



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



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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, ¹H and ¹³C 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(H₂O)] (DfgH₂ = 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(H₂O)] (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, ¹H NMR spectral studies of new compounds are also reported.

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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 B₁₂ [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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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. Bis-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: $[\text{Co}(\text{DfgH})_2\text{BrL}]$ (**2**) and $[\text{Co}(\text{DmgH})_2\text{CIL}']$ (**3**), where $\text{DfgH}_2 =$ diphenylglyoxime, $\text{DmgH} =$ 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 $\text{C}_2\text{H}_5\text{OH}$ 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 $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_2$ (fw 219.09): C, 60.20; H, 5.90; N, 19.17.

^1H and ^{13}C NMR spectra for L : (400 MHz, CDCl_3), $\delta = 1.89$ (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): $\delta = 16.305$ (C, CH_3), 26.249 (C, CH_3), 52.342 (C, CH_2), 91.799 (C, $>\text{C}=\text{N}$), 122.910 (2C, Py), 144.267 (C, $>\text{C}<$), 149.905 (2C, Py), 156.675 (C, $>\text{C}-\text{OH}$), 164.849 (C, $>\text{C}=\text{O}$).

2.2.2. Preparation of the complexes

$[\text{Co}(\text{DfgH})_2\text{BrL}]$ (**2**) was prepared by reacting $[\text{Co}(\text{DfgH})_2\text{Br}(\text{H}_2\text{O})]$ (0.001 mol, 0.64 g) dissolved under heating in 30 ml of a $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ 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 $\text{C}_{39}\text{H}_{35}\text{N}_7\text{O}_6\text{CoBr}$ (fw 836.26): Co, 7.04; C, 55.99; H, 4.21; N, 11.72.

$[\text{Co}(\text{DmgH})_2\text{CIL}']$ (**3**) was prepared by reacting $[\text{Co}(\text{DmgH})_2\text{Cl}(\text{H}_2\text{O})]$ (0.001 mol, 0.34 g) dissolved under heating in 20 ml of a mixture of $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (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 $\text{C}_{19}\text{H}_{27}\text{N}_7\text{O}_6\text{CoCl}$ (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 $0.30 \times 0.10 \times 0.10$ mm, $0.20 \times 0.15 \times 0.10$ mm and $0.25 \times 0.10 \times 0.10$ mm respectively. Experimental data for **1** and **2** were collected on an Xcalibur CCD -axis diffractometer and a graphite monochromator using Mo $K\alpha$ radiation. Experimental data for **3** were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo $K\alpha$ 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, 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 $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. 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 $\text{C}=\text{N}$ bond and $\text{C}-\text{N}$ bonds between each carbonyl groups of 2,4-pentanedione and isonicotinic hydrazide NH_2- and $-\text{NH}-$ group were formed. One water molecule saturated the double bond $-\text{CH}=\text{C}(\text{CH}_3)-$ of 2,4-pentanedione fragment, so the addition of one hydroxyl group at the carbon atom $>\text{C}(\text{CH}_3)-$ 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 $[\text{Co}(\text{DfgH})_2\text{BrL}]$ (**2**) (Fig. 2) and $[\text{Co}(\text{DmgH})_2\text{CIL}']$ (**3**) (Fig. 3) have been synthesized by interaction of previously obtained $[\text{Co}(\text{DfgH})_2\text{Br}(\text{H}_2\text{O})]$ ($\text{DfgH}_2 =$ diphenylglyoxime) or $[\text{Co}(\text{DmgH})_2\text{Cl}(\text{H}_2\text{O})]$ ($\text{DmgH}_2 =$ dimethylglyoxime) [7] with 2,4-pentanedione isonicotinoylhydrazone (**1**) in a basic methano-

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