, Taisiya S. Sukhikh, Artem S. Bogomyakov, Liliya A. Sheludyakova, Ludmila G. Lavrenova

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FIRST EXAMPLES OF Co(II), Ni(II) AND Cu(II) COORDINATION COMPOUNDS

WITH 1-(PYRID-2-YL)-1H-TETRAZOLE: SYNTHESIS, STRUCTURE AND PROPERTIES

Alina D. Ivanova^{a,*}, Yury V. Grigoriev^b, Vladislav Yu. Komarov^{a,c}, Taisiya S. Sukhikh^a,

Artem S. Bogomyakov^{c,d}, Liliya A. Sheludyakova^a, Ludmila G. Lavrenova^{a,c}

^aNikolaev Institute of Inorganic Chemistry SB RAS, Russia, 630090 Novosibirsk, Akademika Lavrentieva ave., 3 ^bResearch Institute for Physical Chemical Problems of Belarusian State University, Belarus, 220006 Minsk, Leningradskaya str., 14 ^cNovosibirsk State University, Russia, 630090 Novosibirsk, Pirogova str., 2 ^dInternational Tomography Center SB RAS, Novosibirsk, Russia, Institutskaya str., 3a *e-mail: ivanova@niic.nsc.ru*

ABSTRACT

Coordination compounds of cobalt(II), nickel(II), and copper(II) with a poly nitrogen-containing heterocyclic ligand 1-(pyrid-2-yl)-1*H*-tetrazole (1-Pytz) such as $[Cu(1-Pytz)_2Cl_2]_n$, $[M(1-Pytz)_2(H_2O)Cl_2]$ (M = Co, Ni), $[M(1-Pytz)_2(C_2N_3)_2]_n$ (M = Co, Ni) have been synthesized. The compounds have been studied by means of infrared diffuse reflectance spectroscopy, single-crystal and powder X-ray diffraction, and static magnetic susceptibility. The studies on the $\mu_{eff}(T)$ for the $[Cu(1-Pytz)_2Cl_2]_n$, $[Co(1-Pytz)_2(C_2N_3)_2]_n$ and $[Ni(1-Pytz)_2(C_2N_3)_2]_n$ polynuclear complexes in the temperature range of 2-300 K have shown that exchange interactions between spins of metal ions are weak.

Keywords: 3d metals 1-(pyrid-2-yl)-1*H*-tetrazole Complex X-ray structure Magnetic properties

1. Introduction

Tetrazole derivatives are promising objects for studying in the field of coordination chemistry. Owing to the presence of four nitrogen atoms in the tetrazole ring capable of forming coordination bonds, the use of tetrazoles as ligands allows one to obtain a wide range of metal complexes with specific properties [1–4]. Among tetrazole-containing mononuclear metal complexes, compounds have been found that exhibit low temperature spin crossover (SCO), including photoinduced SCO, as well as luminescent properties [5–8]. A number of complexes of the Co(II), Ni(II), Cu(II) halides with 1-alkyltetrazoles having a layered structure exhibit exchange interactions of ferromagnetic nature [9–11].

Coordination polymers and organometallic backbones that form multinuclear metal complexes with tetrazole derivatives are characterized by high heat resistance, high porosity, the

Journal Pre-proofs ability of a selective sorbtion of gases, etc. [12–18]. At that, the manifold structural features and properties of the obtained complexes is connected not only with the presence of a tetrazole fragment in the ligand molecule, but also, to a considerable extent, with the structure of the substituent in the tetrazole ring and the nature of the metal used as a complexing agent [1].

