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Cobalt(II) scorpionate-like complexes obtained from *in situ* synthesized ligand created in [Co(0)–1-hydroxymethyl-3,5-dimethylpyrazole–$VOSO_4$–NH_4SCN] system

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Novel cationic–anionic $\{[Co^{II}(NCS)L^S]^{n+}[X]^{n-}\}$ $X = [V_6O_{11}(CH_3O)_8]^{2-}$, $[Co^{II}(NCS)_4]^{2-}$ (**1** and **2**) and neutral $[Co^{II}(NCS)_2L^S]$ (**3**) complexes have been isolated in one pot synthesis from [Co^0–L–$VOSO_4$–NH_4SCN] (L = 1-hydroxymethyl-3,5-dimethylpyrazole) system. The anion $[V^{IV}{}_2V^{V}{}_4O_{11}(CH_3O)_8]^{2-}$ was found to be a new mixed valence Lindqvist type cluster. The redox reactions resulted in atypical compositions and structures of the products as well as in an *in situ* formation of tris(3,5-dimethylpyrazolylmethyl)amine (L^S), which is a scorpionate-type ligand. The coordination numbers of cobalt(II) in the species were found to be five (**1**), five and four (**2**) and six (**3**). The compounds were characterized by analytical, spectroscopic (FT-IR and UV–Vis) and X-ray methods. For the complex containing two different transition metals (**1**) and that with one transition metal but in two different geometrical environments (**2**), the digital filtration method applied made it possible to elucidate two independent crystal fields.

1. Introduction

Pyrazole-based ligands play an important role in biology and chemistry [1,2]. For example, a pyrazole entity was found to be a component of various biological molecules taking part in, e.g. genetic processes [1–3]. Besides, pyrazole rings can be considered models for histidine residues of proteins [3]. Metal complexes containing pyrazole ligands have been well established in literature [4–8] and have various application areas [1–3]. For example, they can mimic an active site of metalloenzymes [1,3].

As pyrazole derivatives have found various successful applications in bioinorganic chemistry, in this work our interest has been focused on using them in models for metal implant corrosion [9,10]. Toxic effects of metals released from orthopedic implants upon dissolution are very well documented [9,10].

Recently, in an attempt to understand the process of cobalt oxidation in the presence of biological ligands, we investigated solid state products isolated from a [Co–1-hydroxymethyl-3,5-dimethylpyrazole–M^{n+}] system [11,12]. We have found that a combination of both redox and condensation processes in the [Co^0–1-hydroxymethyl-3,5-dimethylpyrazole–Zn^{2+}] system resulted in the formation of a cationic–anionic complex of Co(II) pyrazolylamine and Zn(II) urotropine, respectively. Both organic ligands were formed *in situ* [11]. Since in the [cobalt(0)–organic ligand–M^{n+}] system the metallic ion seems to be one of the crucial factors taking part in the process of zerovalent metal oxidation, in this work we have changed Zn(II) into the VO^{2+} group. Vanadium, apart from having a biological significance of its compounds [13], is used as a component in implant alloys (in contrast to zinc) [14].

In this work, we have applied and modified a general procedure for the isolation of complexes starting from zerovalent metals [15]. In this method, the presence of NH_4^+ ion as one of the reagents plays the role of a proton reservoir for the reduced atmospheric oxygen, which finally leads to water formation and $M^0 \rightarrow M^{n+}$ metal oxidation [15].

Here, we have reported physicochemical characteristics of three subsequently isolated complexes with various coordination numbers of the cobalt(II) ion. Each of these complexes contains an *in situ* formed scorpionate ligand (L^S) while only one of them has an earlier unknown vanadate cluster. Moreover, unlike our earlier studies reporting exclusively a cationic–anionic species formation [11,12], one complex was found to be in a neutral form.

The results of this work can be further evidence that the reactions of metallic cobalt as a substrate can result in isolating products of unique compositions and structures.

2. Experimental

2.1. Materials and measurements

All reagents were purchased from commercial sources and used without further purification. The experiments were carried out in air atmosphere. Cobalt powder, $VOSO_4$ and 1-hydroxymethy-3,

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Table 1
Crystal data and structure refinement for the studied compounds **1**–**3**.

	1	**2**	3
Chemical formula	$C_8H_{24}O_{19}V_6 \cdot 2(C_{19}H_{27}CoN_8S) \cdot 4(C_7H_8)$	$2(C_{19}H_{27}CoN_8S) \cdot C_4CoN_4S_4 \cdot CH_4O$	$C_{20}H_{27}CoN_9S_2$
Formula weight	1007.70	1240.24	516.56
T (K)	295(2)	295(2)	295(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.7321(9)	10.5710(7)	12.7916(9)
b (Å)	12.5025(9)	15.4554(11)	12.6345(9)
c (Å)	18.6712(11)	18.8732(13)	16.3674(12)
α (°)	83.034(5)	86.767(6)	90
β (°)	78.492(6)	85.263(6)	104.593(6)
γ (°)	69.014(7)	74.293(6)	90
V (Å^3)	2288.7(3)	2956.3(4)	2559.9(3)
Z	2	2	4
D_{calc}	1.462	1.393	1.340
μ (mm^{-1})	1.06	1.09	0.86
Crystal size (mm)	0.41 × 0.18 × 0.03	0.32 × 0.28 × 0.26	0.33 × 0.24 × 0.16
θ_{max} (°)	24.7	24.1	24.1
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	21816, 7771, 2834	32235, 9284, 5701	17 565, 4043, 2867
T_{min}, T_{max}	0.827, 0.973	0.666, 0.761	0.719, 0.823
R_{int}	0.113	0.092	0.042
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.147, 0.91	0.061, 0.178, 1.01	0.046, 0.115, 1.08
Data/restraints/parameters	7771/0/550	9284/2/668	4043/0/295
Goodness of fit on F^2	0.908	1.008	1.076
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.33	0.63, −0.43	0.39, −0.30

5-dimethylpyrazole were purchased from Aldrich Chemical Company. Elemental analyses were performed with a Perkin Elmer Elemental Analyzer 2400 CHN and an AES-ICP 3410 emission spectrometer (Co) using appropriate Aldrich standards. IR spectra were recorded on Perkin-Elmer FTIR 1600 (4000–400 cm^{-1}) and Perkin-Elmer FTIR 2000 (600–100 cm^{-1}) spectrophotometers in KBr pellets and Nujol mull, respectively.

Electronic reflectance spectra (range 50000–5000 cm^{-1}) were measured on a Cary 500 Scan (Varian) UV–VIS–NIR Spectrophotometer. In order to obtain accurate values of the band positions, the spectra were analyzed using a variable digital filter method [16,17] with the following filter parameters: the number determining a degree of resolution enhancement: $\alpha = 200.0$; the integer number determining the filter width: $N = 10$; the increment between points (step): $K = 100$ cm^{-1}.

Magnetic moments were measured using an MSB-MKI instrument (Sherwood Scientific Ltd.) at ambient temperature with $Co[Hg(SCN)_4]$ as standard.

