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# SYNTHESIS AND CRYSTAL STRUCTURE OF COBALT(III) COMPLEXES WITH SUBSTITUTED 2-[(BENZIMIDAZOLE-1-YL) IMINOMETHYL]PHENOLS

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Two Co(III) complexes are synthesized based on 2-{(E)-[2-(hydroxy(alkyl)amino)benzimidazole-1-yl]iminomethyl}phenol ($H_3L^1$ and $H_3L^2$, alkyl is ethyl or propyl). By the elemental analysis and IR spectroscopy it is established that the obtained complexes have the compositions $[Co(H_2L^1)(HL^1)]\cdot 2C_2H_5OH$ and $[Co(H_2L^2)(HL^2)]CH_3OH\cdot 1/2H_2O$. Their crystal and molecular structures are determined by single crystal X-ray diffraction (XRD). From the XRD data it is found that the complexes crystallize in the triclinic space group $P\overline{1}$ as solvates with alcohol and water molecules. In mononuclear molecules of both complexes, two trischelate ligands in mono- and dianionic forms are coordinated to the Co(III) cation. The coordination environment of the cobalt atom $CoN_4O_2$ corresponds to a distorted octahedron in both compounds.

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**Keywords:** azomethines, benzimidazole, cobalt(III) complexes, single crystal XRD.

## INTRODUCTION

Azomethine compounds – benzimidazole derivatives and metal complexes on their bases [1, 2]–are of constant scientific interest due to a wide range of their biological activity [3, 4]. These Schiff bases and their metal complexes have multiple applications in medicine owing to their antimicrobial [5-7], antimalarial [8], antiphlogistic [9, 10], and antineoplastic activities [11-14].

Furthermore, Schiff bases, including those containing benzimidazole moieties, and their metal complexes are used as catalysts in the chemical industry [15] and as corrosion inhibitors for some alloys and metals, especially in acidic media [16, 17].

Being potential polydentate ligand systems, azomethine compounds as the derivatives of 2-hydroxy-, 2-tosylaminobenzaldehydes and aminoazoles are of special interest for the synthesis of mono- and polynuclear metal complexes [18-22].

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There are practically no publications in the scientific literature on metal complexes of azomethine compounds the derivatives of 2-hydroxy-, 2-tosylaminobenzaldehydes, and N-aminobenzimidazoles. One can cite only few works where mono- and binuclear complexes based on these ligands were obtained [23, 24]. A series of mono- and polynuclear metal complexes with different heterocyclic ligands, which contain benzimidazole or imidazole moieties and alcohol groups, were synthesized [25-33].

We have previously prepared cobalt(II) and copper(II) complexes with 2-{(E)-[2-(4-hydroxy butylamino)benzimidazole-1-yl]iminomethyl}phenol and studied their structure and properties [34]. In continuation of this work, here we report the results of the synthesis and structural study of cobalt(III) complexes with 2-{(E)-[2-(2-hydroxyethylamino)benzimidazole-1-yl]iminomethyl}phenol ($\mathbf{H_3L^1}$) and 2-{(E)-[2-(3-hydroxypropylamino)benzimidazole-1-yl]iminomethyl}phenol ($\mathbf{H_3L^2}$).

## EXPERIMENTAL

In the synthesis, we used commercially available solvents, cobalt(II) acetate tetrahydrate (CAS No.: 6147-53-1), salicylic aldehyde (CAS No.: 90-02-8), 3-aminopropanol (CAS No.: 156-87-6), and triethylamine (CAS No.: 121-44-8) (Alfa Aesar) without further purification.

The C, H, N elemental analysis was carried out on a Carlo Erba Instruments TCM 480 device. The metal analysis was performed by the weight method. The melting point was measured by a Kofler bench. The IR spectra of the samples were recorded on a Varian 3100-Excalibur FTIR instrument in a range of 4000-400 $\text{cm}^{-1}$ by the disturbed total internal reflection method. The $^1$H NMR spectra were recorded on a Bruker Avance-600 (600 MHz) in DMSO-$d_6$. $^1$H chemical shifts are given relative to residual deuteron solvent signals.

