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Synthesis and structure of new mononuclear octahedral cobalt(III) dioximates derived from isonicotinic hydrazide

Maria Cocu [a], Ion Bulhac [a], Eduard Coropceanu [a], Elena Melnic [b], Sergiu Shova [a,b], Olga Ciobanica [a], Victoria Gutium [a], Paulina Bourosh [b,*]

[a] *Institute of Chemistry, Academy of Sciences of Moldova, Academiei str. 3, MD2028 Chisinau, Republic of Moldova*
[b] *Institute of Applied Physics, Academy of Sciences of Moldova, Academiei str. 5, MD2028 Chisinau, Republic of Moldova*

HIGHLIGHTS

- New Schiff base resulting from isonicotinic hydrazide and 2,4-pentanedione.
- Compounds comprise novel ligand and its dehydrated derivative.
- Mononuclear octahedral complex $[Co(DfgH)_2BrL]$ with the substitution of the water molecule by new ligand.
- Co(III) complex $[Co(DmgH)_2ClL']$, where L′ represents a dehydrated derivative of L.
- The crystal structures were studied.

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ABSTRACT

New organic ligand L (**1**) resulting from isonicotinic hydrazide and 2,4-pentanedione has been prepared and investigated by physicochemical methods, including elemental analysis, ^{1}H and ^{13}C NMR, IR spectroscopy and X-ray studies.

The X-ray investigation revealed that the condensation of 2,4-pentanedione with isonicotinic hydrazide is accompanied by the formation of a five-membered ring including three carbon atoms of 2,4-pentanedione and two nitrogen atoms of the isonicotinic hydrazide fragment.

The reaction between $[Co(DfgH)_2Br(H_2O)]$ ($DfgH_2$ = diphenylglyoxime) and L resulted in the formation of the mononuclear octahedral complex $[Co(DfgH)_2BrL]$ (**2**) with the substitution of the water molecule in the apical position by the ligand L. The reaction starting from $[Co(DmgH)_2Cl(H_2O)]$ (DmgH = dimethylglyoxime) and L resulted in the mononuclear octahedral Co(III) complex with the composition $[Co(DmgH)_2ClL']$ (**3**), where L′ unexpectedly represents a dehydrated derivative of L. The two coordination compounds are characterized by X-ray diffraction method. The IR, ^{1}H NMR spectral studies of new compounds are also reported.

1. Introduction

The Schiff bases and their metal complexes have been used in various biological systems, as polymers and dyes, and as antifertility and enzymatic agents [1]. These Schiff base metal derivatives are of considerable interest, because they are used as model complexes for biological systems and thus contribute to the knowledge of their structure and behavior [2].

Recently, isonicotinic hydrazide and its derivatives have been the subject of interest to researchers of different profiles. Many of these ligands and their complexes have shown a wide spectrum of biological activity, such as antibacterial and antiviral activities; some of them have already been used in medical practice. Derivatives of isonicotinic acid and its hydrazide (INH) are well known for their highly specific antituberculous activity.

An important role in chemistry of biologically active compounds is played by transition metal dioximates. The complexation ability of -dioximes with *d*-metals attracts researchers not only for synthesis models of vitamin B_{12} [3], but also for a wide range of synthetic, analytical, and structural possibilities. Studies to obtain new materials based on transition metal complexes with a porous structure, such as biocatalysts [4,5], are carried out to synthesize coordination compounds with new composition, structure, and properties. Coordination compounds with dioximes as ligands can be mono-, di- or polynuclear [3,4,6].

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* Corresponding author. Tel.: +373 22 73 81 54; fax: +373 22 72 58 87.
E-mail address: bourosh.xray@phys.asm.md (P. Bourosh).

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Using the building blocks in the preparation of the coordination compounds, allows the assembly of complex molecules, which by straightforward pathway synthesis is more difficult. *B*is-dioxime blocks of synthesis with a water molecule in axial position, due to its liability are a successful start point for obtaining new materials, through substitution by various ligands. Often the relative liability of such group may be a major drawback to the use of this method [7].

The introduction of various organic molecules in metal complexes as ligands can significantly change their properties.

In this paper we describe the synthesis and properties of L = 2,4-pentanedione isonicotinoyl hydrazone (**1**) and its complexes with dioximates of a trivalent Co metal ion: [Co(DfgH)$_2$BrL] (**2**) and [Co(DmgH)$_2$ClL′] (**3**), where DfgH$_2$ = diphenylglyoxime, DmgH = dimethylglyoxime and L′ represents the dehydrated derivative of L.

2. Experimental

2.1. Chemicals

All chemicals were of reagent grade and used as purchased without further purification.

2.2. Syntheses of ligand and complexes

*2.2.1. Preparation of the Schiff base L (**1**)*

2,4-pentanedione isonicotinoylhydrazone (L) was prepared by reacting isonicotinic hydrazide (0.012 mol, 1.5 g) dissolved in 7 ml of C_2H_5OH with 2,4-pentanedione (0.045 mol, 1.1 ml) in 1:1 molar ratio. The reaction mixture was heated at 65 °C for 15 min. White crystals formed after 4 days. The crystals were separated by filtration, washed with ethanol and diethyl ether. Yield 1.16 g, 50%, m.p. 131–133 °C. *Anal.* Found: C, 60.30; H, 5.80; N, 18.92. Calc. for $C_{11}H_{13}N_3O_2$ (fw 219.09): C, 60.20; H, 5.90; N, 19.17.

^1H and ^{13}C NMR spectra for L: (400 MHz, $CDCl_3$), δ = 1.89 (s, 6H, CH_3), 2.83–3.01 (d, 2H, CH_2), 6.66 (s, 1H, OH) and 7.58–8.63 ppm (d, 4H, Py). (400 MHz, $CDCl_3$): δ = 16.305 (C, CH_3), 26.249 (C, CH_3), 52.342 (C, CH_2), 91.799 (C, >C=N), 122.910 (2C, Py), 144.267 (C, >C<), 149.905 (2C, Py), 156.675 (C, >C—OH), 164.849 (C, >C=O).

2.2.2. Preparation of the complexes

[Co(DfgH)$_2$BrL] (**2**) was prepared by reacting [Co(DfgH)$_2$Br(H$_2$O)] (0.001 mol, 0.64 g) dissolved under heating in 30 ml of a CH_3OH:H_2O mixture (1:1) with L (0.001 mol, 0.23 g) dissolved in 20 ml CH_3OH. The resulting mixture was heated at 70 °C for 10 min, and then the brown solution was filtered and left for slow evaporation at room temperature. The brown needle-like crystals were separated by filtration. Yield: 0.46 g, 55%. *Anal.* Found: Co, 6.84; C, 55.67; H, 4.05; N, 11.61. Calc. for $C_{39}H_{35}N_7O_6CoBr$ (fw 836.26): Co, 7.04; C, 55.99; H, 4.21; N, 11.72.