2.2. Single crystal X-ray diffraction studies

X-ray diffraction data were collected on a KUMA Diffraction KM-4 four-circle single crystal diffractometer equipped with a CCD detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data were treated with the CRYSALIS Data Reduction Program (version 1.172.32.6), taking into account an absorption correction. The intensities of the reflection were corrected for Lorentz and polarization effects. The crystal structures were solved by direct methods [18] and refined by a full-matrix least-squares method using SHELXL-97 program [18] (Table 1). All non-hydrogen atoms were refined using anisotropic displacement parameters. The H-atoms were visible on Fourier difference maps, but placed by geometry and allowed to ride on the parent atom.

2.3. Preparation of complexes

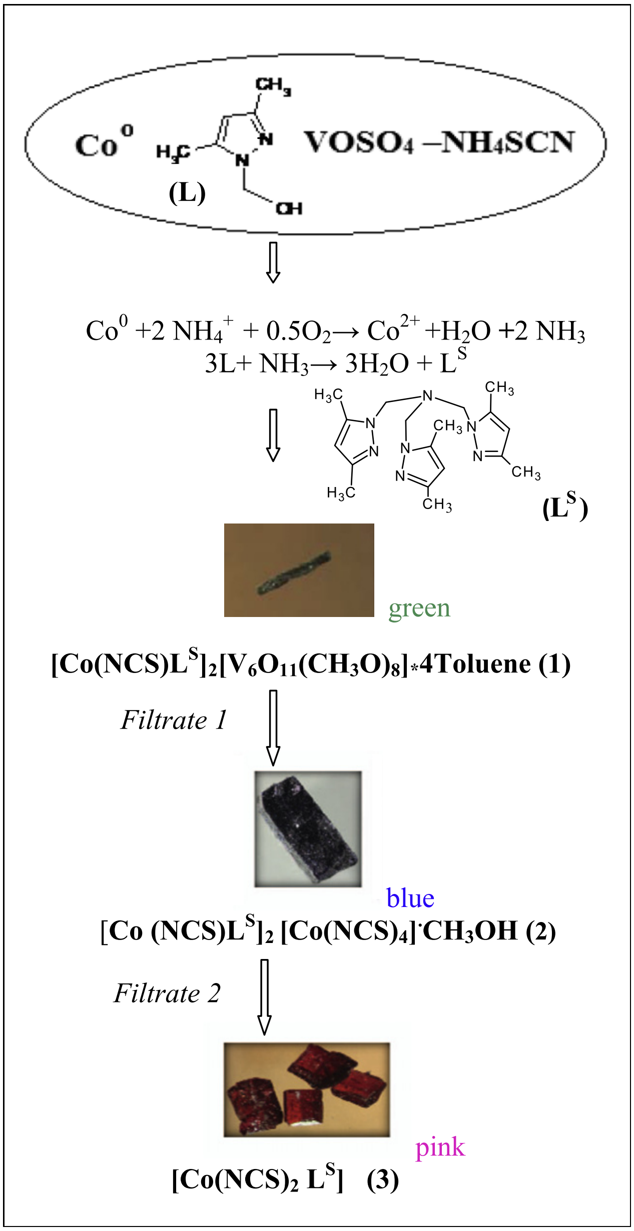
All the compounds (**1**–**3**) were synthesized according to the general procedure [15]. The reagents: metallic Co, $VOSO_4$, NH_4SCN and organic ligand L were used in 1:1:2:4 M ratio, respectively. Cobalt powder (0.0296 g, 0.5 mmol) was added to 30 cm^3 of a methanolic solution of $VOSO_4$ (0.0815 g, 0.5 mmol) and NH_4SCN (0.0769 g, 1 mmol). Finally, a metanolic solution (5 cm^3) of 1-hydroxymethyl-3,5-dimethylpyrazole (0.2525 g, 2.0 mmol) was added. The mixture was heated to 50–60 °C and stirred magnetically until a dissolution of the cobalt powder (*ca.* 5 h). The resulting solution was of a dark violet color. After 3 days, deep green crystals **1** appeared, which were filtered off and recrystallized from the mixture of toluene and CH_2Cl_2 (4:1). Subsequently, under a slow evaporation of filtrate 1 at room temperature, blue crystals **2** precipitated after 4 days and were filtered off and recrystallized from methanol. Finally, a pink crystalline compound **3** precipitated from the resulting filtrate 2 (Scheme 1) after 1 week. It was filtered off and recrystallized from warm methanol.

All the isolated compounds (**1**–**3**) were repeatedly recrystallized to obtain products suitable for X-ray crystallographic measurements.

Compound (**1**) yield: 18.9%. Elemental analyses for $C_{74}H_{110}N_{16}S_2O_{19}Co_2V_6$: *Anal.* Calc.: C, 44.60; H, 5.60; N, 11.12; Co, 5.75; V, 15.16. Found: C, 44.36; H, 5.38; N, 11.47; Co, 5.53; V, 14.95%; IR spectrum: 2972(vw), 2059(s), 1550(m), 1467(m), 1425(w), 1390(m) 1302(w),1276(w), 1247(m), 1180(w), 1130(w), 1037(m), 949(vs), 764(m), 774(m), 689(w), 669(m), 647(vw), 628(m) 595(m,br), 548(sh), 482(m,br), 441s,sh), 417(s,sh), 366(w,sh), 354(w), 327(m), 291(m), 238(m), 206(w), 191(m, sh), 157(m), 145(w), 133(w), 121(m).

Compound (**2**) yield: 38%. Elemental analyses for $C_{43}H_{58}N_{20}S_6OCo_3$: *Anal.* Calc.: C, 41.64; H, 4.71; N, 22.59; Co, 14.30. Found: C, 41.53; H, 4.37; N, 23.03; Co, 14.83%; IR spectrum: 3132(vw), 2914(vw), 2054(vs), 1628(vw), 1553(s), 1466(s), 1419(m), 1387(m,sh), 1375(m,sh), 1302(m), 1246(m), 1180(w), 1128(m), 1065(m,sh), 1044(m, sh), 985(w), 945(m), 891(m), 837(w), 808(m,sh), 796(m,sh), 690(m), 670(m), 659(m), 625(m), 594(m), 548(m), 498(m), 481(m), 440(s), 408(m,br), 353(m,sh), 318(s,sh), 305(s,sh), 288(s,sh), 239(m), 223(w), 189(s,sh) 182(s,sh), 149(m), 140(m), 133(w), 112(w).

Compound (**3**) yield: 21%. Elemental analyses for $C_{20}H_{27}N_9S_2Co$: *Anal.* Calc.: C, 46.50; H, 5.27; N, 24.41; Co, 11.41. C, 46.93; H, 5.37; N, 24.03; Co, 11.80%; IR spectrum: 2920(vw), 2073(vs), 1554(s), 1463(s)(, 1435(m,sh), 1419(m), 1396(m), 1246(w), 1174(m), 118(m), 1045(s), 1016(m), 974(m), 890(m), 796(s), 689(m),



Scheme 1. Isolation procedure for (**1**–**3**).

669(s), 630(s), 599(s), 570(m), 513(w), 488(m), 478(m), 456(m), 422(m), 405(m), 365(w), 325(m), 268(s), 246(s), 224(s,sh), 205(s,sh), 196(s), 152(m,sh), 142(w), 132(w), 121(m), 110(w).