**2-[(1-Aminobenzimidazole-2-yl)amino]ethanol** (**1a**) was synthesized using the procedure from [34].

**3-[(1-Aminobenzimidazole-2-yl)amino]propan-1-ol** (**1b**). A mixture of 1-aminobenzimidazole-2-sulphonic acid (4.26 g, 0.02 mol) [35] and 3-aminopropanol (4 mL, 0.052 mol) was heated for 1 h at 160-165 °C, cooled to 90 °C, added with 5 mL of water, stirred, and left in a fridge for 4 h. The precipitate formed was filtered off and washed with 5 mL of ice water. Yield: 2.56 g (62%). The complex was recrystallized from acetonitrile. Colorless crystals were obtained, m.p. = 119-121 °C.

Found (%): C 58.12, H 7.00, N 27.24. For $C_{16}H_{16}N_4O_2$ calculated (%): C 58.24, H 6.84, N 27.17. $^1$H NMR spectrum (DMSO-$d_6$; δ, ppm): 1.68-1.73 (m, 2H, $CH_2\underline{CH_2}CH_2OH$), 3.39-3.48 (m, 4H, $\underline{CH_2}CH_2\underline{CH_2}OH$), 4.91 (s, 1H, OH), 5.54 (s, 2H, $NH_2$), 6.42 (t, $^3J$ = 5.4 Hz, 1H, NH), 6.87-6.91 (m, 2H, $H^{5,6}$), 7.05-7.13 (m, 2H, $H^{4,7}$).

**2-{(E)-[2-(2-Hydroxyethylamino)benzimidazole-1-yl]iminomethyl}phenol** ($\mathbf{H_3L^1}$). To a solution of **1a** (1.92 g, 0.01 mol) in 15 mL of isopropanol, 2-hydroxybenzaldehyde (1.22 g, 0.01 mol) was added. The mixture was boiled in the presence of a catalytic amount (2 drops) of piperidine for 3 h and cooled. The precipitate was filtered off, washed with diethyl ether, recrystallized from butanol, and dried. Yield: 2.54 g (86%). Colorless crystals were obtained, m.p. = 241-242 °C.

Found (%): C 64.90, H 5.51, N 19.02. For $C_{16}H_{16}N_4O_2$ calculated (%): C 64.85, H 5.44, N 18.91. IR spectrum (ν, $\text{cm}^{-1}$): 3113-2700 (OH, NH), 1622, 1601 (CH=N). $^1$H NMR spectrum (DMSO-$d_6$; δ, ppm): 3.48-3.52 (m, 2H, $CH_2$), 3.61-3.65 (m, 2H, $CH_2$), 4.90 (t, $^3J$ = 5.4 Hz, 1H, $CH_2\underline{OH}$), 6.93-7.09 (m, 5H, $H^{3'-5'}$, $H^{5(6)}$, NH), 7.28 (d, $^3J$ = 7.8 Hz, 1H, $H^{6'}$), 7.35 (td, $^3J$ = 8.0 Hz, $^4J$ = 1.8 Hz, 1H, $H^{6(5)}$), 7.54 (d, $^3J$ = 7.8 Hz, 1H, $H^4$), 8.13 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1H, $H^7$), 9.21 (s, 1H, CH=N), 10.28 (s, 1H, OH).

**2-{(E)-[2-(3-Hydroxypropylamino)benzimidazole-1-yl]iminomethyl}phenol** ($\mathbf{H_3L^2}$). The complex was prepared similar to $\mathbf{H_3L^1}$ [34] from 3-[(1-aminobenzimidazole-2-yl)amino]propan-1-ol (**1b**) (2.06 g, 0.01 mol) and 2-hydroxybenzaldehyde (1.22 g, 0.01 mol). Yield: 2.73 g (88%). The complex was recrystallized from butanol. Pale yellow crystals were obtained, m.p. = 224-225 °C.