In this connection, pyridyltetrazoles, whose coordination to the metal can be effected by nitrogen atoms belonging both to the tetrazole ring, and to the pyridine one, are of interest as potential ligands. In contrast to 5-pyridyltetrazoles, whose coordination chemistry has been thouroughly studied [19–29], the complex compounds of 1-(pyrid-2-yl)-1*H*-tetrazole (1-Pytz), first synthesized more than 20 years ago [30], have not been obtained up till now. The only theoretical investigation of Ir(III) complex with 1-Pytz has been reported [31]. Moreover, synthesized metal complexes of 1-(pyrid-2-yl)-1*H*-tetrazole with any substituents are limited to one example, viz. Be compound with a hydroxy-pyridyl derivative, whose crystal structure was not determined [32]. The compounds described in this paper represent the examples of first synthesized complexes with the 1-Pytz ligand.

This work is a continuation of our studies concerning the coordination chemistry of tetrazole derivatives and is devoted to the synthesis and studies of the structure and properties of Cu (II), Co (II), Ni (II) complexes with 1-(pyrid-2-yl)-1H-tetrazole.

2. Experimental

2.1. Materials and instrumentation9

All the reagents were obtained from Sigma Aldrich and used without purification. The elemental analysis (C, H, N) was performed at the Analytical laboratory of Nikolaev Institute of Inorganic Chemistry, SB RAS using a EuroVector EURO EA 3000 (Italy) analyzer. The ¹H and ¹³C NMR spectra were registered using a Bruker Avance 500 NMR spectrometer. The observed chemical shifts were referenced to solvent signals ($\delta_{\rm H}$ 2.50, $\delta_{\rm C}$ 39,43 ppm). The IR absorption spectra were registered using a Scimitar FTS 2000 spectrometer in the range from 400 to 4000 cm⁻¹. The samples under investigation were prepared in the form of suspensions in Nujol and in fluorinated oils. Diffuse reflectance spectra were registered using a Shimadzu UV-3101 PC scanning spectrophotometer at a room temperature. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves have been obtained using a NETZSCH STA429 thermoanalyzer in a dynamic nitrogen atmosphere in the temperature range from a room temperature up to 500 °C (aluminum oxide at a heating rate amounting to 10 °C/min, and a weighed sample portion ranging from 1 to 3 mg). Temperature-dependent magnetic susceptibility measurements were carried out using a MPMSXL Quantum Design SQUID

Journal Pre-proofs magnetometer within the temperature range from 2 to 330 K with magnetic field of up to 5 kOe. The observed susceptibility data were corrected for the sample holder and underlying diamagnetism by using Pascal's constants. The values of the effective magnetic moment were calculated according to formula $\mu_{eff} = \left(\frac{3k}{N_A \mu_B^2} \cdot \chi T\right)^{\frac{1}{2}} \approx (8\chi T)^{\frac{1}{2}}$, where χ is the molar magnetic susceptibility corrected for diamagnetism, k is the Boltzmann constant, N_A is the Avogadro's number, μ_B is the Bohr magneton.

2.2. Synthesis

2.2.1. Synthesis of 1-(pyrid-2-yl)-1H-tetrazole (1-Pvtz).

A glacial acetic acid (48 g, 0.8 mol) was added under stirring to a suspension of 2aminopyridine (9.4 g, 0.1 mol) and sodium azide (7.8 g, 0.12 mol) in triethylorthoformate (43.8 g, 0.3 mol). The mixture was heated under stirring at 100 °C for 3 h. The reaction mixture was cooled to a room temperature, and then a concentrated hydrochloric acid (12 mL) was added. The reaction mixture was filtered, and filtrate was concentrated under reduced pressure. A crude residue was washed with water (~100 mL) and dried at a room temperature under vacuum to obtain the pure target compound in form of a colorless powder (13.4 g, 0.091 mol, 91%). Mp: 129-130 °C (Lit. 125-126,5 °C [33]). C₆H₅N₅ (147.14): C 49.05 (calc. 48.98); H 3.61 (calc. 3.43); N 47.37 (calc. 47.60)%. ¹HNMR (500 MHz, (CD₃)₂SO, δ: 7.64-8.66 (m, 4H, CH_{pyridine}), 10.19 (s, 1H, CH_{tetrazole}) ppm.¹³C NMR (125 MHz, (CD₃)₂SO, δ:114.9, 125.3, 140.5, 141.5, 146.4, 149.2 ppm.