3. Results and discussion

Two cationic–anionic (**1**–**2**) and one neutral (**3**) complexes were obtained in one pot synthesis from the system: [Co^0–1-hydroxymethyl-3,5-dimethylpyrazole (L)–$VOSO_4$–$NH_4(SCN)$] (Scheme 1).

All the isolated compounds (**1**–**3**) contained cobalt exclusively on +2 oxidation state and with its various coordination numbers (CN): 5 for compound **1**, 5 and 4 for compound **2**, and 6 for compound **3**.

The oxidation of Co^0 with atmospheric oxygen in the presence of NH_4^+ cations leads to cobalt(II) formation and releasing water and ammonia (Scheme 1) [11,12,15]:

The ammonia molecules were further used for the synthesis of scorpionate ligands (L^S), which are products of an *in situ* condensation of NH_3 with 1-hydroxymethyl-3,5-dimethylpyrazole (L) [11,12] (Scheme 1). The resulting product (L^S–tris(1-(3,5-dimethylpyrazolylmethyl)amine)) was found to be a tetradentate scorpionate-like ligand [3] – analog of poly(pyrazol-1-yl)borates [2].

3.1. Crystal structure of cobaltoscorpionates

3.1.1. Crystal structure of $[Co(NCS)L^S]_2[V_6O_{11}(CH_3O)_8]\cdot 4C_7H_8$ (1)

Complex **1** crystallizes in $P\bar{1}$ triclinic space group (Table 1) with one $[Co(NCS)L^S]^+$ ion, half of the $[V_6O_{11}(CH_3O)_8]^{2-}$ anion and two toluene molecules in the asymmetric unit of the unit cell. The $[V_6O_{11}(CH_3O)_8]^{2-}$ anion lies in inversion centers, whereas the other species are located in general positions.

A molecular structure of the $[Co(NCS)L^S]^+$ ion is very similar to that published earlier, containing chloride ligand [11,12]. One tris(1-(3,5-dimethylpyrazolylmethyl)amine (L^S) and one $(SCN)^-$ anion create a five-coordination sphere around the Co^{2+} ion. The central ion is significantly displaced from the basal plane of the trigonal bipyramid (Fig. 1a). The shortest and the longest Co–N distances are observed in vertical positions of the trigonal bipyramid (Table 2).

Examples of organic vanadium (IV/V) oxo- and methoxobridged complexes with nuclearity higher than two are rare in literature

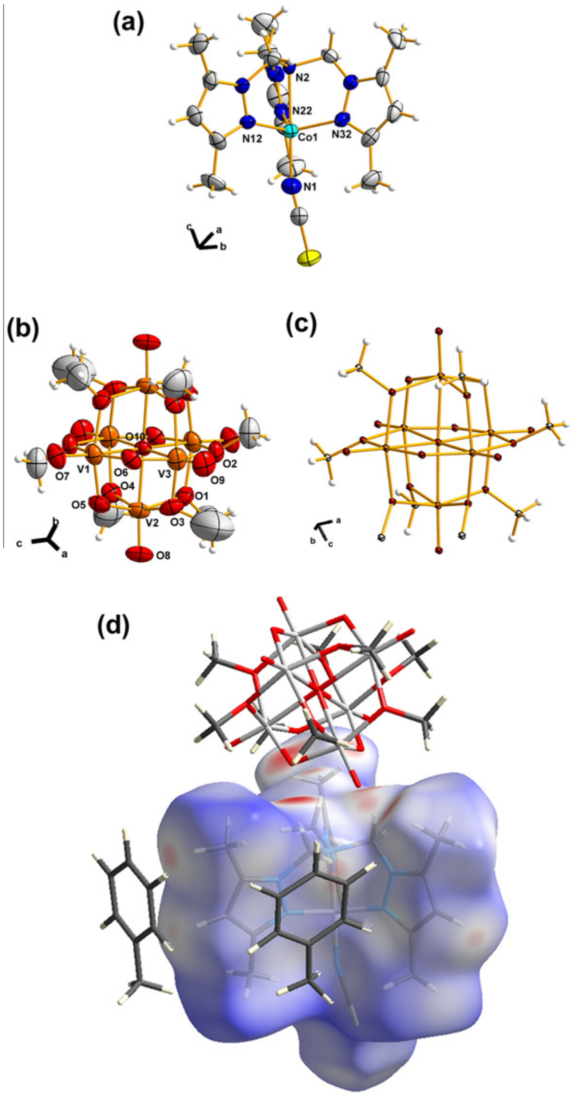


Fig. 1. (a) The structure of the hexavanadate $[V_6O_{11}(CH_3O)_8]^{2-}$ anion in **1** and (b) in referenced compound [17]. (c) Coordination sphere of the Co^{2+} ion in compound **1**. (d) Normalized Hirshfeld surface of the $[Co(NCS)L^S]^+$ ion and interacting species.

Table 2
Selected geometric parameters (Å, °).

1			
Co1–N1	1.977(6)	V2–O1	2.000(5)
Co1–N32	2.031(5)	V2–O10	2.2431(12)
Co1–N22	2.037(6)	V2–V1^{i}	3.014(2)
Co1–N12	2.052(5)	V2–V3	3.1134(19)
Co1–N2	2.290(4)	V3–O9	1.600(5)
V1–O7	1.588(5)	V3–O6	1.787(4)
V1–O6^{i}	1.849(4)	V3–O3	1.827(5)
V1–O5^{i}	1.864(4)	V3–O2	1.985(5)
V1–O1	1.963(5)	V3–O4	1.987(5)
V1–O2	2.003(5)	V3–O10	2.2504(12)
V1–O10	2.2053(13)	V3–V1^{i}	3.0164(19)
V1–V2^{i}	3.014(2)	O4–V2^{i}	1.928(5)
V1–V3^{i}	3.0164(19)	O5–V1^{i}	1.864(4)
V2–O8	1.593(5)	O6–V1^{i}	1.849(4)
V2–O5	1.769(5)	O10–V1^{i}	2.2053(13)
V2–O3	1.923(5)	O10–V2^{i}	2.2431(12)
V2–O4^{i}	1.928(5)	O10–V3^{i}	2.2504(13)
2			
Co1–N1A	1.958(5)	Co2–N51	2.028(4)
Co1–N21	2.033(4)	Co2–N61	2.034(5)
Co1–N11	2.043(4)	Co2–N2	2.292(4)
Co1–N31	2.050(4)	Co3–N4D	1.931(5)
Co1–N1	2.287(3)	Co3–N6F	1.952(6)
Co2–N1B	1.974(5)	Co3–N5E	1.955(6)
Co2–N41	2.027(4)	Co3–N1C	1.961(5)
3			
Co1–N2	2.007(3)	Co1–N21	2.152(3)
Co1–N1	2.075(3)	Co1–N11	2.174(3)
Co1–N31	2.119(3)	Co1–N3	2.261(2)

Symmetry code: (i) $-x$, $-y+1$, $-z+1$.