Found (%): C 65.82, H 5.90, N 17.95. For $C_{17}H_{18}N_4O_2$ calculated (%): C 65.79, H 5.85, N 18.05. IR spectrum (ν, $\text{cm}^{-1}$): 3120-2700 (OH, NH), 1620, 1602 (CH=N). $^1$H NMR spectrum (DMSO-$d_6$; δ, ppm): 1.76-1.81 (m, 2H,

$CH_2\underline{CH_2}CH_2OH$), 3.42-3.54 (m, 4H, $\underline{CH_2}CH_2\underline{CH_2}OH$), 4.77 (t, $^3J$ = 5.1 Hz, 1H, $CH_2\underline{OH}$), 6.91-7.37 (m, 7H, $H^{3'-6'}$, $H^{5,6}$, NH), 7.52 (d, $^3J$ = 7.5 Hz, 1H, $H^{4(7)}$), 8.11 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.2 Hz, 1H, $H^{7(4)}$), 9.19 (s., 1H, N=CH), 10.29 (s, 1H, OH).

**Synthesis of complexes 2, 3.** $[Co(H_2L^1)(HL^1)]\cdot 2C_2H_5OH$ complex (**2**). To a solution of 2-{(E)-[2-(2-hydroxyethylamino)benzimidazole-1-yl]iminomethyl}phenol (**$H_3L^1$**) (0.60 g, 0.002 mol) in a mixture of 30 mL of ethanol and 5 mL of DMF, a solution of cobalt acetate tetrahydrate (0.25 g, 0.001 mol) in 5 mL of ethanol and sodium methoxide (0.1 g, 0.002 mol) was added. The mixture was boiled for 2 h and cooled. The precipitated crystals were filtered off, washed twice with 5 mL of ethanol, and dried at 150 °C. Yield: 0.33 g (45%). Dark brown crystals suitable for XRD were obtained, m.p. > 250 °C.

Found (%): C 58.50, H 5.36, Co 8.02, N 15.23. For $C_{36}H_{41}CoN_8O_6$ calculated (%): C 58.38, H 5.58, Co 7.96, N 15.13. IR spectrum (ν, $cm^{-1}$): 3170-2700 (OH), 1685 (CH=N).

$[Co(H_2L^2)(HL^2)]CH_3OH\cdot 1/2H_2O$ complex (**3**). To a solution of 2-{(E)-[2-(3-hydroxypropylamino)benzimidazole-1-yl]iminomethyl}phenol (**$H_3L^2$**) (0.62 g, 0.002 mol) in 30 mL of methanol, a solution of cobalt acetate tetrahydrate (0.25 g, 0.001 mol) in 10 mL of methanol and triethylamine (0.2 g, 0.002 mol) was added. The mixture was stirred for 3 h at 20-25 °C. The precipitate of the complex was filtered off, washed twice with 5 mL of methanol. Yield: 0.40 g (55%). Brown crystals were obtained, m.p. > 250 °C.

Found (%): C 58.52, H 5.91, Co 8.32, N 15.62. For $C_{35}H_{38}CoN_8O_{5.5}$ calculated (%): C 58.58, H 5.34, Co 8.21, N 15.61. IR spectrum (ν, $cm^{-1}$): 3179-2754 (OH), 1680 (CH=N).