2.2.2 Synthesis of $[Cu(1-Pytz)_2Cl_2]_n(1)$

A solution of 1-Pytz (0.15 g, 0.001 mol) in acetone (10 mL) was added to a solution of CuCl₂·2H₂O (0.09 g, 0.0005 mol) in ethanol (10 mL) heated to 60 °C. The reaction mixture was stirred at 60 °C and, after evaporation to $\frac{1}{2}$ of the initial volume, cooled to 0–5 °C. The resulting blue-green precipitate [Cu(1-Pytz)₂Cl₂]_n (0.15 g, 71.0%) was filtered off, washed with a small amount of chilled ethanol and dried in air at a room temperature. Anal. Calc. for CuC₁₂H₁₀N₁₀Cl₂(428.73): C, 33.6; H, 2.4; N, 32.7. Found: C, 33.7; H, 2.3; N, 32.3%.

2.2.3. Synthesis of $[Co(1-Pytz)_2(H_2O)Cl_2]$ (2)

A solution of 1-Pytz (0.37 g, 0.0025 mol) in 10 ml of acetone was added under stirring to a solution of CoCl₂·6H₂O (0.31 g, 0.0013 mol) in 7 ml of ethanol. The reaction mixture was stirred at 60°C and evaporated to ¼ of the initial volume. The solution with no precipitate was held at a room temperature. The crystals of [Co(1-Pytz)₂Cl₂(H₂O)] with admixture of [Co(H₂O)₂Cl₂] (revealed via XRPD, vide infra) formed after 24 hours were filtered off and dried



at room temperature in air. For elemental analysis, the crystals were ground to nomogeneous state. Anal. Calc. for CoC₁₂H₁₂N₁₀Cl₂O (442.13): C, 32.6; H, 2.7; N, 31.7. The best phase mixture fit is 90.0 mol.% $[Co(1-Pytz)_2(H_2O)Cl_2]$ and 10.0 mol.% $[Co(H_2O)_2Cl_2]$, CoC_{10.8}H_{11.2}N_{9.0}O_{1.1}Cl₂ (414.51): C, 31.3; H, 2.7; N, 31.4, Found: C, 31.7; H, 3.1; N, 30.0%.

2.2.3. Synthesis of $[Ni(1-Pytz)_2(H_2O)Cl_2]$ (3)

A solution of 1-Pytz (0.15 g, 0.001 mol) in acetone (10 mL) was added to a solution of NiCl₂·6H₂O (0.12 g, 0.0005 mol) in ethanol (10 mL) heated to 60 °C. The reaction mixture was stirred at 60 °C and, after evaporation to 1/2 of the initial volume, cooled to 0-5 °C. The resulting precipitate of [Ni(1-Pytz)₂Cl₂(H₂O)] (0.14 g, 63.0%) was filtered off, washed with a small amount of chilled ethanol and dried in air at a room temperature. Anal. Calc. for NiC₁₂H₁₂N₁₀Cl₂O (441.89): C, 32.6; H, 2.7; N, 31.7. Found: C, 32.3; H, 2.8; N, 31.5%.

2.2.4.Synthesis of $[Co(1-Pytz)_2(C_2N_3)_2]_n$ (4)

A solution of 1-Pytz (0.29 g, 0.002 mol) in acetone (10 mL) was added to a solution of Co(NO₃)₂·6H₂O (0.12 g, 0.0005 mol) and NaN(CN)₂ (0.27 g, 0.003 mol) in a mixture of ethanol (15 mL) – water (5 mL). The reaction mixture was stirred at 60 °C and after evaporation to $\frac{1}{2}$ of the initial volume was held in a refrigerator. The crystals of $[Co(1-Pytz)_2(C_2N_3)_2]_n$ (0.2 g, 82.0%) formed after 24 hours were filtered off and dried at a room temperature in air. Anal. Calc. for CoC₁₆H₁₀N₁₆ (485.29): C, 39.6; H, 2.1; N, 46.2. Found: C, 39.6; H, 2.1; N, 45.7%.