[19–22]. Generally, they are formed during oxidation of VO^{2+} cation or reduction of vanadium(V) [19,21,22]. Here, a polyoxovanadate cluster decorated with six bridging and two terminal methoxo groups has been formed. Such hexavanadate cluster, have been recently studied due to their peculiar coordination features [23], the spin frustrated structure [24], and fluorescence of surfactants [25]. In the structure of **1**, the polyoxymethoxo vanadate anion contains eight μ_2-methoxo and four μ_2-oxo bridges (Fig. 1a and b). Such a geometry requires a mixed-valence state of vanadium ions, i.e. four V^V and two V^{IV}. The $[V_6O_{11}(CH_3O)_8]^{2-}$ anion formally belongs to a highly symmetrical Lindqvist structure $[M_6O_{19}]^{n-}$ [26] with eight oxygen atoms substituted with methoxo groups [26]. The mixed valence $[V^{IV}_2V^V_4O_{11}(OR)_8]^{2-}$ cluster exhibits two coordination numbers: 5 and 6 for V(IV) and V(V) ions, respectively. The arrangement of the methoxo and oxo ligands are similar to that found in [27] (Fig. 1a and b). Eight positions (6 ordered + 2 disordered) of the CH_3O– group have been determined (Fig. 1b) [27]. Considering only a mutual position of the methoxo groups, it was found that $[V_6O_{11}(CH_3O)_8]^{2-}$ anion forms a different isomer, i.e. of C_i point group symmetry when compared with the recently reported hexavanadate of approximately C_s point group symmetry [27].

Oxygen atoms of a hexavanadate anion are attractive sites for the formation of an intermolecular hydrogen bonding. Many weak hydrogen bonds are found between $[Co(L^S)(NCS)]^+$ and $[V_6O_{11}(CH_3O)_8]^{2-}$ anions (*Table* S1 and Fig. 1d). Two toluene molecules are also involved in weak intermolecular interactions of C–H···π type. In turn, the first two C–H···π interactions listed in *Table* S1 can be classified to group II of Malone's classification [28], whereas the other two belong to group V.

*3.1.2. Crystal structure of $[Co(NCS)L^S)]_2[Co(NCS)_4]\cdot CH_3OH$ (**2**)*

Complex **2** crystallizes in $P\bar{1}$ triclinic space group (Table 1). Two $[Co(NCS)L^S]^+$ cations, one $[Co(NCS)_4]^{2-}$ anion and one methanol molecule exist in the asymmetric unit of the unit cell (Fig. 2). The methanol molecule is disordered over two symmetry independent positions, i.e. C1M–O1M and C2M–O2M. The distance between C1M and O2M is unusually short and equals to 2.637 Å. However, no effects associated with such a hydrogen bonding interaction were observed in the infrared spectrum. Therefore, in the model of the crystal structure of **2**, the methanol molecule is disordered over two positions with a site occupancy factor 0.5 each, rather than two molecules occupying symmetry independent positions.

Two symmetry independent Co^{2+} ions have five coordinate spheres, each with one tris(1-(3,5-dimethylpyrazolylmethyl)amine) (L^S) and one $(NCS)^-$ anion creating a trigonal bipyramid around the central ion. However, the Co^{2+} ion is displaced from the basal plane of the bipyramid. Therefore, axial Co–N distances significantly differ from each other in both symmetry independent $[Co(NCS)(L^S)]^+$ ions (Table 2). The structure of complex **2**, apart from two $[Co(NCS)(L^S)]^+$ cations, contains one $[Co(NCS)_4]^{2-}$ anion

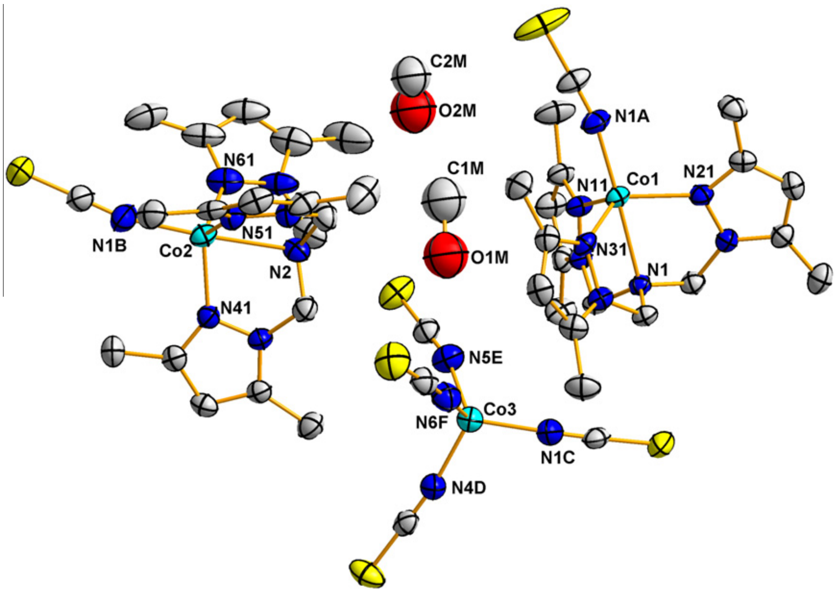


Fig. 2. Asymmetric unit of the unit cell of $[Co(L^S)(NCS)]_2[Co(NCS)_4]\cdot CH_3OH$ (**2**).

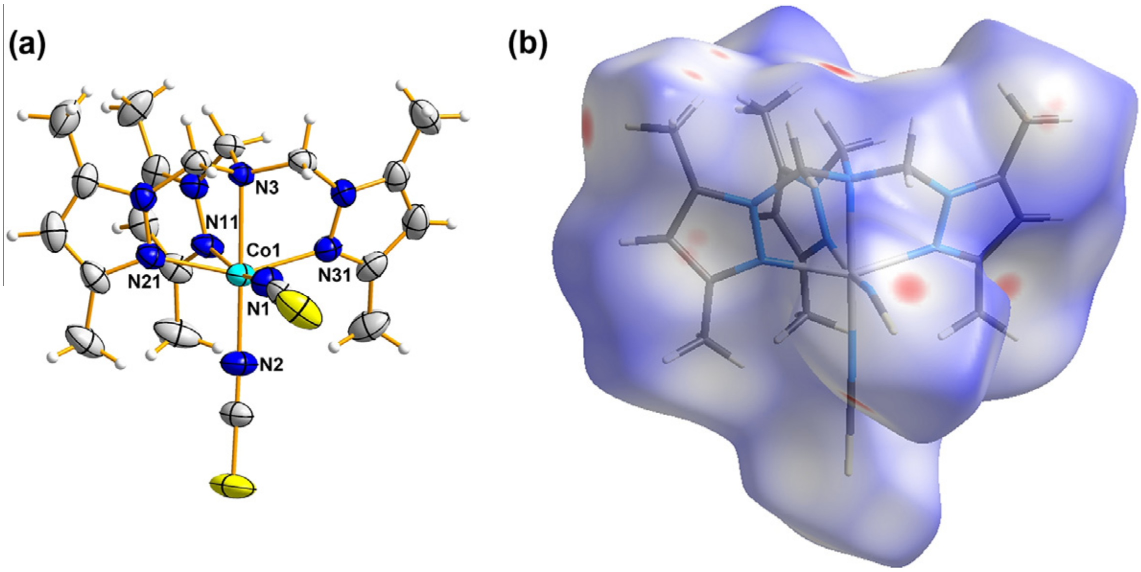


Fig. 3. (a) Coordination sphere of the Co^{2+} ion in compound **3**. (b) Normalized Hirshfeld surface of the $[Co(NCS)_2L^S]$ molecule.

of an approximately tetrahedral configuration. The tetrahedrally coordinated Co(II) ion with N-bonded $(NCS)^-$ ions is responsible for the deep blue color ("cobalt blue") [29] of the crystals of **2**.

