



## Synthesis, crystal structure and properties of $[\text{Co}(\text{L})_2](\text{ClO}_4)_2$ (**L** = 1,3-bis(1*H*-benzimidazol-2-yl)-2-oxapropane)

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(Received 15 April, revised 26 July, accepted 28 July 2014)

**Abstract:** The reaction of 1,3-bis(1*H*-benzimidazol-2-yl)-2-oxapropane (**L**) with  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in absolute ethanol yielded the bis[1,3-bis(1*H*-benzimidazol-2-yl)-κ<sup>N3</sup>-2-oxapropane]cobalt(2+) diperchlorate chelate complex ( $[\text{Co}(\text{L})_2](\text{ClO}_4)_2$ , **1**). Complex **1** was characterized by elemental analysis, magnetic moment and molar conductivity measurements, thermogravimetric analysis, FT-IR, UV-Vis and mass spectrometry, and its solid-state structure was determined by single crystal X-ray diffraction. According to the elemental and thermogravimetric analysis data, no water either coordinated or uncoordinated is present in **1**. Complex **1** has 1:2 M:L ionic characteristic according to the molar conductivity value. In the complex, the distances between the cobalt and the ethereal oxygen atoms (Co1–O2: 2.805(3); Co2–O1: 2.752(2) Å) show semi-coordination bonding and the Co(II) ion is six-coordinated with a  $\text{N}_4\text{O}_2$  ligand set, resulting in a distorted octahedron.

**Keywords:** bis-benzimidazole; oxapropane; cobalt(II) perchlorate; semi-coordination; X-ray diffraction; spectroscopy.

### INTRODUCTION

Bis-benzimidazoles are to be known strong chelating agents coordinating through both of the C=N nitrogen atoms. In addition, they have polymer-forming characteristics as typical multidentate ligands.<sup>1,2</sup>

Complexes of bridged bis-benzimidazole ligands with transition metals were examined as potential models of the structure of the metal-binding sites in metalloproteins, such as hemerythrin, hemocyanin, tyrosinase or azurin.<sup>3–10</sup>

The crystal structure of 1,3-bis(1*H*-benzimidazol-2-yl)-2-oxapropane (**L**) was reported by Chen *et al.*<sup>11</sup> Moreover, the crystal structures of some metal complexes of **L** were reported. For example, Cu(II)-dipicrate,<sup>12</sup> Zn(II)-diperchlorate,<sup>13</sup> various Cu(II) salts,<sup>14</sup> Co(II)-dipicrate,<sup>15</sup> Mn(II)-dipicrate<sup>16</sup> complexes

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doi: 10.2298/JSC140415081T

were studied, as well as Cu(II) perchlorate mixed complex with bipyridine<sup>17</sup> complexes. In addition, Ni(II) and Zn(II) complexes of 1-benzyl derivative of **L**, 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxapropane, were reported.<sup>18,19</sup> Matthews *et al.* synthesized and characterized a series of asymmetric benzimidazolyl-2-oxapropane derivatives and their Cu(II), Zn(II), Cd(II), Hg(II) and Ag(I) complexes.<sup>20</sup> Co(II)<sup>21</sup> and Cd(II)<sup>22</sup> complexes of 1,3-bis(1-ethylbenzimidazol-2-yl)-2-oxapropane was also reported. CoCl<sub>2</sub> complex of **L** was used in the polymerization of butadiene as co-catalyst in combination with methylaluminumoxane (MAO) and it was shown to catalyze the polymerization with high selectivity.<sup>23</sup> In most of the above mentioned complexes, the ligands acted as tridentate.

In this study, the crystal structure of the Co(ClO<sub>4</sub>)<sub>2</sub> complex of **L**, bis[1,3-*bis*-(1*H*-benzimidazol-2-yl-κ*N*<sup>3</sup>)-2-oxapropane]cobalt(2+) diperchlorate (C<sub>32</sub>H<sub>28</sub>N<sub>8</sub>O<sub>10</sub>Cl<sub>2</sub>Co, **1**, Fig. 1), is reported. The structure of **1** was also characterized by elemental analysis, molar conductivity, FT-IR, UV-Vis, mass spectrometry and thermogravimetric analysis.