[Co(DmgH)$_2$ClL′] (**3**) was prepared by reacting [Co(DmgH)$_2$Cl(H$_2$O)] (0.001 mol, 0.34 g) dissolved under heating in 20 ml of a mixture of CH_3OH:H_2O (1:1) with L (0.001 mol, 0.23 g) dissolved in 20 ml of CH_3OH. The resulting mixture was heated at 80 °C for 10 min, then filtered and left for slow evaporation at room temperature. The brown prismatic crystals were separated by filtration. Yield: 0.32 g, 40%. *Anal.* Found: Co, 10.64; C, 41.62; H, 4.86; N, 17.92. Calc. for $C_{19}H_{27}N_7O_6CoCl$ (fw 801.38): Co, 10.83; C, 41.96; H, 5.0; N, 18.03.

2.3. Analyses and physical measurements

Elemental analyses were performed by standard micro methods. The IR spectra were obtained on a FT IR Spectrum-100 Perkin–Elmer spectrometer in Vaseline in the range of 4000–400 cm^{-1} and ATR in the range of 4000–650 cm^{-1}. Melting points were measured in a Boethius melting point apparatus and were uncorrected.

*2.4. Crystal data for **1–3***

Crystal dimensions for **1–3** are 0.30 × 0.10 × 0.10 mm, 0.20 × 0.15 × 0.10 mm and 0.25 × 0.10 × 0.10 mm respectively. Experimental data for **1** and **2** were collected on an Xcalibur CCD -axis diffractometer and a graphite monochromator using Mo Kα radiation. Experimental data for **3** were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. Frames for **3** were integrated and corrected for Lorentz and polarization effects using DENZO [8]. The scaling, as well as the global refinement of crystal parameters, was performed by SCALEPACK [8]. The absorption correction was introduced by a semi-empirical method from symmetry equivalent reflections [9]. Final unit cell dimensions for **1**–**3** were obtained and refined on an entire data set. All calculations necessary to solve the structures and to refine the proposed model were carried out with the SHELX program [10]. The non-hydrogen atoms were treated anisotropically (full-matrix least squares method on F^2). The carbon bounded H atoms were placed in calculated positions and were treated using a riding model approximations with $U_{iso}(H) = 1.2U_{eq}(C)$, while the oxygen bounded H-atoms were found from differential Fourier maps at an intermediate stage of the refinement, and their positions were constrained using the AFIX 83 instruction in SHELX for oxime and hydroxyl groups. These hydrogen atoms were refined with the isotropic displacement parameter $U_{iso}(H) = 1.5U_{eq}(O)$. The X-ray data and the details of the refinement for **1–3** are summarized in Table 1, the selected geometric parameters are presented in Table 2, and hydrogen-bonding geometry is given in Table 3.

3. Results and discussion

Condensation of isonicotinic hydrazide and 2,4-pentanedione in a molar ratio of 1: 1 resulted in the formation of a novel V-shaped organic ligand L (**1**) that consists of two cycles, the six-membered pyridine, and the five-membered hydroxyl-and-dimethyl-substituted diazole one joined *via* a carbonyl bridge (Scheme 1). An analogous cyclization was observed for the formation of pyrazoles by condensation of various 1,3-diketones and hydrazines, acylhydrazines or sulfonyl hydrazines, described in [11].

During the condensation, one azomethine C=N bond and C—N bonds between each carbonyl groups of 2,4-pentanedione and isonicotinic hydrazide NH$_2$— and —NH— group were formed. One water molecule saturated the double bond —CH=C(CH$_3$)— of 2,4-pentanedione fragment, so the addition of one hydroxyl group at the carbon atom >C(CH$_3$)— took place. The ligand was isolated as air-stable white needle-like crystals which are soluble in chloroform, DMF, dimethylsulfoxide, ethanol, and methanol, and low soluble in water, hexane, and diethyl ether (melting point 131–133 °C).

The product was characterized using elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy, which confirmed the formation of a cycle composed of five atoms: three carbon atoms of acetylacetone and two nitrogen atoms of the isonicotinic hydrazide fragment, which is in agreement with the formulas in Scheme 1.

New mononuclear octahedral cobalt(III) complexes [Co(DfgH)$_2$BrL] (**2**) (Fig. 2) and [Co(DmgH)$_2$ClL′] (**3**) (Fig. 3) have been synthesized by interaction of previously obtained [Co(DfgH)$_2$Br(H$_2$O)] (DfgH$_2$ = diphenylglyoxime) or [Co(DmgH)$_2$Cl(H$_2$O)] (DmgH$_2$ = dimethylglyoxime) [7] with 2,4-pentanedione isonicotinoylhydrazone (**1**) in a basic methano-

Table 1
Crystal data and structure refinement parameters for **1–3**.

	1	**2**	**3**
Empirical formula	$C_{11}H_{13}N_3O_2$	$C_{39}H_{35}Br_1Co_1N_7O_6$	$C_{19}H_{25}Cl_1Co_1N_7O_5$
Formula weight	219.24	836.58	525.84
Temperature (K)	293(2)	293(2)	100(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	*P* − 1	$P2_1/a$
Z	8	2	4
Unit cell dimensions			
a (Å)	10.8965(8)	11.4105(9)	13.6760(3)
b (Å)	13.2845(8)	14.3341(10)	10.9670(4)
c (Å)	15.2176(9)	14.4005(11)	15.0540(5)
α (°)	90	109.116(7)	90
β (°)	90	111.750(7)	99.8240(9)
γ (°)	90	99.581(6)	90
Cell volume (Å^3)	2202.8(2)	1952.7(3)	2224.8(1)
D_{calc} (g cm^{-3})	1.322	1.423	1.570
μ (mm^{-1})	0.094	1.517	0.939
F (000)	928	856	1088
Reflections collected/unique	6355/2047	9994/7219	14,417/4128
Reflections with ($I>2\sigma(I)$)	1582	2819	3834
Parameters	145	487	289
R_1, wR_2[$I>2\sigma(I)$]	0.0415, 0.1247	0.0402, 0.0702	0.0436, 0.1104
R_1, wR_2(all data)	0.0541, 0.1297	0.1316, 0.0939	0.0475, 0.1130

lic medium under heating, L′ unexpectedly represents a dehydrated derivative of L .

In complexes **2** and **3**, the water molecule from the apical position was substituted by L/L′ ligands (Scheme 2).

Complexes were isolated as air-stable brown needle-like crystals for **2** and brown prisms for **3**. They are soluble in DMF and DMSO, less soluble in water and insoluble in ethanol and methanol. The complexes are neutral with the metal charge entirely neutralized by the Br^- and Cl^- anions. In each case, the products were characterized using IR spectroscopy and elemental analysis. Complexes **2** and **3** were also analyzed by ^{1}H and ^{13}C NMR spectroscopy. The structure of compounds **1**–**3** was determined using X-ray analysis.