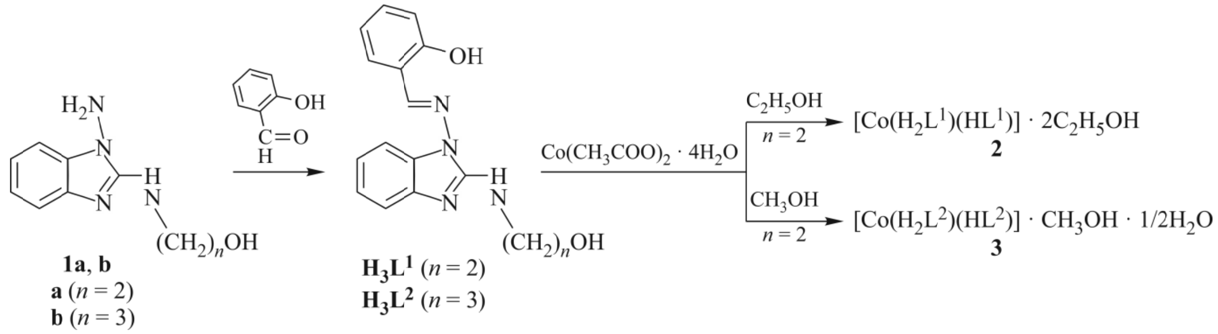
**Single crystal XRD.** Single crystal XRD of **2** and **3** was performed on a Smart Apex II CCD diffractometer ($MoK_\alpha$ radiation, graphite monochromator). For all compounds, a semi-empirical absorption correction was applied using the SADABS program [36]. The structures were solved by direct methods and refined by full-matrix LSM in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms at carbon atoms of organic ligands and of OH groups were generated geometrically and refined in the riding model. Hydrogen atoms of NH groups were determined from difference Fourier maps and fixed using the AFIX 43 function. The structure of **2** was solved with regard to the disorder of the $OH–CH_2$ moiety of one of the ligands over two positions with occupancies of 0.774(6) and 0.226(6). Slightly overestimated *R* factors in the solution of **2** are due to a poor crystal quality. The structure of **3** was solved with regard to the disorder of the solvate water molecule over two positions through the inversion center with equal occupancies (0.5). All calculations were performed using the SHELX [37] and Olex 2 software [38]. Crystallographic parameters and structure refinement details are given in Table 1. Intra- and intermolecular interactions were analyzed using the PLATON program [39]. Atomic coordinates and complete structural data have been deposited with the Cambridge Crystallography Data Center (CCDC Nos. 2085807 (**2**), 2085808 (**3**)).

## RESULTS AND DISCUSSION

Azomethine compounds **$H_3L^1$** and **$H_3L^2$** were synthesized by condensating equimolar amounts of salicylic aldehyde and, respectively, 2-[(1-aminobenzimidazole-2-yl)amino]ethanol (**1a**) or 3-[(1-aminobenzimidazole-2-yl)amino]propan-1-ol (**1b**) in isopropyl alcohol (Scheme 1).

Cobalt complex $[Co(H_2L^1)(HL^1)]\cdot 2C_2H_5OH$ (**2**) was prepared by boiling a solution of **$H_3L^1$** and cobalt acetate tetrahydrate in a mixture of ethanol and DMF. Cobalt complex $[Co(H_2L^2)(HL^2)]CH_3OH\cdot 1/2H_2O$ (**3**) was synthesized by boiling a solution of **$H_3L^2$** and cobalt acetate tetrahydrate in methanol. Both complexes were obtained in the air.

The structures of initial amino alcohols **1a**,**b** and synthesized azomethines **$H_3L^1$** and **$H_3L^2$** were determined from the data of elemental analysis, IR, and $^1H$ NMR spectroscopy. In the $^1H$ NMR spectra of **1a**,**b**, **$H_3L^1$**, and **$H_3L^2$**, the signals of all protons corresponding to their structures were found and assigned. The proton signals from the OH group of azomethine **$H_3L^1$** appear as a triplet at 4.90 ppm and a singlet at 10.28 ppm, and proton signals from NH groups are observed as