Additionally, in the crystal structure of **2**, several hydrogen bondings are found (Table S2). Similarly to **3** (*vide infra*), both the lone pair at the sulfur atom and electron cloud between carbon and nitrogen atoms are the acceptors. Also, one C–H$\cdots\pi$ interaction is found (Table S2). It belongs to group III of Malone's classification of the X–H$\cdots\pi$ interactions [28].

3.1.3. Crystal structure of $[Co(NCS)_2(L^S)]$ (3)

Complex **3** crystallizes in $P2_1/n$ monoclinic space group (Table 1). The Co^{2+} ion coordinates the tetradentate tris(1-(3,5-dimethylpyrazolylmethyl)amine) [30], and two NCS^- anions (Fig. 3). Compound **3** exists as a molecular crystal, because the inorganic anions fully compensate the positive charge of the cobalt ion in $[Co(NCS)_2(L^S)]$. The ligands are bound to Co^{2+} by the nitrogen atoms, forming chromophore of tetragonal geometry (CoN_2N_4). It appears to be the first time that the product isolated from the system [Co(0)–L–M′–NH_4^+] L = 1-hydroxymethyl-3,5-dimethylpyrazole (L) is a neutral cobalt(II) complex. Moreover, it appears that here, for the first time, hexacoordinate cobalt(II) with ligand L^S created *in situ* was found. In the Cambridge Structural Database nine mono- and dinuclear complexes with L^S (N,N,N-substituted 3,5-dimethylpyrazole amine) ligand have been deposited but only two of them form hexacoordinate cobalt(II) complexes, however, they are not both neutral and monomeric [31–34].

The deformation towards tetragonality of the octahedral geometry around the central metal ion in **3** (Table 2) can be related to the polidentate coordination mode of the organic ligand and mixed ligand complex formation. Indeed, the Co–(NCS) distances are significantly shorter than the other Co–N(organic ligand) distances.

In the crystal structure of **3**, there are no conventional hydrogen bonds. The shortest contacts are listed in Table S3. All these interactions of C–H$\cdots$(NCS) type are weak and they can be seen on the normalized Hirshfeld surface (Fig. 3b) [35,36]. It is worth noting that both the lone pair at the sulfur atom and the electron cloud between carbon and nitrogen atoms are acceptors in the intermolecular interactions. These interactions are arranged in the chain patterns described by the unitary graph-sets (Table S3) [37,38]. All the chains are formed along three different directions towards the 2_1 screw axis or *n* glide plane.

In the crystal structure of **3**, the C24–H24$\cdots$C35^{iv} and C17–H17B$\cdots$C34^{v} interactions are of the C–H$\cdots\pi$ type (Table S3). They both can be classified to group III of Malone's classification of X–H$\cdots\pi$ interactions [28,34].

3.2. Infrared spectra

The comparison of selected vibrational bands of free 1-hydroxymethyl-3,5-dimethylpyrazole (L) and **1–3** are important for the confirmation of the *in situ* formation of a new ligand, i.e. tris(1-(3,5-dimethylpyrazoylmethyl)amine) (L^S). The spectrum of the free ligand L is completely different from that of the coordinated one. In the starting (L) the OH stretching band lies at 3152 cm^{-1} and is very broad due to the inter- and intramolecular hydrogen bonding (O…H…N). The O–H band disappears in the spectra of **1–3**. Additionally, the appearance of new, medium stretching ν(C–N) vibration typical of tertiary amine at 1273 cm^{-1} (**1**), 1265 cm^{-1} (**2**) 1267 cm^{-1} (**3**) can be related to the presence of L^S [39,40]. The IR spectra of (**1–3**) exhibited also a new, very strong band at 2051 cm^{-1} (**1**), 2054 cm^{-1} (**2**) 2073 cm^{-1} (**3**), confirming the presence of the $(NCS)^-$ entity in the complexes [39,41]. The $(NCS)^-$ group may coordinate to metal through nitrogen or sulfur atoms [39,41–43]. The absorption bands which occur in the range of 2143–2039 cm^{-1} (CN stretching), 827–806 cm^{-1} (CS stretching for N-bonded) and δ(NCS) near at 480 cm^{-1} (for N-bonded) corroborate the X-ray data on the monodentate coordination of N-bonded isothiocyanate ligand to Co(II) in **1–3** [39,41–43].

In addition, the IR spectrum of **1** reveals bands corresponding to the presence of polyoxoalkoxo vanadates. The strongest bands are located in the 950–1100 cm^{-1} region: the O–CH_3 (1000–1100 cm^{-1}) and the V=O (950–1000 cm^{-1}) stretching modes [24]. A further absorption band located in the 550–650 cm^{-1} region is attributed to V–O–V bending [24]. Finally, two bands in the 400–450 cm^{-1} region are tentatively assigned to V–O stretching [24]. The IR spectrum of **1** shows vibration of V=O (949 cm^{-1}) [44], V–O–V bridging fragments (743, 548 cm^{-1}) [44] and also V–OCH_3 from fragments (594 and 417 cm^{-1}) [39,44]. Coordination of (L^S) to Co(II) is also demonstrated in the far-IR region (400–100 cm^{-1}). In this region, new bands arising from the stretching vibrations ν of (Co–N) at (441, 238 cm^{-1}) (**1–2**) [39,41,45] and ν(Co–NCS) at 270 cm^{-1} (**1**), 288 cm^{-1} (**2**) and 268 cm^{-1} (**3**) [39,41,42,46,47] were observed.

3.3. Electronic spectra

The electronic spectra are collected in Table 3 and Figs. 4–6.

The spectra of **1–3** are complicated mainly due to the presence of more than one crystal field both in **1** (Co(II)-d^7 and V(IV)-d^1) and **2** (Co(II) ions in the environment of different symmetries. Generally, for heterometallic transition metal complexes and homometallic of different symmetries more than one crystal field can be expected. Their detection is not a simple task due to overlapping bands of low intensity. The complication also arises from some distortions of the metal environment from the ideal polyhedron (Tables 1 and 2). However, using a digital filter method, they can be identified with an assumption of the independent absorption of the metallic centers [48,49]. Indeed, the crystallographic data confirmed that the distances are large enough for such an assumption.

Thus, the electronic spectra of (**1–3**) enhanced with the digital filtration have been successfully analyzed adopting the respective energy diagrams for $[CoN_4{}^SN]^+$ (D_{3h}), $[CoN_4{}^SN_2]$ (D_{4h}) and $[VO(O)_4]$ (C_{4v}) and $[Co(NCS)_4]$ (T_d) chromophores.

In the cationic–anionic complex **1**, two central metal atoms, i.e. Co(II) (d^7) and V(IV) (d^1) are present. The digitally resolved spectra allowed detecting an individual absorption in the trigonal bipyramidal (D_{3h}) Co(II)(d^7) (*vide supra*) and square pyramidal (C_{4v}) V(IV) (d^1) crystal fields (Fig. 4).