3.1. Infrared spectra

The IR spectrum of isonicotinic hydrazide exhibits amide group frequencies at 1660, 1550, and 1220 cm^{-1}. In the IR spectrum of L (**1**), a strong band at 1623 cm^{-1} is observed, which may be assigned to (C=O) of the isonicotinic group stretching vibrations, and three bands at 3110, 2972, and 1314 cm^{-1} assignable to the aliphatic hydrogen-bonded OH group ν (OH), ν(=C—H) and ν(C—O), respectively. The band at 1330 cm^{-1} may be assigned to the bending vibrations of the NH group. The bands at 1407 and 1443 cm^{-1} can be attributed to vibrations ν(CH_2) and ν(C=C), respectively. The absence of bands at 3150–3400 cm^{-1} in the IR spectrum of L indicates that the NH_2 group reacts with the aldehyde.

The IR spectrum of **2** contains a band at 3675 cm^{-1} attributable to the stretching vibrations of the free O—H bond. The bands at 2988, 2972, and 2901 cm^{-1} can be attributed to vibrations $\nu_s(CH_2)$, $\nu_s(CH_3)$ and $\nu_{as}(CH_3)$. The presence of the dioximic ligands proven by the bands $\nu(C{=}N)_{oxime}$ at 1630, ν(NO) at 1289 and 1134, γ(OH) at 967, ν(CNO) at 736, ν_{as} (Co—N) at 509 and ν_s(Co—N) at 440 cm^{-1}. The bands in the region 1443 and 1378 cm^{-1} are attributed to vibrations of δ(CH_3). Aromatic ring vibrations are characterized by the bands at 1486, 1027, and 892 cm^{-1}.

The IR spectrum of complex **3** shows the absorption of the monodeprotonated DmgH ligand in the region of 1646 cm^{-1}, which can be attributed to the $\nu(C{=}N)_{oxim}$ group, at 1241 of $\nu(NO)_{ionizate}$ and 1090 cm^{-1} of $\nu(OH)_{DH}$, 724 of δ(CNO), 513 of ν_{as}(Co—N) and 435 cm^{-1} characteristic of ν_s(Co—N) bond. The band at 1563 cm^{-1} can be attributed to the stretching vibrations of C=C bonds of the aromatic fragment and the band with medium intensity at 1711 cm^{-1} to the ketone group. The bands at 1423 and 1381 cm^{-1} correspond to bending vibrations of the methyl groups.

3.2. ^{1}H and ^{13}C NMR spectra

The ^{1}H NMR and ^{13}C NMR spectra of L in $CDCl_3$ solutions showed the presence of all atoms of hydrogen and carbon predicted by molecular formula **1** (Fig. 1).

In the ^{1}H NMR spectra of L solution in $CDCl_3$, eight groups of signals were recorded, which were attributed to protons of two CH_3 groups δ = 2.83–3.01 (d) ppm, one OH group δ = 1.89 (s) ppm, one CH_2 group δ = 6.66 (s) ppm and four signals of hydrogen atoms of the pyridine cycle belonging to δ = 7.58–8.63 ppm.

The ^{13}C NMR spectra data (DEPT135, HMBC, HMQC) of L solution in $CDCl_3$ indicate the presence of 11 carbon atoms at δ = 16.305 (C, CH_3), 26.249 (C, CH_3), 52.342 (C, CH_2), 91.799 (C, >C=N), 122.910 (2C, Py), 144.267 (C, >C<), 149.905 (2C, Py), 156.675 (C, >C—OH), 164.849 (C, >C=O).

In the ^{1}H NMR spectrum of complex **2** the following data may be assigned to signals of ligand L: 1.83 ppm (CH_3), 2.81–3.01 ppm (CH_2), 6.79 ppm (OH), 7.76, 8.42 ppm (pyridine ring). The signals at 7.14–7.39 ppm indicate the presence of diphenylglyoxime benzene rings.

In the ^{1}H NMR spectrum for **3**, the signal from 2.34 ppm is assigned to the methyl groups and is slightly shifted compared to the uncoordinated ligand field. The signal at 18.44 ppm corresponds to protons of the OH oxime groups and indicates the formation of hydrogen bonds between the two monoanions of dioxime.

3.3. Description of structures

The CSD [12] revealed the structure of only one related compound, 5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-l [13], which has been synthesized by addition of isoniazide to a solution of benzoylacetone. In addition to this compound in CSD [12] there are structures of two derivatives of pyrazol-1-yl) (pyridinyl) methanone [14,15] and structures of two ferrocenyl compounds containing ligands of this class [16,17]. Single crystal

Table 2
Selected bond distances and angles for **1-3**.