**Scheme 1.** Synthesis of complexes **2** and **3**.

**TABLE 1.** Crystallographic Parameters and Structure Refinement Details for **2** and **3**

| Parameter | [Co($H_2L^1$)($HL^1$)]·2EtOH (**2**) | [Co($H_2L^2$)($HL^2$)]·MeOH·0.5$H_2O$ (**3**) |
|---|---|---|
| Chemical formula | $C_{36}H_{41}CoN_8O_6$ | $C_{35}H_{38}CoN_8O_{5.5}$ |
| *M*, g/mol | 740.70 | 717.66 |
| *T*, K | 150(2) | |
| Crystal symmetry | Triclinic | |
| Space group | $P\overline{1}$ | |
| *a*, *b*, *c*, Å | 9.3045(8), 13.4659(12), 15.3385(14) | 9.1887(8), 12.9332(11), 15.1822(13) |
| α, β, γ, deg | 65.438(2), 72.401(2), 82.328(2) | 111.352(2), 104.658(2), 95.441(2) |
| *V*, Å$^3$ | 1666.0(3) | 1590.3(2) |
| *Z* | 2 | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.477 | 1.499 |
| μ, mm$^{-1}$ | 0.576 | 0.600 |
| $\theta_{max}$, deg | 26.37 | 27.48 |
| $T_{min}$ / $T_{max}$ | 0.5810 / 0.7457 | 0.6340 / 0.7457 |
| Measured / independent reflections with $I > 2\sigma(I)$ | 14241 / 6619 / 3359 | 14225 / 6966 / 5009 |
| $R_{int}$ | 0.0946 | 0.0444 |
| Refined parameters | 472 | 455 |
| *GOOF* | 1.005 | 1.022 |
| $R_1$ / $wR_2$ ($I > 2\sigma(I)$) | 0.0945 / 0.1616 | 0.0533 / 0.1175 |

a multiplet at 6.93-7.09 ppm. In the $^1$H NMR spectrum of **$H_3L^2$**, proton signals from the OH group appear as a triplet at 4.77 ppm and a singlet at 10.29 ppm, and proton signals from the NH group appear as a multiplet at 6.91-7.37 ppm.

In the IR spectra of **$H_3L^1$** and **$H_3L^2$**, broad low-intensity absorption bands ν(OH) and ν(NH) are observed in a range of 3130-2700 cm$^{-1}$ and ν(CH=N) in a range of 1620-1622 cm$^{-1}$. The elemental analysis data confirm the composition of the obtained azomethine compounds.

Cobalt(III) complexes **2** and **3** synthesized in the air are brown crystals with m.p. > 250 °C. According to the elemental analysis data, they have the composition [Co($H_2L^1$)($HL^1$)]·2$C_2H_5OH$ (**2**) and [Co($H_2L^2$)($HL^2$)]$CH_3OH$·1/2$H_2O$ (**3**), crystallizing with alcohol and water molecules. In their IR spectra, broad low-intensity absorption bands ν(OH) are observed in a range of 3179-2700 cm$^{-1}$ and intense absorption bands ν(CH=N) in a range of 1680-1685 cm$^{-1}$, which shift to a high-frequency region relative to the respective bands in **$H_3L^1$** and **$H_3L^2$**. Absorption bands corresponding to ν(NH) in the IR spectra of the complexes are not observed. These changes in the IR spectra evidence the formation of chelate structures of cobalt complexes **2** and **3**.

The crystal structures of cobalt(III) complexes **2** and **3** were determined by single crystal XRD. The compounds crystallize in the triclinic space group $P\overline{1}$. Complex **2** is a solvate with two ethanol molecules; complex **3** is a solvate with one methanol molecule and a half of water molecule. Atoms in the molecules of the complexes are in general positions. Both these complexes are mononuclear molecules formed by the cobalt(III) cation and trischelate mono- and dianionic forms of ligands, [Co($H_2L$)($HL$)] (Figs. 1*a* and 2*a*). In both compounds, the coordination environment of the cobalt atom