2.2.5.Synthesis of $[Ni(1-Pytz)_2(C_2N_3)_2]_n$ (5)

A solution of 1-Pytz (0.29 g, 0.002 mol) in acetone (10 mL) was added to a solution of Ni(NO₃)₂·6H₂O (0.12 g, 0.0005 mol) and NaN(CN)₂ (0.27 g, 0.003 mol) in a mixture of ethanol (15 mL) – water (5 mL). The reaction mixture was stirred at 60 °C, and after the evaporation to ¹/₂ of the initial volume, the formed precipitate of $[Ni(1-Pytz)_2(C_2N_3)_2]_n$ (0.16 g, 66.0%) was filtered off and dried at a room temperature in air. Anal. Calc. for NiC₁₆H₁₀N₁₆ (485.05): C, 39.6; H, 2.1; N, 46.2. Found: C, 39.7; H, 2.1; N, 46.5%.

2.3. X-ray structure determination

Crystals of 1 and 3 suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation of the mother liquor from the corresponding syntheses; crystals of 2 and 4 were harvested directly from the solid product. Single-crystal XRD data for compounds 1, 2, 3, 4 were registered using a Bruker Apex DUO diffractometer equipped with a 4K CCD area detector employing graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) (Table S1). The φ -and ω -

scan techniques were used to measure intensities. Data reduction and absorption correction were performed using APEX2 suite [34]. The crystal structure were solved using a SHELXT [35] and refined using a SHELXL [36] programs with OLEX2 GUI [37]. Atomic displacement parameters for nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions, and refined with the use of a riding model. In structures of 2 and 3, H atoms of coordinated water were located from Fourier difference map and were refined with restraints on O-H bonds (DFIX 0.86 0.01) and fixed Uiso at 1.5 times of the corresponding O atoms. The H–O–H angles of 106(2) and 103(2)° for 2 and 3 respectively were reasonable, while the O–H bonds were directed to hydrogen bond acceptors N and Cl.

Powder XRD was carried out using a Shimadzu XRD-7000 diffractometer (CuKa radiation, Ni filter, 20 angle range from 5° to 60°) using point NaI scintillation detector SC-1003 (for 1, 3, 5; 20 scan step 0.030°) or linear Dectris MYTHEN2 R 1K (for 2, 4; 20 reduction step 0.014°) detector at ambient conditions. Polycrystalline samples of 1-5 were slightly ground up with heptane in an agate mortar, the resulting suspensions were deposited on the polished side of a glass holder, and a smooth $\sim 100 \ \mu m$ layers formed after drying. X-ray powder diffraction patterns of the complexes are given in ESI (Fig. S1 - S5) Simulated X-ray powder diffraction patterns of compounds 1, 3-5 are in good agreement with the experimental X-ray powder diffraction patterns. Diffraction patterns (measured for 4 independent samples) of 2 revealed that along with the $[Co(1-Pytz)_2(H_2O)Cl_2]$ phase (the crystal structure determined in the present work) it contains an impurity phase, which was recognized as $[Co(H_2O)_2Cl_2]$ [38] (CHN-based admixture phase content is ~10 mol.%, ~4 wt.%). Similarity of the diffraction patterns of 4 and 5 indicates their isostructurality.