	1	**2**	**3**
Co(1)—N(1)	–	1.980(4)	1.967(2)
Co(1)—N(4)	–	1.880(4)	1.904(2)
Co(1)—N(5)	–	1.897(4)	1.918(2)
Co(1)—N(6)	–	1.890(4)	1.883(2)
Co(1)—N(7)	–	1.891(4)	1.889(2)
Co(1)—Br(1)/Cl(1)	–	2.3792(9)	2.2318(7)
O(1)—C(6)	1.228(2)	1.224(5)	1.204(4)
O(2)—C(7)	1.396(2)	1.392(7)	–
N(1)—C(1)	1.330(2)	1.342(5)	1.350(4)
N(1)—C(5)	1.327(2)	1.325(5)	1.351(4)
N(2)—N(3)	1.398(2)	1.406(5)	1.389(4)
N(2)—C(6)	1.352(2)	1.326(6)	1.382(4)
N(2)—C(7)	1.507(2)	1.502(6)	1.403(4)
N(3)—C(9)	1.278(2)	1.271(6)	1.321(4)
O(3)—N(4)	–	1.338(5)	1.352(3)
O(4)—N(5)	–	1.333(4)	1.354(3)
O(5)—N(6)	–	1.336(4)	1.335(3)
O(6)—N(7)	–	1.330(4)	1.336(3)
N(4)—C(12)	–	1.308(6)	1.290(3)
N(5)—C(13)	–	1.305(5)	1.296(3)
N(6)—C(14)	–	1.304(5)	1.301(4)
N(7)—C(15)	–	1.295(5)	1.302(4)
C(1)—C(2)	1.384(2)	1.375(6)	1.387(4)
C(2)—C(3)	1.386(2)	1.378(6)	1.383(4)
C(3)—C(4)	1.389(2)	1.386(6)	1.386(4)
C(3)—C(6)	1.509(2)	1.506(6)	1.511(4)
C(4)—C(5)	1.375(2)	1.380(6)	1.381(4)
C(7)—C(8)	1.533(2)	1.518(7)	1.362(5)
C(7)—C(11)	1.508(2)	1.504(8)	1.484(5)
C(8)—C(9)	1.476(2)	1.477(7)	1.415(4)
C(9)—C(10)	1.484(2)	1.488(7)	1.493(4)
C(12)—C(13)	–	1.466(6)	1.472(4)
C(14)—C(15)	–	1.469(6)	1.469(5)
N(1)—Co(1)—Br(1)/Cl(1)	–	178.4(1)	176.91(6)
N(4)—Co(1)—N(1)	–	92.3(2)	92.29(9)
N(4)—Co(1)—N(5)	–	81.5(2)	80.25(9)
N(4)—Co(1)—N(6)	–	176.8(2)	178.25(90)
N(4)—Co(1)—N(7)	–	98.3(2)	98.45(10)
N(4)—Co(1)—Br(1)/Cl(1)	–	89.0(1)	90.80(7)
N(5)—Co(1)—N(1)	–	91.1(2)	92.10(9)
N(5)—Co(1)—N(6)	–	98.8(2)	98.69(10)
N(5)—Co(1)—N(7)	–	179.8(2)	177.52(9)
N(5)—Co(1)—Br(1)/Cl(1)	–	90.1(1)	88.41(7)
N(6)—Co(1)—N(1)	–	91.0(2)	89.14(9)
N(6)—Co(1)—Br(1)/Cl(1)	–	87.8(1)	87.77(7)
N(7)—Co(1)—N(1)	–	88.9(2)	90.06(9)
N(7)—Co(1)—N(6)	–	81.04(2)	82.55(10)
N(7)—Co(1)—Br(1)/Cl(1)	–	89.9(1)	89.50(7)
C(1)—N(1)—C(5)	116.3(1)	117.9(4)	118.3(2)
Co(1)—N(1)—C(1)	–	121.4(3)	121.3(2)
Co(1)—N(1)—C(5)	–	120.6(3)	120.3(2)
C(6)—N(2)—N(3)	122.9(1)	121.4(4)	118.3(2)
C(6)—N(2)—C(7)	124.3(1)	125.5(4)	130.7(3)
N(3)—N(2)—C(7)	112.8(1)	112.0(4)	111.0(2)
N(2)—N(3)—C(9)	107.9(1)	108.1(4)	104.9(2)
O(3)—N(4)—C(12)	–	120.5(4)	119.1(2)
Co(1)—N(4)—O(3)	–	123.0(3)	123.1(2)
Co(1)—N(4)—C(12)	–	116.4(3)	117.7(2)
O(4)—N(5)—C(13)	–	121.3(4)	119.5(2)
Co(1)—N(5)—O(4)	–	121.6(3)	123.4(2)
Co(1)—N(5)—C(13)	–	117.0(3)	116.9(2)
O(5)—N(6)—C(14)	–	121.3(4)	122.5(2)
Co(1)—N(6)—O(5)	–	122.1(3)	122.0(2)
Co(1)—N(6)—C(14)	–	116.6(3)	115.4(2)
O(6)—N(7)—C(15)	–	121.5(3)	122.1(2)
Co(1)—N(7)—O(6)	–	121.7(3)	122.0(2)
Co(1)—N(7)—C(15)	–	116.8(3)	115.9(2)
N(1)—C(1)—C(2)	124.5(2)	122.0(4)	122.4(3)
C(1)—C(2)—C(3)	118.6(2)	120.2(4)	119.0(3)
C(2)—C(3)—C(4)	117.1(1)	117.6(5)	119.1(3)
C(2)—C(3)—C(6)	126.3(1)	119.7(5)	122.2(3)
C(4)—C(3)—C(6)	116.2(1)	122.5(5)	118.7(3)
C(5)—C(4)—C(3)	119.7(2)	119.0(4)	119.1(3)
N(1)—C(5)—C(4)	123.8(2)	123.3(4)	122.3(3)
O(1)—C(6)—N(2)	120.7(1)	122.6(5)	123.8(3)
O(1)—C(6)—C(3)	118.3(1)	119.5(5)	122.1(3)
N(2)—C(6)—C(3)	121.0(1)	117.8(5)	114.1(3)
N(2)—C(7)—C(8)	99.9(1)	99.7(4)	105.5(3)
N(2)—C(7)—C(11)	110.9(1)	111.3(5)	123.4(3)
C(11)—C(7)—C(8)	113.2(1)	114.3(6)	130.8(3)
O(2)—C(7)—N(2)	110.5(1)	108.6(5)	–
O(2)—C(7)—C(11)	113.0(1)	113.0(5)	–
O(2)—C(7)—C(8)	108.6(1)	109.0(6)	–
C(9)—C(8)—C(7)	104.6(1)	105.0(5)	107.0(3)
C(8)—C(9)—C(10)	122.9(1)	124.6(5)	128.3(3)
N(3)—C(9)—C(8)	114.8(1)	113.9(5)	111.6(3)
N(3)—C(9)—C(10)	122.3(1)	121.4(5)	120.3(3)
N(4)—C(12)—C(13)	–	113.4(4)	112.5(2)
N(5)—C(13)—C(12)	–	111.4(4)	112.6(2)
N(6)—C(14)—C(15)	–	113.5(3)	113.6(2)
N(7)—C(15)—C(14)	–	112.7(4)	112.5(3)

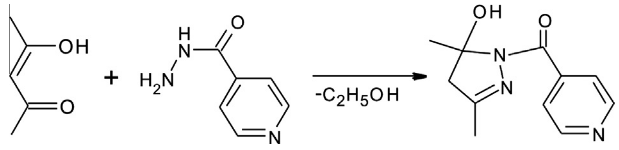
X-ray structure study of compound **1** established that it differs from the nearest compound [13] by the substituent at position 5 of the pyrazole. (5-Hydroxy-3,5-dimethyl-4,5-dihydro-1H-pyrazol-1-yl)(pyridin-4-yl)methanone **1** is a chiral molecule which contain two heterocyclic rings (Fig. 1).

The dihedral angle between the mean planes of the pyrazole and pyridine rings equals to 29.6°. The five-membered ring is almost planar (±0.018 Å), with the C(10) atom whose deviation does not exceed −0.015 Å, and the deviations of the O(2) and C(11) atoms from this plane are 1.151 and −1.269 Å. This structure provides a -coupling between the aromatic system and other fragments of the molecule, although the interatomic distance between C(3) and C(6) atoms is not greatly reduced (1.509(2) Å). The X-ray investigation revealed that formation of L is the result of condensation of 2,4-pentanedione with isonicotinic hydrazide. The same form is found in [13], in which the values of interatomic distances N(2)—N(3), N(2)—C(7), N(3)—C(9), C(7)—C(8), and C(8)—C(9) are 1.408, 1.501, 1.270, 1.537, and 1.483 Å according to the numbering in Fig. 1. However, in [13] the dihedral angle of the mean plane of the pyrazole ring with the pyridine ring equals to 45.0°, and the deviation of the atoms from mean plane of the five-membered ring is ±0.047 Å, while C(10) atom is slightly deviated from the plane (−0.058 Å), and the deviations of the O(2) and C(11) atoms are −1.267 and 1.095 Å. The interatomic distances C(6)—O(1) in **1** and in (5-hydroxy-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)(pyridin-4-yl)methanone monohydrate [13] are 1.228(2) and 1.229 Å, respectively, and indicate in favor of double bond, and the values found for C(6)—N(2) and C(6)—C(3) (1.352(2), 1.509(2) in **1** and 1.345, 1.502 Å in [13]) are also slightly different. In this case, at the C(6) atom, a slight difference was observed in both the valence angles N(2)C(6)C(3)–121.0(1) in **1** and 119.8° in [13] and torsion angles C(6)N(2)C(7)O(2) 64.1(1) in **1** and 64.9° in 5-(5-hydroxy-3-methyl-1-(4-pyridylcarbonyl)-5-trifluoromethyl-2(Z)-pyrazoline-4-ylidenehydrazino)-1H-4-(ethoxycarbonyl)pyrazole [14] and C(6)N(2)C(7)C(11) –62.0(1) in **1** and 56.7° in [13]. Therefore, it was revealed that there are steric hindrances determined by the formation of a rigid intramolecular hydrogen bond O(2)—H···O(1) (Table 3) in [13].