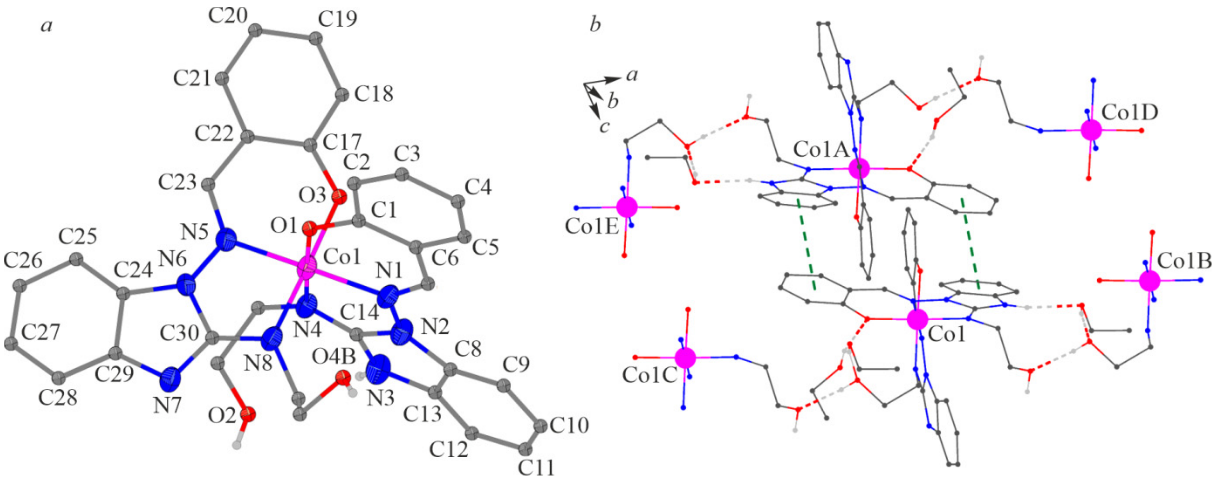


**Fig. 1.** Molecular structure (*a*) and the fragment of the crystal packing (*b*) of **2** (hydrogen atoms at carbon atoms are omitted; thermal ellipsoids are shown at a 50% probability (*a*); H bonds and π–π stacking interactions are denoted by dotted lines (*b*); the symmetry of the indexed atoms corresponds to 2–*x*, 1–*y*, –*z* (A), 1+*x*, *y*, *z* (B), –1+*x*, *y*, *z* (C), 3–*x*, 1–*y*, –*z* (D), 1–*x*, 1–*y*, –*z* (E)).