3. Results and discussion

3.1. Synthesis and characterization

It is well-known that a heterocyclization of primary amines with sodium azide and triethyl orthoformate is a convenient method for obtaining a wide range of 1-substituted tetrazoles [39]. We have used this method to obtain 1-(pyrid-2-yl)-1H-tetrazole (1-Pytz). The reaction proceeds smoothly in glacial acetic acid under heating and at a ratio of 2-aminopyridine : triethylorthoformate : sodium azide : acetic acid amounting to 1 : 3 : 1.2 : 8, which results in obtaining the target 1-Pytz with a 91% yield (Scheme 1). According to the thermogravimetry (TG) and scanning differential calorimetry (DSC) data, the 1-Pytz melts at a temperature of about 129 ° C. Upon further heating of the sample, both thermal decomposition and partial evaporation thereof is observed (Fig. S6). The total mass loss upon heating to 500°C amounted to about 82%.



Scheme 1. Synthesis of 1-(pyrid-2-yl)-1*H*-tetrazole.

The synthesis of 1-Pytz complexes has been performed using different solvents at different M : 1-Pytz ratios, depending on the nature of the complexing metal. According to XRD data, all the compounds obtained are crystalline ones; they are stable in air for a long time. The presence of water molecules in the complexes has been determined using elemental analysis, XRD, and IR spectroscopy.





3.2. Crystal structures

According to single crystal X-Ray analysis, compound 1 exhibits a square planar (shape similarity factor [40, 41] S(D4h) = 0.46) coordination environment of Cu (CuCl₂N₂) by two 1-Pytz ligands and two chloride ions (Fig. 1). The coordination sphere is complemented to an octahedral one ($S(O_h) = 3.13$) by shortened Cu···Cl contacts (3.02 Å) between the neighboring molecules.

Compounds 2 and 3 are isostructural to each other. They contain two 1-Pytz ligands, two chloride ions, and one aqua ligand (Fig. 2) which form the coordination sphere of the metal (MCl₂N₃O) with $S(O_h) = 1.04$ and 0.91 for 2 and 3 respectively. Compound 4 has a polymeric

Structure owing to ortaging $N(UN)_2$ ligands (Fig. 3). The coordination environment of Co (CoN₆) represented by four N(CN)₂ and two 1-Pytz ligands is close to a regular octahedron ($S(O_h)$ = 0.02). Compound 5 was not characterized by single crystal XRD analysis; powder XRD analysis revealed that compound 5 is isostructural with compound 4.



Fig. 1. The structure of 1. Atomic displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are shown as spheres.



Fig. 2. The structure of 2 and 3 by the example of the latter. Atomic displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are shown as spheres.



Fig. 3. The structure of **4**. Atomic displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are shown as spheres.

The 1-Pytz ligand in complexes 1-4 tends to act as a monodentate and bidentate ligand that coordinates via N⁴ atom (IUPAC atom numbering) of the tetrazole moiety or both N⁴ and N of the pyridine moiety (for atom numbering, see Fig. S7). The monodentate ligand exhibits a conformation with a torsion angle N–N–C–N between the tetrazole and pyridine moieties close to 180° (Table 1). A close analogue of 1-Pytz, viz. 2-(1H-1,2,4-triazol-1-yl)pyridine (1-Pytrz) and its derivatives, exhibit a similar coordination mode and a similar conformation in most structurally characterized complexes (see, for example, [42-44]). In complexes 2 and 3, one of 1-Pytz ligands has such a conformation that differs from the others in the rotation of the pyridine moiety along C–N¹ bond so that the torsion N–N–C–N angle is close to zero. This conformation promotes a chelate coordination mode of the ligand. A few complexes with 1-Pytrz, e.g. [Re(1-Pytrz)(CO)₃Br] [45] exhibit a similar chelate coordination mode of the ligand. This mode is likely destabilized by intramolecular steric repulsion interactions between H atoms of C-H groups (Fig. S7). Two intramolecular C–H···N contacts contribute little to the thermodynamic stability of the monodentate conformation. Thus, there is competition between the two different conformations of 1-Pytz and its analogues: the monodentate one and the chelate one. The tendency to the chelate conformation of 1-Pytrz is facilitated by the presence of auxiliary donor groups forming a five-membered metallocycle with the N atom inherent in the tetrazole or pyridine ring, *e.g.* the carboxylate group [46]. In addition to the reduced steric repulsion between

H atoms, the monodentate coordination mode should be preferable owing to a more negative charge at the N^4 atom of the tetrazole comparing to the N^2 one [47, 48].