Thus, geometry of **1** (Fig. 1) does not differ from that found in [2], but a similar V-shaped conformation of the ligand during complexation, provides its coordination to transition metal ions in both monodentate and chelate modes with the formation of metallocycles or executing a bridging function, using donor atoms N(1), N(3), O(1) and O(2). It is known that derivatives of pyridinecarboxylic acids, which have, along with the nitrogen atom of the pyridine ring, other donor groups, reveal the different coordination modes to the metal depending on the environment, the nature of the complexating metal, and competing ligands.

Table 3
Hydrogen bond distances (Å) and angles (°) for **1–3**.

D—H···A	d(D—H)	d(H···A)	d(D···A)	(DHA)	Symmetry transformation for acceptor
1					
O(2)—H(2A)···O(1)	0.82	2.57	3.043(2)	118	*x*, *y*, *z*
O(2)—H(2A)···N(1)	0.82	2.14	2.860(2)	146	$-x + 1/2$, $-y$, $z + 1/2$
2					
O(2)—H(2A)···O(1)	0.82	1.99	2.800(5)	168	$-x + 1$, $-y + 1$, $-z - 1$
O(4)—H(4)···O(5)	0.82	1.68	2.474(4)	164	*x*, *y*, *z*
O(6)—H(6)···O(3)	0.82	1.67	2.465(4)	164	*x*, *y*, *z*
3					
O(3)—H(3A)···O(6)	0.82	1.70	2.489(3)	161	*x*, *y*, *z*
O(4)—H(4A)···O(5)	0.82	1.73	2.514(3)	160	*x*, *y*, *z*



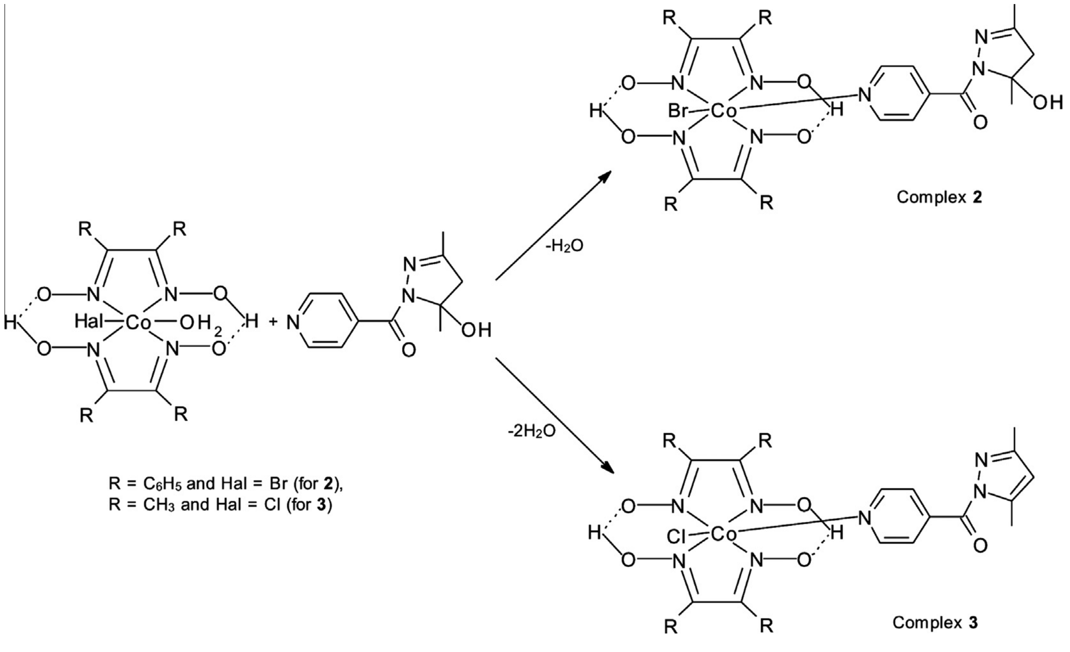
Scheme 1. Mode of formation V-shaped organic ligand L (**1**).

In addition, on the basis of the CSD study [12], it was revealed that this type of ligands coordinate to the metal ion mainly via the nitrogen atom of the heterocycle. In catena-(bis(μ$_2$-isonicotinamide)-(phthalato)-di-silver(I) trihydrate) complex [18] the isonicotinamide ligand coordinates by N, O donor atoms to two different metal atoms as a bridging linker, but in the Mn(II) complex catena-(bis(μ$_2$-isonicotinehydrazido)-(isonicotinehydrazido)-triaquachloro-di-manganese trichloride isonicotinehydrazide solvate) [19] it coordinates through the isonicotinehydrazido set of O,N,N atoms and 2-pyridine-2-carbaldehyde(isonicotinoyl) hydrazone) in the bis(μ$_2$-pyridine-2-carbaldehyde(isonicotinoyl) hydrazone)-hexachlorotetrakis(dimethylsulfoxide)-tri-manganese(II) complex [20]. Involvement in the coordination through two atoms resulting in a five-membered metallocycle is ensured by different rotations around single bonds. But, in most cases, the isonicotinamide derivatives coordinate in a monodentate mode via the nitrogen atom of the heterocycle.

In the formation of the crystal structure it is important zig–zag chains generation along the *c* axis in which the main one is the hydrogen bond O(2)—H···N(1) ($-x + 1/2$, $-y$, $z + 1/2$), O(2)···N(1) 2.860(2) Å (Table 3 and Fig. 2). The structure also provided a weak hydrogen bond which stabilizes this chain and a weaker hydrogen bond C(8)—H(1)···O(1) ($-x + 1/2$, $y + 1/2$, z) (C(8)···O(1) 3.526(5) Å) which is responsible for the binding of these chains into layers along the crystallographic *a* axis.