In general, for a high spin regular trigonal bipyramidal (D_{3h}) $[CoL^5(NCS)]^+$ species ^4F term (Co(II) d^7 conf.) splits into $^4A_1''$, $^4A_2''$, $^4E''$, $^4E'$ and ^4P – into $^4A_2'(P)$ and $^4E''(P)$ [48,52,53]. The reflectance spectrum of **1** (Fig. 4) exhibits well-resolved bands in the spectral range 6700–24000 cm^{-1} attributed to the characteristic transitions of the high-spin five coordinate cobalt(II) complex of the trigonal bipiramidal geometry (Table 3). The data are in line with the spectra obtained by others: $\{N_2O_3\}$ [50], $\{N_4Br\}$ [51], $\{CoN_4Cl\}$ [29,52,53], and by us [11,12] (**3**).

In the 10000–30000 cm^{-1} absorption region, the oxovanadium(IV) species of C_{4v} symmetry are characterized by three low intensity bands assigned to the following electronic transitions: $^2B_2 \rightarrow {}^2E$ $(d_{xy} \rightarrow d_{xy,}d_{yz)}$ and $(^2B_2 \rightarrow {}^2B_1$ $(d_{xy} \rightarrow d_{x_2-y_2})$ and $^2B_2 \rightarrow {}^2A_1(d_{xy} \rightarrow d_{z_2})$ [44,48,55]. The spectrum of **1** shows the bands at 13700, 22300 and 25600 cm^{-1} (Fig. 4). Vanadium complexes containing V=O moiety exhibit electronic spectra which are distinct from other vanadium(IV) compounds [48,54,55]. In some cases, the symmetry of the $[(V{=}O)O_4]$ (C_{4v}) is decreasing and, consequently, the degeneracy of e_g $(d_{x_2-y_2},\ d_{z_2})$ orbitals is removed [24,54,55].

In the spectrum of **2** (Fig. 5), two crystal fields, i.e. the described above trigonal pyramidal $[Co(NCS)(L^S)]^+$ and an anionic tetrahedral $[Co(NCS)_4]^{2-}$ can be also expected. The bands in the spectrum of **2** (Fig. 5) are asymmetrical. However, the filtration process allowed us to obtain their positions (Table 3). The transitions at 11700, 17500, 24300 and 24300 cm^{-1} belong to five coordinate Co(II) [11,12,40,48,52,53]. The bands at 15400 cm^{-1} and two shoulders at 19800 and 22500 cm^{-1} can be assigned to the tetrahedral $[Co(NCS)_4]^2$ ion [42,43,48] (Fig. 5).

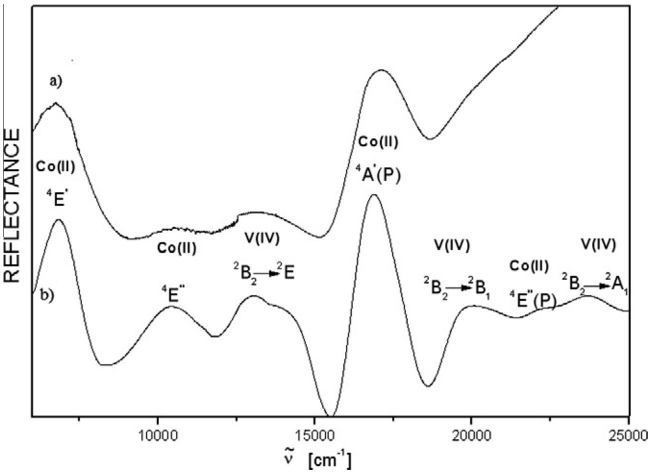


Fig. 4. Reflectance spectra (a) of $[Co(NCS)L^S]_2[V_6O_{11}(CH_3O)_8]{\cdot}(CH_3C_6H_5)_4$ (**1**) and the effect of the digital filtration (b).

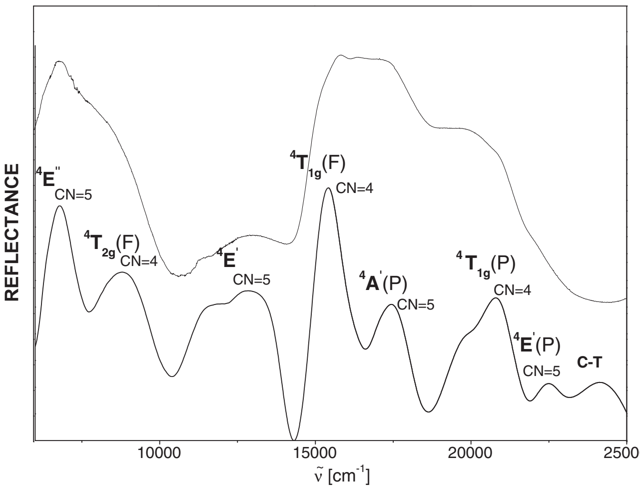


Fig. 5. Reflectance spectra (a) of $[Co(NCS)L^S]_2[Co(NCS)_4]{\cdot}CH_3OH$ (**2**) and the effect of the digital filtration (b).

The spectrum of complex **3** with broad, weakly structured bands reveals splitting upon filtration. The mode of the splitting points to a lowered O_h symmetry towards tetragonality of the $[CoN_6]$ chromophore. Six coordinate cobalt(II) complexes in O_h symmetry exhibit three spin typical transitions: $^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(\nu_1)$, $^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)(\nu_2)$, $^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)(\nu_3)$ [48,49,53] (Fig. 6 and Table 3). However, the analysis of the bands revealed their splitting, showing a significant lowering symmetry supported by a structural analysis. The spectrum of $[CoL^S(NCS)_2]$ **3** is similar to those of other Co(II) complexes with a tetragonal $[CoA_2B_4]$ chromophore [49].

Table 3
Electronic spectra of the **1–3** and the literature data for cobalt(II) complexes with L^S ligands.

Compound	Band position (ν_{max}, cm^{-1})									
$[Co(NCS)L^S]_2[V_6O_{11}(CH_3O)_8] * 4$Toluene (**1**)	6700	10500	13100		17100				24100sh
Filtration effect	6820	10450	13110	16900	20070			22300	23750
$[Co(NCS)L^S]_2[Co(NCS)_4] * CH_3OH$ (**2**)	6820		13000		16700		19700		23000br
Filtration effect	6770	8740	11660	12840	15430	17520	19830	22800	24190
$[Co(NCS)_2L^S]$ (**3**)		9500br					20000		24200br
Filtration effect		9660	11620	13040	15690	17160	20740		24170
$[CoClL^S][ZnLCl_2]$ [19]	6790	10630			16664	18725			24080
$[CoClL^S][CdBr_4]$ [20]	6820	11550			16870br				23720

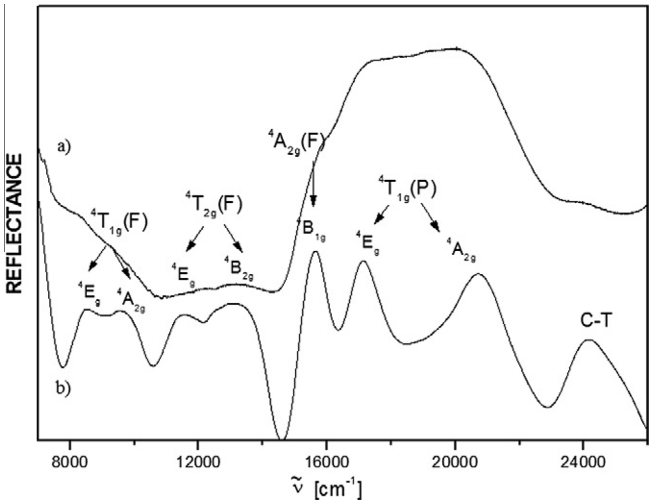


Fig. 6. Reflectance spectra (a) of complex $[Co(NCS)_2L^S]$ (**3**) and the effect of the digital filtration (b).