Compounds 2 and 3 exhibit intermolecular hydrogen bonds such as O–H…N (2.78 Å) with the pyridine nitrogen, and O–H…Cl (3.05 Å) (Fig. 4). The former bind the molecules into pairs, whereas the latter bind them into a layer. The layers are linked to give a 3D structure *via* π - π head-to-tail interactions between the tetrazole and pyridine moieties (Fig. S9) with an intercentroid distance of 3.82 Å.



Fig. 4. The structure of a layer consisting of hydrogen bonded molecules of 2 and 3 by the example of the latter that exhibits intermolecular hydrogen bonds shown in dashed green (O–H···Cl) and blue (O–H···N) lines. Hydrogen atoms not participating in the hydrogen bonds are omitted.

Structures 1 and 4 exhibit π - π stacking interactions between the tetrazole and pyridine moieties (Fig. S9) in a head-to-head manner (the intercentroid distance amounting to 3.88 Å) for 1, and in a head-to-tail manner (the intercentroid distances amounting to 3.62 and 4.56 Å) for 4.

Table 1. Selected bond distances (Å), torsion angles (degrees) and the shortest distances N	1M
(Å) in the structures 1, 2, 3, 4. For the distances, the standard uncertainty is less than $2 \cdot 10^{-3}$	<mark>Å.</mark>

	M-N(1-Pytz)	$M-A$ (Cl, $N(CN)_2$)	M–O (H ₂ O)	N–N–C–N (<i>1-Pytz</i>)	MM
1	2.00	2.29, 3.02	_	177.5(2)	3.88
2	2.11, 2.17, 2.19	2.36, 2.40	2.11	169.1 <mark>(1)</mark> , 7.8 <mark>(2)</mark>	6.40
3	2.06, 2.11, 2.12	2.35, 2.39	2.07	169.0 <mark>(2)</mark> , <mark>7.0(2)</mark>	6.34
4	2.16	2.11, 2.11	_	176.7 <mark>(1)</mark>	7.26

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The main vibrational frequencies in the IK spectra of 1-Pytz and complexes 1-5are presented in Table 2. The spectra of 1-Pytz and the complexes within a highfrequency spectral range from 3120 to 3039 cm⁻¹ exhibit stretching vibration bands inherent in CH groups. Spectra of 2 and 3 in the range of 3494–3211 cm⁻¹ show the bands of stretching vibrations v (O-H) inherent in intrasphere water molecules. Changes in the positions of the bands are observed in the spectra of complexes 1-5 in the range of stretching and bending vibrations of the ring (1600–1470 cm⁻¹), which indicates the fact that the 1-Pytz ligand coordinates to the metal through nitrogen atoms, which is in a good agreement with the obtained X-ray diffraction data. The bands in the spectrum of NaN(CN)₂, in the range of 2100–2300 cm⁻¹, are shifted during complexation mainly to the high-frequency region. This suggests bidentate-bridged coordination of cyanamide ions [49, 50], which is confirmed by X-ray diffraction data. In the low-frequency spectral range, in the case of the synthesized complexes there are bands that are not observed in the free ligand spectrum. The bands in the range of 270-230 cm⁻¹ exhibited in the spectra of all the complexes can be attributed to M-N stretching vibrations, whereas the bands observed in the range of 310-280 cm⁻¹ in the spectra of 1-3 can be attributed to stretching vibrations v(M–Cl). Data analysis table 2 shows that the IR spectra of complexes 4 and 5 are very close in all spectral regions.