The asymmetric units of **2** and **3** comprise halogen dioximates of Co(III) with L and L′ (Figs. 3 and 4). The structures of molecular complexes **2** and **3** fall into the Chugaev's class of compounds [21] with the general formula [MX(DioxH)$_2$A], where M is Co(III) ion, DioxH$^-$ is the charged residue of α-dioxime (dimethylglioximate-ion DmgH$^-$, 1,2-cyclohexanedionedioximate ion NioxH$^-$ or α-benzyldioximate ion DfgH$^-$), A is a neutral molecule derived from isonicotinic hydrazide (L or L′), X is the monoanion Br$^-$ or Cl$^-$.

The structure of Cu(II) dimethylglyoximate with isonicotinamide [Cu(DmgH)$_2$(Inia)] [22], Fe(II) α-benzildioximates with nicotinamide and ethyl ester of isonicotinic acid [Fe(DfgH)$_2$(3-CONH$_2$-Py)$_2$] and [Fe(DfgH)$_2$(4-COOC$_2$H$_5$-Py)$_2$] [23], dimethylglyoximates and 1,2-cyclohexanedionedioximates Co(II) and Co(III) with isonicotinamide [Co^{II}(DmgH)$_2$(Inia)$_2$], [Co^{III}(DmgH)$_2$(Inia)$_2$][PF$_6$], [Co^{III}(NioxH)$_2$(Inia)$_2$][PF$_6$] and [Co^{III}Cl(DmgH)$_2$(Inia)] Inia-isonicotinamide [24] and dimethylglyoximates Co(III) with



Scheme 2. Synthesis of complexes **2** and **3**.

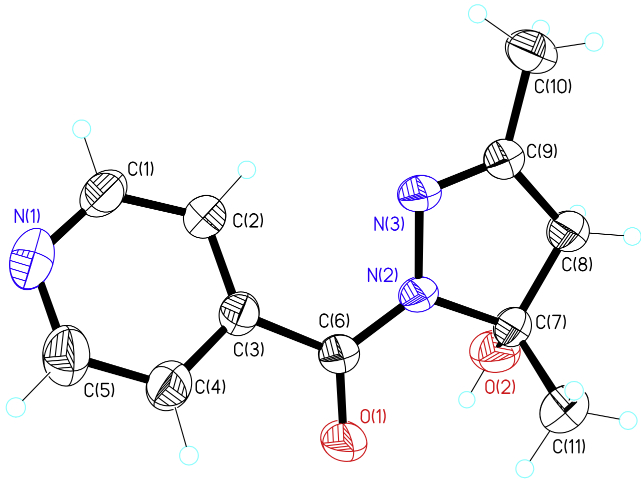


Fig. 1. ORTEP drawing for new organic molecule **1** with a numbering scheme. Thermal ellipsoids are shown at a 50% probability level.

isonicotinic acid (Ina) $[Co^{III}Cl(DmgH)_2(Ina)]$ were previously described [25,26].

Molecular complexes of Co(III) (**2** and **3**) have a typical octahedral coordination of the metal atom (Figs. 3 and 4). The chelate type coordination via nitrogen atoms of $DfgH^-$ or $DmgH^-$ is present in the equatorial plane of both complexes. Two dioxime residues are combined through intramolecular O—H···O hydrogen bonds (O···O 2.475(3) and 2.465(3) in **2**, 2.489(3) and 2.514(3), in **3**, Table 3) in a pseudomacrocyclic system. The interatomic distances Co—N (DfgH/DmgH) in complexes **2** and **3** (1.880(3)–1.892(3) and 1.883(2)–1.918(2) Å respectively) are consistent with those in the complexes of Co(III) (in $[CoCl(DmgH)_2(Inia)]$ [24] Co—N 1.885(1)–1.908(1) Å). Despite the organic molecules L/L′ have several donor centers, both ligands act as monodentate neutral ligands and coordinate with the metal atom by the nitrogen atom of the pyridine fragment.

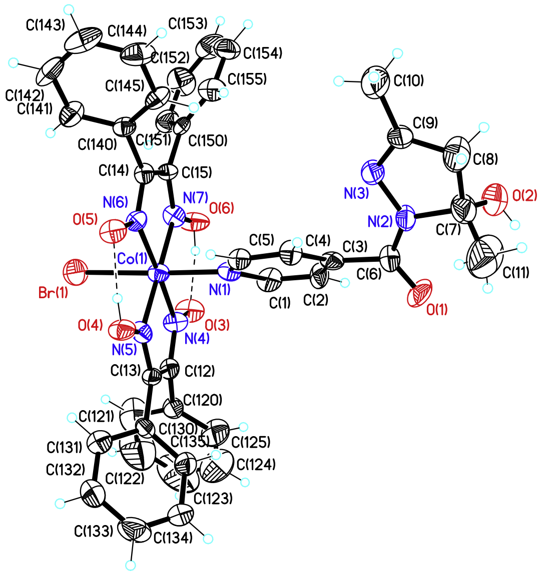


Fig. 3. ORTEP drawing for **2** with a numbering scheme and the shortest intramolecular O···O distances shown by dashed lines. Thermal ellipsoids are shown at a 50% probability level.

Thus, the coordination polyhedron of the central metal ion is completed to an octahedron by nitrogen atoms of L/L′ molecules and Br^-/Cl^- anions. The interatomic distances Co—N (L/L′) significantly depend on the types of atoms which are in the *trans*-apical position: Co—N (L/L′ 1.980(3) and 1.967(2) Å in **2** and **3**. In this case, the *trans*-position to L in **2** is occupied by Br^- ion, but in **3** the *trans*-position to the L′ is Cl^- ion. These interatomic distances are consistent with those found in dioximates of cobalt(III) with monodentate pyrazine (Pz), pyrazincarboxamide (Pzca) and isonicotinamide (Co(1)—N(Pz) 1.957(2), Co(1)—Cl(1) 2.2428(7) Å in $[CoCl(DmgH)_2(Pz)]$ [27]; Co(1)—N(Pzca) 1.998(3), Co(1)—Br(1) 2.3703(6) Å in $[CoBr(DfgH)_2(Pzca)]$, Co(1)—N(Pzca) 1.968(2), Co(1)—Cl(1) 2.2221(8) Å in $[CoCl(NioxH)_2(Pzca)]$ and