The magnetic moment of complex **3** ($\mu_{eff} = 4.37\ \mu_B$) was found in the range supporting a hexacoordinate symmetry of the Co(II) ion [46]. The electronic spectra of the range above 30000 cm^{-1} have been assigned both to intraligand (pyrazole $\pi \rightarrow \pi^*$) and L → M CT transitions [30,42,43,56].

4. Summary and conclusions

The dissolution of metallic cobalt in methanol in the presence of pyrazole derivative, VO^{2+} as $VOSO_4$ and NH_4^+ ions in the form of $NH_4(SCN)$, resulted in a simultaneous appearance of the following remarkable effects:

- Transformation of the metallic cobalt to Co(II) in the atmospheric oxygen resulted in two novel cationic–anionic $\{[Co^{II}(NCS)L^S]^{n+}[X]^{n-}\}$ $X = [V_6O_{11}(CH_3O)_8]^{2-}$, $[Co^{II}(NCS)_4]^{2-}$ **1** and **2** and one neutral $[Co^{II}(NCS)_2L^S]$ **3** complexes isolated from one pot synthesis, with an organic ligand L^S formed *in situ*. In the first two complexes, the cationic part exhibits a formation of relatively rare five coordinate Co(II) [57].
- The new isomer of *octa*methoxo-cluster $[V_6O_{11}(CH_3O)_8]^{2-}$ **1** formed *via* redox and condensation processes belongs to a series of highly interesting alkoxo-polyoxovanadium species of the Lindqvist structure.
- In compounds **1** and **2**, the central ion is significantly displaced from the basal plane of the trigonal bipyramid in $[Co(NCS)(L^S)]^+$ cation.
- The electronic spectra of **1** and **2** have been successfully analyzed in two independent CF approximations, adopting the respective energy diagrams for cobalt(II) in $[CoN_4{}^SN]^+(D_{3h})$, vanadium(IV) in $[VOO_4(C_{4v})]$ and Co(II) in $[Co(NCS)_4]$ (T_d) chromophores.
- For complex **3**, it appears to be the first time that the product isolated from the $[Co(0)–L–M^{n+}–NH_4^+]$ system (L–1-hydroxymethyl-3,5-dimethylpyrazole) is both a neutral and hexacoordinate species.
- Isothiocyanate is a monodentate ligand and it coordinates by a nitrogen atom to cobalt(II) ion. A short nitrogen-carbon distance alike long carbon–sulfur distance indicate $(N{\equiv}C–S)^-$ structure of the isothiocyanate in all the presented compounds.

The comparison of the results with those of our earlier findings [11,12] shows the following pattern: the cationic part consists of Co(II) ion coordinating both L^S and the inorganic anions (I^-, Cl^- NCS^-). Moreover, the “anionic metal” in cation–anion complexes always adopts its favorite geometry, i.e. tetrahedral for Zn(II) [11], Cd(II) [12], and a polyoxometallate form for vanadium (this work). However, unlike in other studied systems, the process takes place through a subsequent precipitation of the species. Furthermore, in contrast to previous studies where only cationic–anionic products were isolated, here, one pot synthesis resulted in the formation of a neutral complex as a final product.

In summary, the isolation of the complexes with such unusual compositions and architecture can be ascribed to the redox ($Co^0 \rightarrow Co^{II}$) processes and the accompanying *in situ* formation of the pyrazole derivative ligand.

Evidently, the direct synthesis as a model of implant corrosions results in the formation of interesting although still weakly predictable species and is worthy of further investigation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.021.

References

[1] (a) F. Mani, Coord. Chem. Rev. 120 (1992) 325;
(b) F.K. Keter, J. Darkwa, Biometals 25 (2012) 9;
(c) R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.
[2] S. Trofimenko, Coord. Chem. Rev. 93 (1993) 943.
[3] (a) C. Santini, M. Pellei, Curr. Bioact. Compd. 5 (4) (2009) 243;
(b) M. Pellei, G. Papini, G. Lobbia, C. Santini, Curr. Bioact. Compd. 5 (2009) 321.
[4] (a) W.L. Driessen, Recl. J. The Royal Netherlands Chem. Soc. 12 (1982) 441;
(b) W.L. Driessen, S. Gorter, W.G. Haanstra, L.J. Laarhoven, J. Reedijk, K. Goubitz, F.R. Seljée, Recl. Trav. Chim. Pays-Bas 112 (1993) 309;
(c) W.L. Driessen, B. Maase, J. Redijk, H. Kooijman, M.T. Lakin, A.L. Spek, Inorg. Chim. Acta 300–302 (2000) 1099;
(d) F. Paap, E. Bouwman, W.L. Driessen, R.A. de Graaff, J. Reedijk, J. Chem. Soc., Dalton Trans. (1985) 737.
[5] A.R. Oki, J. Sanchez, R.J. Morgan, J. Coord. Chem. 36 (1995) 167.
[6] (a) B. Barszcz, T. Głowiak, J. Jezierska, K. Kurdziel, Inorg. Chem. Commun. 5 (2002) 1056;
(b) B. Barszcz, T. Głowiak, J. Jezierska, A. Tomkiewicz, Polyhedron 23 (2004) 1309.
[7] (a) A. Boixassa, J. Pons, X. Solans, M. Font-Bardia, J. Ros, Inorg. Chem. Acta 355 (2003) 254;
(b) A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardia, J. Ros, Inorg. Chem. Acta 340 (2002) 49.
[8] R. Touzani, M. Haibach, A.J. Nawara-Hultzsch, S.E. Kadiri, T.J. Emge, A.S. Goldman, Polyhedron 30 (2011) 2530.
[9] I. Iavicoli, G. Falcone, M. Alessandrelli, R. Cresti, V. De Santis, S. Salvadori, A. Alimonti, G. Carelli, J. Trace Elem. Med. Biol. 20 (2006) 25.
[10] A. Sargeant, T. Goswiami, Mater. Des. 28 (2007) 155.
[11] A. Adach, M. Daszkiewicz, B. Barszcz, M. Cieślak-Golonka, G. Maciejewska, Inorg. Chem. Commun. 13 (2010) 361.
[12] A. Adach, M. Daszkiewicz, B. Barszcz, Struct. Chem. 21 (2010) 331.
[13] (a) D. Rehder, Coord. Chem. Rev. 182 (1999) 297;
(b) M. Aureliano, D.C. Crans, J. Inorg. Biochem. 103 (2009) 536;
(c) E.J. Baran, J. Inorg. Biochem. 80 (2000) 1.
[14] C. Faleiro, I. Godinho, U. Reus, M. de Sousa, Biometals 9 (1996) 321.
[15] (a) V.G. Makhankova, O.V. Khavryuchenko, V.V. Lisnyak, V.N. Kokozay, V. Dyakonenko, O.V. Shishkin, B.W. Skelton, J. Jezierska, J. Solid State Chem. 183 (2010) 2695;
(b) V.V. Semenaka, O.V. Nesterova, V.N. Kokozay, R.I. Zybatyuk, O.V. Shishkin, R.B. Carlos, J. Gómez-García, J.M. Clemente-Juan, J. Jezierska, Polyhedron 29 (2010) 1326.
[16] G. Bierman, H. Ziegler, Anal. Chem. 58 (1986) 536.
[17] J. Myrczek, Spectrosc. Lett. 23 (1990) 1027.
[18] G.M. Sheldrick, Acta Crystallogr., Sect. A A64 (2008) 112.
[19] C. Drouza, A. Kermidas, J. Inorg. Biochem. 80 (2000) 75.