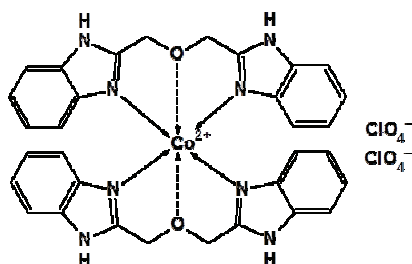


Fig. 1. Chemical diagram of the title compound.

#### EXPERIMENTAL

Elemental analysis data were obtained using a Thermo Finnigan Flash EA 1112 analyzer. The molar conductivity was measured on a WTW Cond315i conductivity meter in DMF at 25 °C. The magnetic moment measurement was realized on a Sherwood Scientific MK1 apparatus at room temperature by the Gouy method. The UV-Vis spectra were performed on a Perkin Elmer Lambda 25 UV/Visible spectrometer in ethanol (10<sup>-4</sup> mol L<sup>-1</sup>). The FT-IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer. The spray ionization-mass spectrometry (ESI-MS) analysis was performed in the positive ion mode using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS instrument. The thermogravimetric (TG) study was realized on a Shimadzu TG-60WS instrument, at a heating rate of 10 °C min<sup>-1</sup> under a dynamic air atmosphere at a flow rate of 50 mL min<sup>-1</sup>.

#### Synthesis of **L**

The ligand was synthesized from a 1:2 mole ratio of diglycolic acid (also known as 2,2'-oxydiacetic acid), 1.34 g, 0.01 mol) and *o*-phenylenediamine (2.16 g, 0.02 mol) in 5.5 M HCl (20 mL) according to the literature.<sup>17,24</sup>

### Synthesis of $[Co(L)_2](ClO_4)_2$

The ligand, **L** (0.209 g; 0.75 mmol), and  $Co(ClO_4)_2 \cdot 6H_2O$  (0.275 g; 0.75 mmol) were dissolved separately in absolute ethanol (10 mL). Then the solutions were mixed and refluxed for 2 h. (After mixing the solutions, a purple turbidity formed). The mixture was filtered and the filtrate was kept at room temperature after the volume was reduced to 10 mL. Purple crystals suitable for X-ray diffraction studies were formed after 3 days. The crystals were filtered and dried at room temperature (0.232 g, yield: 76 %).

### Crystallography

The diffraction measurements were performed at  $20 \pm 1$  °C on a Rigaku RAXIS RAPID imaging plate area detector using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å), with the distance between the crystal and the detector being 127.40 mm (Istanbul University Advanced Analyses Laboratory, Turkey). For the structure solution, 127754 reflections were collected, 6775 were unique ( $R_{int} = 0.050$ ); equivalent reflections were merged. An empirical absorption correction was applied that resulted in transmission factors ranging from 0.57 to 0.84. The data were corrected for Lorentz and polarization effects. The structure of **1** was solved by SIR92<sup>25</sup> and refined with CRYSTALS.<sup>26</sup> The non-hydrogen atoms were refined anisotropically. H atoms were treated as riding, with C–H = 0.95(6) Å and  $U_{iso}(H) = 1.2U_{eq}(C)$  and were constrained refined. All calculations were performed using the CrystalStructure<sup>27</sup> crystallographic software package.

## RESULTS AND DISCUSSION

### General properties

Elemental analysis showed that the composition of **1** is  $[Co(L)_2](ClO_4)_2$ . Complex **1** is 2:1 electrolyte according to the molar conductivity data ( $126 \text{ S m}^2 \text{ mol}^{-1}$ ) in DMF.<sup>28</sup> Thermogravimetric analysis data and elemental analysis showed that there are no coordinated or uncoordinated water in the structure of **1**. It started to decompose at about 250 °C and decomposed exactly above 550 °C to CoO (the weight percentage of CoO in the title compound is 9.1%, Fig. S-1 of the Supplementary material to this paper). The considerable weight loss near 300 °C should be due to the decomposition of the 1,3-bis(1H-benzimidazol-2-yl)-2-oxapropane ligand.