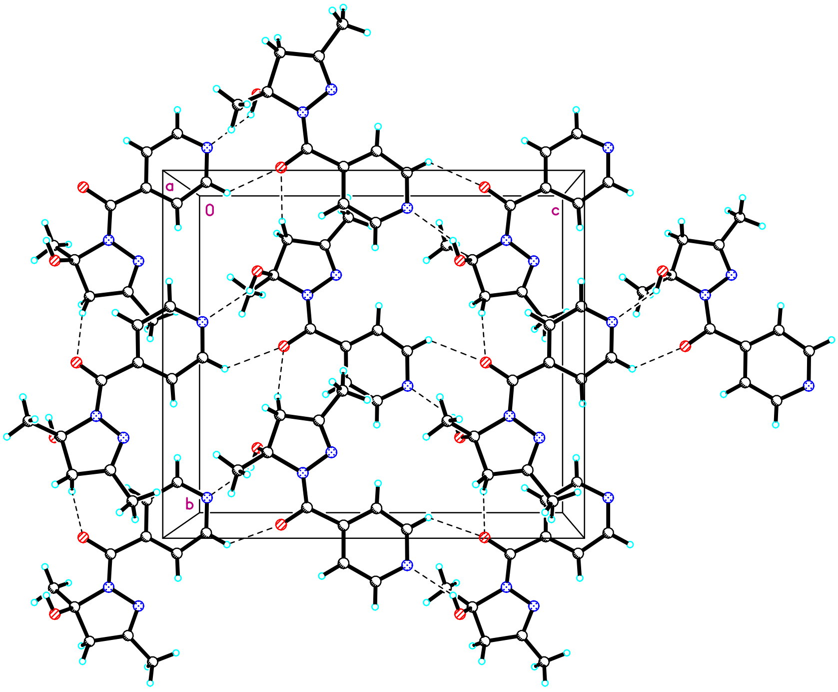


Fig. 2. Fragment of crystal packing in **1**. The hydrogen bonds O—H···N formed zig–zag chains along the *c* axis (shortest intramolecular C—H···O distances are shown by dashed lines).

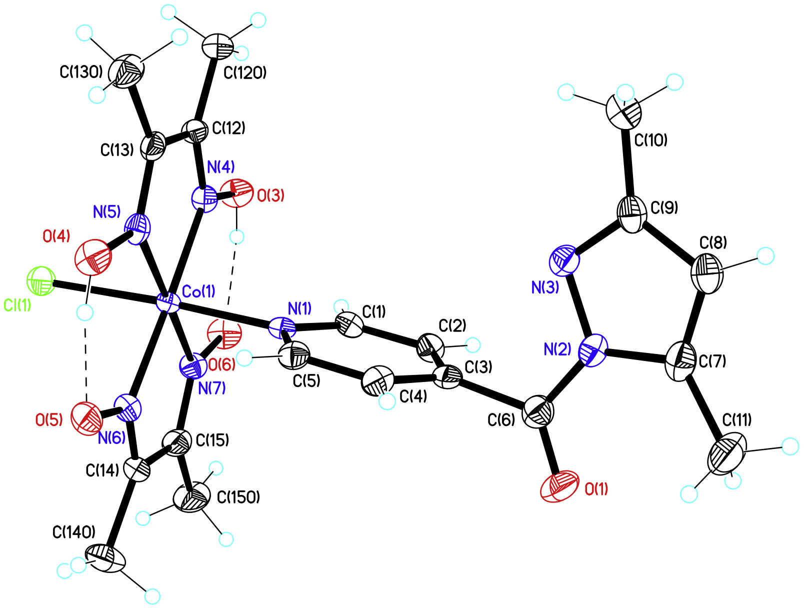


Fig. 4. ORTEP drawing for **3** with a numbering scheme. Shortest intramolecular O···O distances are shown by dashed lines. Thermal ellipsoids are shown at a 50% probability level.

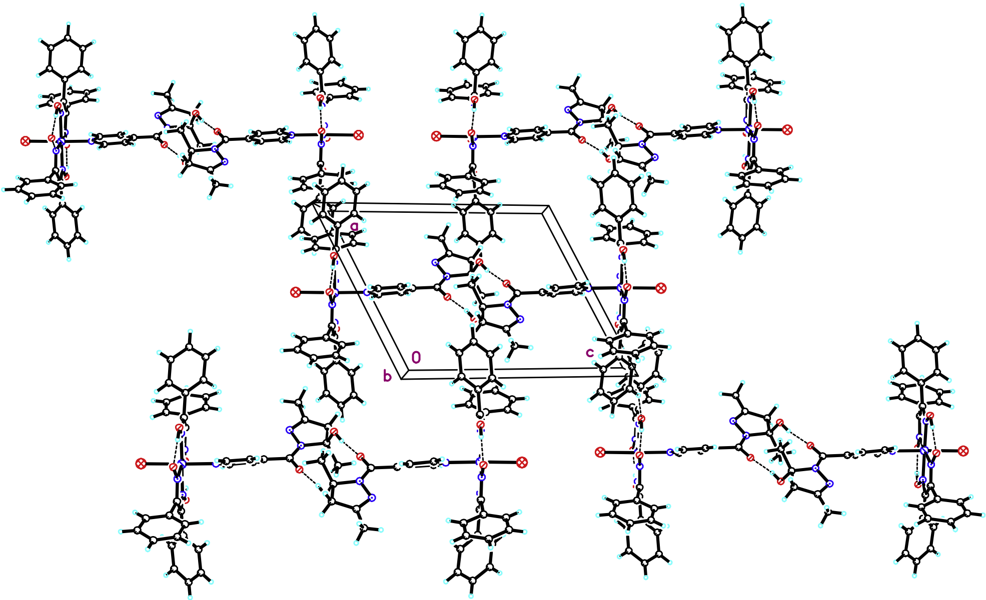


Fig. 5. Fragment of crystal packing in **2**. The centrosymmetric dimers formed by O—H···O hydrogen bond shown by dashed lines.

Co(1)—N(Pzca) 1.968(3), Co(1)—Cl(1) 2.227(1) Å in [CoCl(DmgH)(NioxH)(Pzca)] [28], Co—N(Inia) 1.956(1), Co(1)—Cl(1) 2.2426(4) Å in [Co^{III}Cl(DmgH)$_2$(Inia)] [24]).

The oxidation state +3 of the cobalt ion in **2** and **3** is demonstrated by Co—N and Co—Cl/Br bond lengths. Due to the stabilization of charges, these two dioxime ligands coordinate in a bidentate mode and thus lead to the formation of a five-membered chelate ring around the metal core, which can be stabilized both in a monodeprotonated mode and in a different way: one is neutral, the other is bideprotonated. The L/L′ coordinates only in a neutral mode.

The N—O bond lengths of DfgH and DmgH ligands reveal the monodeprotonated coordination mode of DfgH$^-$ in **2** (O(3)—N(4) 1.341(3), O(4)—N(5) 1.337(3), O(5)—N(6) 1.331(3) and O(6)—N(7) 1.341(3) Å, Table 2 and Fig. 3) and a different mode for DmgH$_2$ and Dmg^{2-} in **3** (O(3)—N(4) 1.352(3), O(4)—N(5) 1.354(3), O(5)—N(6) 1.335(3) and O(6)—N(7) 1.336(3) Å, Table 2 and Fig. 3). In **2** and **3**, the N=C and C—C interatomic distances in oximic ligands (Table 2) are characteristic of metallocycles that are formed in a chelating coordination mode of -dioximes. These data indicate that the composition for compound **3** is [CoCl(Dmg)(DmgH$_2$)(L′)], as in a similar complex with isonicotinamide [24].