[20] H. Kumagai, S. Kawata, S. Kitagawa, K. Kanamori, K. Okamoto, Chem. Lett. (1997) 249.
[21] A.J. Tasiopolos, A.N. Troganis, Y. Deligiannakis, A. Evangelou, T.A. Kabanos, J.D. Woollins, A. Slawin, J. Inorg. Biochem. 79 (2000) 159.
[22] Y. Hayashi, Coord. Chem. Rev. 255 (2011) 2270.
[23] M. Piepenbrink, M.U. Triller, N.H.J. Gorman, B. Krebs, Angew. Chem., Int. Ed. 41 (2002) 2523.
[24] C. Daniel, H. Hartl, J. Am. Chem. Soc. 131 (2009) 5101.
[25] P. Yin, P. Wu, Z. Xiao, D. Li, E. Bitterlich, J. Zhang, P. Cheng, D.V. Vezenov, T. Liu, Y. Wei, Angew. Chem., Int. Ed. 50 (2011) 2521.
[26] G.A. Seisenbaeva, T. Mallah, V.G. Kessler, Dalton Trans. 39 (2010) 7774.
[27] D. Hou, G.-S. Kim, K.S. Hagen, C.L. Hill, Inorg. Chim. Acta 211 (1993) 127.
[28] J.F. Malone, C.M. Murray, M.H. Charlton, R. Docherty, A.J. Lavery, J. Chem. Soc., Faraday Trans. 93 (1997) 3429.
[29] T. Peppel, M. Kockerling, M. Geppert-Lipczyńska, R.V. Ralys, J.K. Lehmann, S.P. Verevkin, A. Heintz, Angew. Chem. 49 (2010) 7116.
[30] K. Fujisawa, S. Chiba, Y. Miyashita, K. Okamoto, Eur. J. Inorg. Chem. (2009) 3921.
[31] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
[32] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.
[33] W.L. Driessen, R.A.G. de Graaff, J. Ochocki, J. Reedijk, Inorg. Chim. Acta 150 (1988) 41.
[34] Z.-H. Zhang, Y.-C.h. Lu, H.-L. Yang, Y. Tang, Chin. J. Inorg. Chem. 21 (2005) 477.
[35] F.L. Hirshfeld, Theor. Chim. Acta 44 (1977) 129.
[36] J.J. McKinnon, D. Jayatilaka, M.A. Spackman, Chem. Commun. (2007) 3814.
[37] M.C. Etter, J.C. MacDonald, J. Bernstein, Acta Crystallogr., Sect. B 46 (1990) 256.
[38] M. Daszkiewicz, Struct. Chem. 23 (2012) 307.
[39] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., John Wiley, New York, 1986.
[40] G. Yang, J. Chem. Crystallogr. 34 (2004) 269.
[41] H.S. Bhojya, N. Siddaramaiah, P.G. Ramappa, Thermochim. Acta 287 (1996) 279.
[42] N.C. Tomson, M.R. Crimer, T. Petrenko, L.E. Rosebrugh, S. Sproules, W.C. Boyd, R.G. Bergman, S. DeBeer, F.D. Toste, K. Wieghardt, J. Am. Chem. Soc. 133 (2011) 18785.
[43] C.L. Yadava, S. Tripathi, I.S. Ahuja, Transition Met. Chem. 11 (1986) 295.
[44] M.R. Prathapachandra Kurup, E.B. Seena, M. Kuriakose, Struct. Chem. 21 (2010) 599.
[45] (a) A.T. Çolak, F. Çolak, O.Z. Yeşilel, D. Akduman, F. Yılmaz, M. Tumer, Inorg. Chim. Acta 363 (2010) 2149;
(b) T. Çolak, O.Z. Yeşilel, G. Pamuk, H. Gúnay, O. Búyukgungo, Polyhedron 30 (2011) 1012.
[46] A. Døssing, P. Engberg, R. Hazell, Inorg. Chim. Acta 268 (1998) 159.
[47] B.K. Singh, R.K. Sharma, B.S. Garg, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 63 (2006) 96.
[48] B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, New York, Tokyo, 1984.
[49] (a) M. Daszkiewicz, Z. Staszak, A. Pietraszko, W. Bronowska, M. Cieślak-Golonka, Struct. Chem. 17 (2006) 599;
(b) M. Puszyńska-Tuszkanow, M. Daszkiewicz, G. Maciejewska, A. Adach, M. Cieślak-Golonka, Struct. Chem. 21 (2010) 315.
[50] Z. Atherton, D.M.L. Goodgame, S. Menzer, D.J. Williams, Polyhedron 18 (1999) 273.
[51] F. Meyer, K. Heinze, B. Nuber, L. Zsolnai, J. Chem. Soc., Dalton Trans. (1998) 207.
[52] Z. He, D.C. Craig, S.B. Colbran, J. Chem. Soc., Dalton Trans. (2002) 4224.
[53] (a) T. Li, A.L. Walker, H. Iaki, Y. Hasegawa, A. Liu, J. Am. Chem. Soc. 127 (2005) 12282;
(b) M. Šebová, V. Jorik, J. Mancoĺ, J. Kožiŝek, R. Boča, Polyhedron 30 (2011) 1163.
[54] M. Badea, R. Olar, V. Uivarosi, D. Marinescu, V. Aldea, S.F. Barbuceanu, G.M. Nitulescu, J. Therm. Anal. Calorim. 105 (2011) 559.
[55] T. Rosu, E. Pahontu, M. Reka-Stefana, D.C. Ilies, R. Georgescu, S. Shova, A. Gulea, Polyhedron 31 (2012) 352.
[56] J. Krzystek, D.C. Swenson, S.A. Zvyagin, D. Smirnov, A. Ożarowski, J. Telser, J. Am. Chem. Soc. 132 (14) (2010) 5241.
[57] M. Dudev, J. Wang, T. Dudev, C. Lim, J. Phys. Chem. B 110 (2006) 1889.