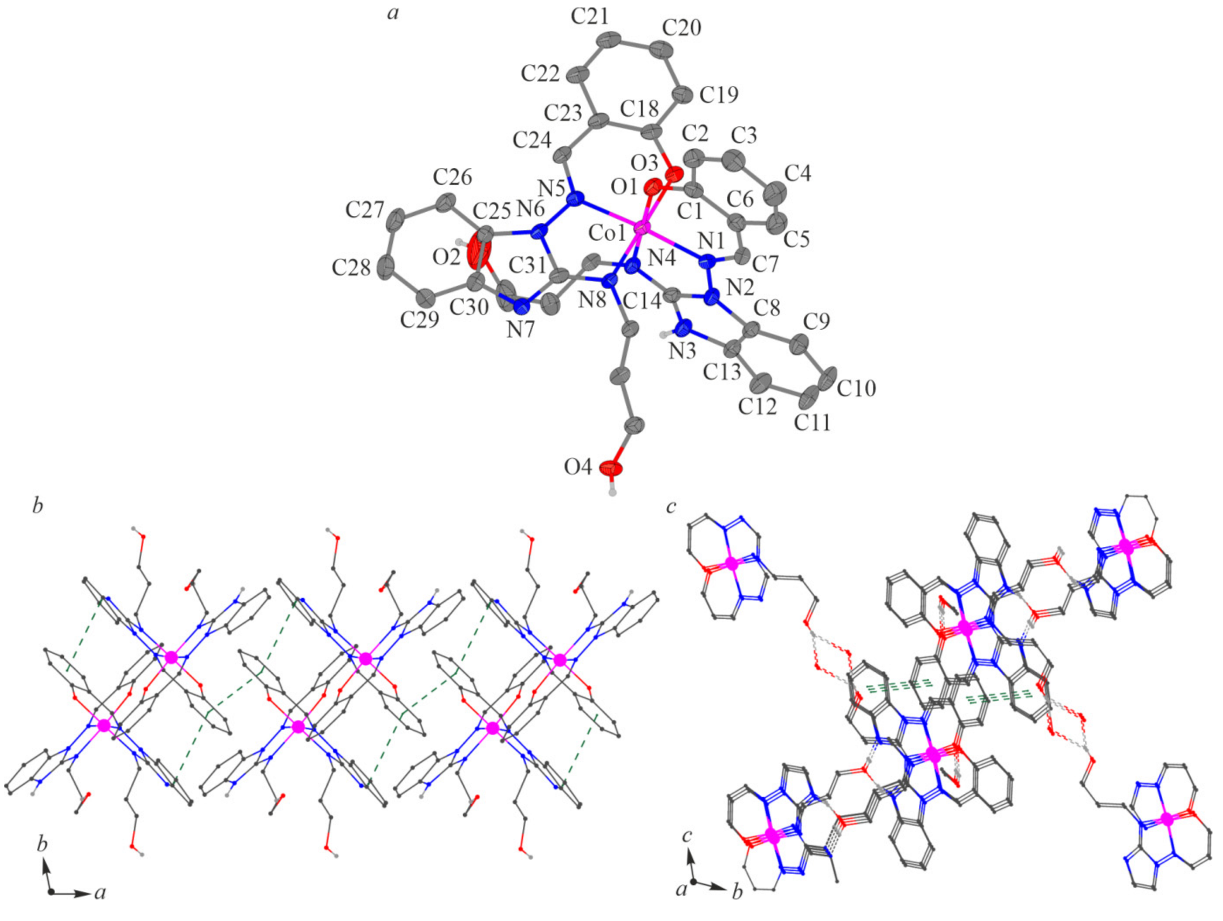


**Fig. 2.** Molecular structure (*a*) and the fragment of the crystal packing (*b*) of **3** (hydrogen atoms at carbon atoms are omitted; thermal ellipsoids are shown at a 50% probability (*a*); H bonds and π–π stacking interactions are denoted by dotted lines (*b*, *c*).

(chromophore $CoN_4O_2$) corresponds to a distorted octahedron, the Co–N distances of 1.895(4)-1.930(4) Å for **2** and 1.893(2)-1.930(2) Å for **3**, Co–O of 1.897(3) Å, 1.899(3) Å for **2** and 1.891(2) Å, 1.899(2) Å for **3** indicate a trivalent state of the metal atom. Apparently, oxidation of initial Co(II) to Co(III) in the complexes occurs when single crystals of these compounds are synthesized or grown in the air. Trischelate ligands form two chelate rings: five-membered ($CoN_2CN$) and six-membered ($CoNC_3O$) lying practically in one plane; the average atomic deviation from the mean square plane of conjugated rings is 0.0629 Å for $Co(H_2L)$ and 0.1174 Å for Co(HL) in **2** and 0.0259 Å for $Co(H_2L)$ and 0.0550 Å for Co(HL) in **3**. The angle between the planes of trischelate ligands is close to 90°, being 81.03(8)° in **2** and 87.44(4)° in **3**.

The crystal packing of both compounds is determined by intermolecular H bonds and π–π stacking interactions (the data were analyzed according to the criteria described in [40]); the main characteristics are listed in Tables 2 and 3 and illustrated in Figs. 1*b* and 2*b*, *c*. In **2**, intermolecular stacking interactions between phenyl moieties of the ligands contribute to the formation of a supramolecular dimer where H bonds result in the formation of a supramolecular chain along the *a* axis (Fig. 1*b*). In **3**, intermolecular stacking interactions between phenyl moieties of the ligands give a supramolecular chain along the *a* axis (Fig. 1*b*). The H bonding of chains between N atoms of imidazole moieties and O atoms of propanol residues result in the formation of a layer in the *bc* plane (Fig. 1*c*). The additional bonding of free propanol residues via the crystallization water molecules contribute to the formation of a 3D supramolecular structure (Fig. 1*c*).