A rigorous analysis of interatomic distances of *trans*-apical ligands from the cobalt and halogen atoms (Br/Cl) in **2** and **3** (Figs. 3 and 4 and Table 2) reveals the stabilization of L and L′ ligands; the L′ in **3** is in dehydrated form of L. In the five-membered ring are the following atom distances: N(2)—N(3) 1.404(4), N(2)—C(7) 1.502(5), N(3)—C(9) 1.272(4), C(7)—C(8) 1.519(5) and C(8)—C(9) 1.466(5) Å

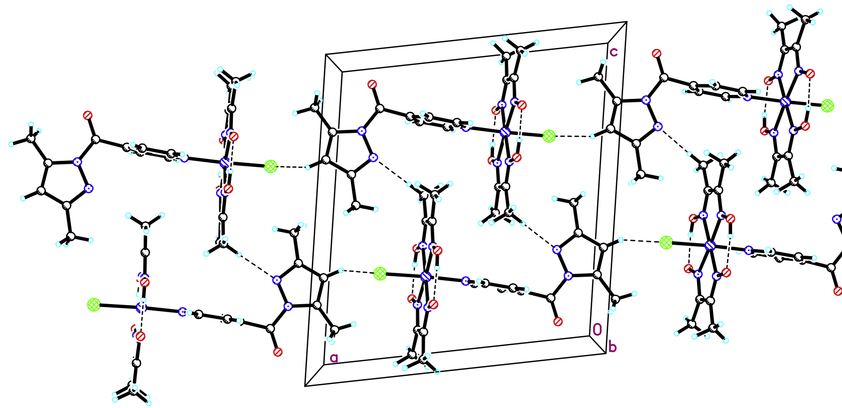


Fig. 6. Fragment of crystal packing in **3**. The chains along the crystallographic *a* -axis formed by C—H···Cl bonds, which are linked in layers along the *c*-axis by the C—H···N bonds shown by dashed lines.

in **2** and N(2)—N(3) 1.389(4), N(2)—C(7) 1.403(4), N(3)—C(9) 1.321(4), C(7)—C(8) 1.362(5) and C(8)—C(9) 1.415(4) Å in **3**. The C(6)—O(1) interatomic distances in **2** and **3** are equal to 1.224(4) and 1. 204(4) Å, which show the double nature of this bond. The values found for C(6)—N(2) and C(6)—C(3) (1.331(4), 1.506(5) in **2** and 1.382(4), 1.511(4) Å in **3**) are slightly different. However, there is a small difference in the valence angles N(2)C(6)C(3)—117.0(4) in **2** and 114.1(3)° in **3**. The mean deviations from the mean planes of the five-membered ring in **2** is ±0.065 Å (the C(10) atom deviation from the mean plane is -0.074 Å, but the O(2) and C(11) shifts -1.353 and 1.009 Å), while in **3** the ring is almost planar, ±0.003 Å (the C(10) and C(11) atoms slightly deviate from the mean plane at 0.043 and 0.134 Å). The torsion angles C(6)N(2)C(7)O(2) and C(6)N(2)C(7)C(11) in **2** are 64.5 and $-60.2°$ and were similar in **1**, but in **3** the angle C(6)N(2)C(7)C(11) is $-6.2°$.

The dihedral angle between the pyridine and diazole rings is 49.5° in L (in **2**), but the dihedral angle between these cyclic units is 88.8° in L′ (in **3**). These differences affect the crystal packing in **2** and **3**.

In compound **2**, the L ligands of two different complexes are joined into a centrosymmetric dimer by the O(2)—H···O(1) $(-x+1, -y+1, -z-1)$ intermolecular hydrogen bonds (Table 3 and Fig. 5). In the crystal, the dimers are linked only through weak intermolecular hydrogen-bond interactions C—H···O(oxime): C(4)—H···O(5) $(-x+1, -y+2, -z)$ (donor···acceptor 3.190 Å), C(2)—H···O(3) $(-x+1, -y+1, -z)$ (donor···acceptor 3.157 Å) и C(152)—H···O(6) $(-x, -y+1, -z)$ (donor···acceptor 3.352 Å).

The absence of classic donor functional groups in complex **3**, except for oxime hydroxyl groups, which are involved in the formation of intramolecular hydrogen bonds O(oxime)—H···O(oxime), suggests that there are weak interactions of the components in the crystal. The analysis of the possible weak interactions identified several C—H···O, C—H···N, C—H···Cl hydrogen bonds, which involve all four oxime oxygen atoms, one nitrogen atom of the pyrazole ring, and the coordinated chloride ion as proton acceptors: C(10)—H···O(3) $(x+1/2, -y+3/2, z)$ (donor···acceptor 3.289 Å), C(8)—H···O(4) $(x+1/2, -y+5/2, z)$ (donor···acceptor 3.365 Å), C(4)—H···O(5) $(x+1/2, -y+5/2, z)$ (donor···acceptor 3.323 Å), C(2)—H···O(6) $(x+1/2, -y+3/2, z)$ (donor···acceptor 3.341 Å), C(12)—H···N(3) $(-x, -y+2, -z+1)$ (donor···acceptor 3.413 Å) and C(8)—H···Cl(1), $(x+1, y, z)$ (donor···acceptor 3.458 Å). Finally, in crystal **3** can be identified two chains formed along the crystallographic *a*-axis by C—H···Cl bonds, which are linked in layers along the *c*-axis by the C—H···N bonds (Fig. 6). The C—H···O(oxime) hydrogen bonds are involved to connect these layers into a 3D network.

4. Conclusions

The interaction of isonicotinic acid hydrazide with 2,4-pentanedione (enolic form) in a molar ratio of 1:1 represents a double process of the condensation-cyclization, resulted in the formation of a Schiff base a novel V-shaped organic ligand L which contains a five-membered cycle with two nitrogen and three carbon atoms. In the condensation process are involved —NH$_2$ groups of hydrazide and >C=O groups of 2,4-pentanedione, while in the cyclization process – the —NH group of hydrazide and C—OH group of 2,4-pentanedione fragment.

In cobalt(III) α-benzyldioximate complex, the Schiff base L coordinates to the metal without chemical modification. In dimethylglyoximate complex, ligand L undergoes modifications, which can be regarded as dehydratation process on C(7)—C(8) bond (Fig. 1), resulting in another double bond in the Schiff base cycle with generation L′.

The ligands L and L′ contain potential five and four electron donor atoms, respectively, but both coordinate to the metal ion through the nitrogen atom of the pyridine heterocycle, which shows a higher affinity relative to examined cobalt dioximates.

Supplementary material

Crystallographic data for **1**–**3** have been deposited with the Cambridge Crystallographic Data Center, CCDC 947227-947229. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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