In the FT-IR spectrum of **1**, a strong band at  $1115 \text{ cm}^{-1}$  could be assigned to the stretching vibrations of the uncoordinated perchlorate anion,  $\nu(Cl=O)$ . In addition, the medium band at  $627 \text{ cm}^{-1}$  is due to the  $\nu_4$  mode of the perchlorate anion.<sup>29–31</sup> The new broad medium band at  $698 \text{ cm}^{-1}$  in the IR spectrum could be attributed to the  $\nu(Co-N)$  coordination band.<sup>32</sup>

Compound **1** shows three absorption bands in the visible region with maxima at 558, 526 and 456 nm. The 558 and 526 nm bands may be assigned to  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$  and  $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$  transitions, respectively, indicating a distorted octahedral geometry. The 456 nm shoulder may be due to ligand to metal charge transfer transitions.<sup>32,33</sup>

The observed magnetic moment value for **1** at room temperature,  $\mu_B = 4.12 \mu_B$ , is near the range reported for distorted octahedral Co(II) complexes having three unpaired electrons (high spin).<sup>33,34</sup>

In the ESI-MS spectrum, the molecular ion peak of **1** appears at  $m/z$  835.90 (19.2 %) as  $[(M+23)-2]^+$  (sodiated molecular ion). The  $m/z$  614.7 fragment is due to  $[\text{CoL}(\text{L}-\text{H})]^+$  ( $[\text{C}_{32}\text{H}_{28}\text{CoN}_8\text{O}_2]^+$ ) and its intensity was 100 %. Furthermore, a fragment at  $m/z$  279.7, corresponding to the ion peak of the ligand, was determined with an intensity of 18 %.

#### Crystal structure of **1**

The details of the X-ray data collection, structure solution and structure refinements are given in Table I. Compound **1** crystallizes in the monoclinic system with space group  $P2_1/n$ . Selected bond distances and angles are listed in Table S-I and selected torsion angles are given in Table S-II in Supplementary material. The ORTEP 3 view of the molecular structure of the title compound is given in Fig. 2; a crystal-packing diagram of **1** is given in Fig. S-2 of the Supplementary material. Crystallographic data has been deposited with the Cambridge Crystallographic Data Base as CCDC reference number 836316 for the  $[\text{Co}(\text{L})_2](\text{ClO}_4)_2$  complex.

TABLE I. X-Ray crystallographic data for **1**

|  |  |
|--|--|
| Empirical formula                            | $\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{CoN}_8\text{O}_{10}$ |
| Molecular weight, $\text{g mol}^{-1}$        | 814.46   |
| Color, habit                                 | Purple, chunk  |
| Crystal system                               | Monoclinic   |
| $a / \text{\AA}$                             | 19.448(2)  |
| $b / \text{\AA}$                             | 9.6228(6)  |
| $c / \text{\AA}$                             | 20.471(2)  |
| $V / \text{\AA}^3$                           | 3576.6(6)  |
| $\beta$ ( $^\circ$ )                         | 110.999(4)   |
| Space group                                  | $P2_1/n$   |
| Z value                                      | 4  |
| $d_{\text{calc}} / \text{g cm}^{-3}$         | 1.512  |
| $\mu(\text{Mo-K}\alpha) / \text{cm}^{-1}$    | 6.97   |
| $F(000)$                                     | 1668.00  |
| Index ranges, $h, k, l$                      | $-23 \leq h \leq 23, -11 \leq k \leq 10, -24 \leq l \leq 24$     |
| $\theta$ range for data collection, $^\circ$ | 2.7–25.0   |
| No. observations ( $I > 3\sigma(I)$ )        | 5899   |
| No. variables                                | 516  |
| Residuals: $R$ ( $I > 3\sigma(I)$ )          | 0.094  |
| Residuals: $R_w$ ( $I > 3\sigma(I)$ )        | 0.053  |
| Goodness of fit indicator                    | 1.161  |

The coordination cations ( $[\text{Co}(\text{L})_2]^{2+}$ ) are stabilized by weak  $\pi \cdots \pi$  stacking between the benzimidazole rings. In addition, no inter- or intra-molecular hydrogen bonding was detected.

The ligand (**L**) is potentially tridentate of NON-type. In many complexes described in the literature, **L** acted as tridentate towards the metal ions coordinating through the ethereal oxygen atom and the C=N nitrogen atoms. Some of the found M–O bond lengths were as follows: Zn–O, 2.35;<sup>13</sup> Mn–O, 2.38;<sup>16</sup> Ni–O, 2.10;<sup>18</sup> Cu–O, 2.53;<sup>17</sup> Cd–O, 2.54 Å.<sup>22</sup> However, in the present study, the distances between the cobalt and the ethereal oxygen atoms [O1–Co2: 2.752(2) and Co1–O2: 2.805(3) Å] are longer than in a coordination bond. Metal–ligand interactions with such long distances are often viewed as semi coordination.<sup>35,36</sup> Likewise, the bending of the oxygen atoms towards the cobalt atom supports semi-coordination. Thus, **L** acted as tridentate towards  $\text{Co}(\text{ClO}_4)_2$  in this study and the Co(II) ion is six coordinate with a  $\text{N}_4\text{O}_2$  ligand set from two ligands and the complex is distorted octahedral.