Compound					Attribution		
1-Pytz	1	2	3	4	5	NaN(CN) ₂	
2		3305	3494				$\nu(H_2O)$
		3211	3387				
			3279				
3120	3154	3145	3146	3130	3126		v(CH)
3100	3095	3078	3108	3111	3107		
3069	3086	3053	3076		3079 sh		
3039	3062		3049				
		1631	1626				$\delta(H_2O)$
1598	1597	1604	1607	1596	1597		R _{ring}
1575	1570	1573	1572	1577	1575		6
1527	1489	1532	1529	1482	1484		
1468		1485	1487				
				2301	2298	2287	$v_s + v_{as}(C - N)$
				2249	2253	2233	v _{as} (C≡N)
				2177	2183	2182	ν _s (C≡N)
		479	483				v(M–O)
	248	254	271	269	287		v(M–N)
	236	232	247	250	266		
	301	338	352				v(M–Cl)
	295пл						

Table 2. Main vibrationa	l frequencies in	the IR spectra of	f 1-Pytz and	complexes 1-5
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Journal Pre-proofs I ne number and the position of the bands in diffuse reflectance spectra 1-5 correspond to the literature data [51] and indicate that all the complexes have an octahedral structure of the coordination polyhedron. The splitting parameters Δ have been estimated. The position of the bands in the spectra, the attribution thereof, as well as the obtained Δ values are presented in Table 3.

N⁰	Compound	λ_{max} , nm	Attribution	Δ ·10 ⁻³ , cm ⁻¹
1	$[Cu(1-Pytz)_2Cl_2]_n$	695	$^{2}E\rightarrow^{2}T_{2}$	14,4
2	$[Co(1-Pytz)_2(H_2O)Cl_2]$	530	${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}(P)$	8,7
		1313	${}^{4}T_{1} \rightarrow {}^{4}T_{2}$	
3	[Ni(1-Pytz) ₂ (H ₂ O)Cl ₂]	400	$^{3}A_{2}\rightarrow ^{3}T_{1}(P)$	8,5
		650	$^{3}A_{2} \rightarrow ^{3}T_{1}(F)$	
		1173	$^{3}A_{2}\rightarrow ^{3}T_{2}$	
4	$[Co(1-Pytz)_2(C_2N_3)_2]_n$	485	${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}(P)$	10,4
		1095	${}^{4}T_{1} \rightarrow {}^{4}T_{2}$	
5	$[Ni(1-Pytz)_2(C_2N_3)_2]_n$	367	$^{3}A_{2}\rightarrow ^{3}T_{1}(P)$	10,4
		590	$^{3}A_{2} \rightarrow ^{3}T_{1}(F)$	
		958	$^{3}A_{2} \rightarrow ^{3}T_{2}$	

Table 3. Characteristics of diffuse reflection spectra for complexes 1–5.

The $\mu_{eff}(T)$ dependence for complex 1 is shown in Fig. 5. The μ_{eff} value at 300 K is 1.78 $\mu_{\rm B}$ and is in good agreement with the theoretical spin only one of 1.73 $\mu_{\rm B}$ for one paramagnetic center with spin S = 1/2 with a g factor of 2. The μ_{eff} almost does not change with lowering temperature downto 70 K, and below 70 K decreases to to 1.29 μ_B at 5 K. The $1/\chi(T)$ dependence obeys the Curie-Weiss law with the best fit values of C and θ of 0.413 K·cm³/mol and -2.9 K. The decreasing of μ_{eff} below 70 K and negative value of the Weiss constant indicate domination of antiferromagnetic exchange interactions between spins of Cu(II) ions. Analysis of the $\mu_{eff}(T)$ dependence with an uniform chain model (spin-Hamiltonian H = $-2J \cdot \sum S_i S_{i+1}$) [52] gives the best fit values of g-factor and exchange coupling parameter J of 2.11±0.01 and - 1.96 ± 0.01 cm⁻¹ respectively.