## CONCLUSIONS

Two new potentially tridentate azomethine compounds 2-{(E)-[2-(2-hydroxyethylamino)benzimidazole-1-yl]iminomethyl}phenol and 2-{(E)-[2-(3-hydroxypropylamino)benzimidazole-1-yl]iminomethyl}phenol, as well as cobalt complexes on their basis are prepared and characterized. The crystal structures of the cobalt complexes were determined from the single crystal XRD data. It is found that both complexes are mononuclear; in them, two trischelate ligands in mono- and dianionic forms are coordinated to cobalt (III) cations. The coordination environment of the cobalt atom in both compounds corresponds to a distorted octahedron. A trivalent state of cobalt ions in the complexes is probably due to oxidation by atmospheric oxygen during their synthesis or crystallization in solution.

**TABLE 2.** Main Parameters of H Bonds in **2** and **3**

| *D*–H···*A*, Å | *D*–H, Å | H···*A*, Å | *D*···A, Å | *D*–H–*A*, deg |
|---|---|---|---|---|
| | | **2** | | |
| O1S–H···O1 | 0.84 | 2.05 | 2.863(5) | 164 |
| O2S–Ha···O4B | 0.84 | 1.93 | 2.748(7) | 164 |
| O2–H2···N7 (2–*x*, 1–*y*, 1–*z*) | 0.84 | 1.89 | 2.704(6) | 162 |
| N3–H3···O2S (1+*x*, *y*, *z*) | 0.88 | 2.06 | 2.911(7) | 163 |
| O4B–H4B···O2 (–1+*x*, *y*, *z*) | 0.84 | 1.96 | 2.797(7) | 171 |
| | | **3** | | |
| O1S–H1S···O3 | 0.84 | 1.96 | 2.790(3) | 171 |
| O2–H2···O1W | 0.84 | 2.35 | 2.852(8) | 159 |
| N3–H3···O4 (1–*x*, –*y*, 1–*z*) | 0.88 | 1.97 | 2.806(4) | 158 |
| O4–H4···N7 (2–*x*, –*y*, 1–*z*) | 0.82(2) | 1.92(3) | 2.738(3) | 175(2) |

**TABLE 3.** Main Parameters of π–π Stacking Interactions in **2** and **3**

| Aromatic ring | | *Cg*–*Cg*, Å | α, deg | *Cg*(*I*)_Perp, Å | *Cg*(*J*)_Perp, Å | *S*, Å |
|---|---|---|---|---|---|---|
| *I* | *J* | | | | | |
| | | | **2** | | | |
| C1–C6 | C8–C13 (2–*x*, 1–*y*, –*z*) | 3.685(3) | 12.7(3) | 3.482(2) | 3.455(2) | 1.283 |
| | | | **3** | | | |
| C18–C23 | C25–C30 (2–*x*, 1–*y*, 2–*z*) | 3.655(2) | 11.54(16) | 3.3136(14) | 3.5037(15) | 1.042 |
| C18–C23 | C18–C23 (1–*x*, 1–*y*, 2–*z*) | 3.727(2) | 0.00(16) | 3.4506(14) | 3.4505(14) | 1.409 |

Note: *Cg*–*Cg* = the distance between the centroids of the rings (Å); α = the dihedral angle between the *I* and *J* planes (deg); *Cg*(*I*)_Perp = the perpendicular distance from *Cg*(*I*) on the *J* ring (Å); *Cg*(*J*)_Perp = the perpendicular distance from *Cg*(*J*) on the *I* ring (Å); *S* is the distance between *Cg*(*I*) and the perpendicular projection of *Cg*(*J*) on the *I* ring (Å).

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## CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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