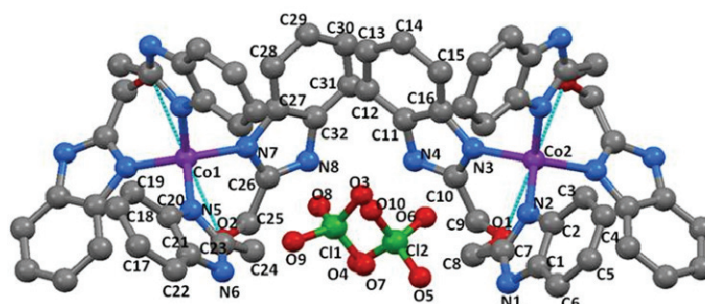


Fig. 2. A molecular drawing of the title compound. H atoms are omitted for clarity.

### CONCLUSIONS

In this study, bis[1,3-bis(1*H*-benzimidazol-2-yl- $\kappa\text{N}^3$ )-2-oxapropane]cobalt(2+) diperchlorate was synthesized and recrystallized from ethanol as single crystals suitable for X-ray study. The complex was characterized by elemental analysis, magnetic moment and molar conductivity measurements, thermogravimetric analysis, and FT-IR, UV–Vis and mass spectrometry. The molar conductivity of **1** measured in DMF falls within the range of values typical for 2:1 electrolytes. The room temperature magnetic moment value,  $\mu_{\text{B}}$ , of 4.12  $\mu_{\text{B}}$  falls within the range of values typical for high spin octahedral Co(II) complexes. The thermogravimetric analysis data showed that there was no coordinated or uncoordinated water molecule in compound **1**, which was supported by elemental analysis. In addition, the structure of **1** was determined by X-ray diffraction. The distances between the cobalt and the ethereal oxygen atoms (Co1–O2: 2.805(3); Co2–O1: 2.752(2) Å) indicate semi-coordination bonding. According to these

data, the chelate complex **1** has four five-membered Co–N–C–CH<sub>2</sub>–O rings, and the Co(II) ion has a distorted octahedral geometry with four nitrogen and two oxygen atoms from two ligands.

#### SUPPLEMENTARY MATERIAL

Analytical, conductivity, magnetic and spectral data, as well as TGA data and packing diagram of the title compound are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

*Acknowledgement.* This work was supported by the Scientific Research Projects Unit of Istanbul University, Turkey.

#### ИЗВОД

#### СИНТЕЗА, КРИСТАЛНА СТРУКТУРА И СВОЈСТВА [Co(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (L = 1,3-БИС(1H-БЕНЗИМИДАЗОЛ-2-ИЛ)-2-ОКСАПРОПАН)

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У реакцији 1,3-бис(1H-бензимидазол-2-ил)-2-оксапропана (L) са Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O у апсолутном етанолу добијен је хелатни комплекс бис[1,3-бис(1H-бензимидазол-2-ил-κN<sup>3</sup>)-2-оксапропан]кобалт(2+)-диперхлорат, [Co(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**). Овај комплекс је окарактерисан помоћу елементарне анализе, мерења магнетног момента и моларне проводљивости, термогравиметријске анализе, FT-IR, UV–Vis и масене спектрометрије. Кристална структура комплекса **1** је одређена методом дифракције X-зрака. На основу термогравиметријске и елементарне анализе нађено је да у комплексу **1** нема координованих и кристалних молекула воде. На основу мерења моларне проводљивости закључено је да су у комплексу **1** кобалт(II) и лиганд координовани у молском односу 1:2. На основу измерених растојања између Co(II) јона и атома кисеоника у аксијалном положају (Co1–O2: 2,805(3); Co2–O1: 2,752(2)) може се закључити да је у овом случају присутна парцијално-координативна веза и да је Co(II) јон хексакоординован са N<sub>4</sub>O<sub>2</sub> лигандним системом, као и то да комплекс **1** има деформисану октаедарску геометрију.

(Примљено 15. априла, ревидирано 26. јула, прихваћено 28. јула 2014)

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