Fig. 5. The $\mu_{eff}(T)$ and $1/\chi(T)$ dependences for complex $[Cu(1-Pytz)_2Cl_2]_n(1)$.

The $\mu_{eff}(T)$ and $1/\chi(T)$ dependencies for complexes 4 and 5 are shown in Fig. 6. The μ_{eff} values are 5.09 and 3.23 μ_B at 300 K and are in good agreement with typical values for one Co(II) and Ni(II) ions for complexes 4 and 5, respectively. The $1/\chi(T)$ dependencies are linear and obey the Curie-Weiss law with the best fit parameters *C* and θ of 3.55 K·cm³/mol and -27.6 K for complex 4 and 1.17 K·cm³/mol and -0.52 K for complex 5. Small Weiss constant value and constancy of the μ_{eff} value in the wide temperature range indicate absence of significant exchange interactions between spins of Ni(II) ions in the complex 5. The large negative Weiss constant and a decreasing of the μ_{eff} below 150 K are caused by spin-orbit coupling, that typical for Co(II) ions in the octahedral environment. The μ_{eff} value at low temperatures is in good agreement with a theoretical one of 3.87 μ_B for one paramagnetic center with spin S = 3/2.



Fig. 6. The $\mu_{eff}(T)$ and $1/\chi(T)$ dependencies for complexes $[Co(1-Pytz)_2(C_2N_3)_2]_n$ (4) (• and \circ) and $[Ni(1-Pytz)_2(C_2N_3)_2]_n$ (5) (• and \Box).

4. Conclusions

By using interaction between 1-(pyrid-2-yl)-1*H*-tetrazole and Co(II), Ni(II) and Cu(II) salts, novel coordination compounds with this ligand have been synthesized. The obtained complexes have been studied by means of infrared diffuse reflectance spectroscopy, single-crystal and powder X-ray diffraction, and static magnetic susceptibility. Depending on the nature of the metal ion, on the anion, and on the synthesis conditions, the ligand can be coordinated both monodentally to the N(4) atom of the tetrazole ring and in a bidentate-cyclic way with the formation of the five-membered metal-containing cycle MCN₃ with the participation of the N(2) nitrogen atom belonging to the tetrazole ring, and the N atom belonging to the pyridine ring, which results in the formation of mononuclear or polynuclear structures. The conclusions about the structure of complex **5** were made based on a comparison of powder X-ray diffraction. It has been shown that, antiferromagnetic exchange interactions occur between spins of copper(II) ions in the [Cu(1-Pytz)₂Cl₂]_n complex at a low temperature and exchange interactions between spins of paramagnetic metal ions in the complexes **4** and **5** are weak.

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Appendix A. Supplementary data

CCDC 2010561-2010564 contain the supplementary crystallographic data. 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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Alina D. Ivanova: Investigation; Yury V. Grigoriev: Investigation; Vladislav Yu. Komarov: Investigation; Taisiya S. Sukhikh: Investigation; Artem S. Bogomyakov: Investigation; Liliya A. Sheludyakova: Investigation; Ludmila G. Lavrenova: Conceptualization, Methodology, Writing -Original Draft.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Novel coordination compounds of cobalt(II), nickel(II), and copper(II) with 1-(pyrid-2-yl)-1*H*-tetrazole have been synthesized. The ligand can be coordinated both monodentally and in a bidentate-cyclic way. The studies on the $\mu_{eff}(T)$ for the polynuclear copper(II) have shown antiferromagnetic exchange interactions between copper(II) ions to occur at a low temperature.

Novel complexes of 3d-metals with 1-(pyrid-2-yl)-1*H*-tetrazole have been synthesized Ligand can be coordinated both monodentally and in a bidentate-cyclic way Polynuclear Cu(II) have shown exchange interactions between Cu(II) ions to occur