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The synthesis and structure of the *tris* (monoethanolamine-O, N) cobalt (II) (4-hydroxybenzoate) monoethanolamine solvate

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Abstract

New cobalt(II) complex of composition $[Co(EtaH)_2(Eta)](L)\cdot EtaH$ (I) (where EtaH is monoethanolamine $NH_2(CH)_2OH$, L= 4-hydroxybenzoate) has been prepared. The crystal structure of the obtained complex is determined by X-ray diffraction analysis. The crystal is monoclinic, a = 12.4429(13), b = 8.9370(9), c = 17.9020(15) Å, β= 99.698(9) °, V = 1962.3(3) Å^3, space group $P2_1/n$, Z = 4. The asymmetric unit consists of mononuclear complex cation $[Co(EtaH)_2(Eta)]^+$ with a distorted octahedron geometry and one 4-hydroxybenzoate anion and EtaH molecules. The $[Co(EtaH)_2(Eta)]^+$ cation contains two neutral and one deprotonated monoethanolamine ligands. Both the two neutral monoethanolamine molecules and monoethanolaminate anion act as bidentate ligands through the amine nitrogen and ethanol oxygen atoms and form five-membered chelate rings. In the $[Co(EtaH)_2(Eta)]^+$ cation the NH_2 and OH groups are disordered over two positions, with a ratio of their occupancies close to 0.5:0.5. In the crystal, the cations and anions are linked by N-H…O, O-H…O and C-H…O hydrogen bonds.

Keywords: cobalt, crystal structure, monoethanolamine, 4-hydroxybenzoic acid, metal complex, X-ray structure analysis

1. Introduction

As we well know biological activity of pharmaceutical preparations may be significantly enhanced by metal complex formation [1, 2] which is especially crucial in case of substances with low activity. In this regard, we are carrying out a systematic study of the mixed-ligand metal complex formation by aromatic carboxylic acids and ethanolamines demonstrating weak antimicrobial [3] and growth stimulating effects [4]. These substances were selected due to their low cost, availability and simplicity of the structure. Benzoic acids are used in a pharmaceutical industry and as conservant and catalyst precursors beyond other applications [5]. Ethanolamines are used in an industry as adhesives, antistatic agents, a corrosion inhibitor in metal-cutting fluids and as an ointment emulsifier [6].

In order to prepare mixed-ligand complex of cobalt with 4-hydroxybenzoic acid and monoethanolamine we carried out a reaction from liquid media containing cobalt (II) chloride salt and these potential ligands. Unfortunately, a desired reaction is failure and instead of target compound we have obtained supramolecular substance on the base of tris-cobalt complex with monoethanolamine and both of potential ligands. We report here a preparation and structure of this supramolecular complex I.

2. Materials and Methods

Synthesis

Cobalt(II) chloride, 4-hydroxybenzoic acid and monoethanolamine (chemically pure grade) were used. A hot solution of 4-hydroxybenzoic acid (1 mmol, 0.137 g) in 10 mL of a water–ethanol mixture (1 : 1 vol/vol) was added to a solution of $CoCl_2\cdot 2H_2O$ (1 mmol, 0.165 g) in 4 mL of the same mixture. Monoethanolamine (4 mmol) was added dropwise to the obtained mixture with continuous stirring. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 15 min. The obtained solution was placed in a not tightly closed box at 25°C. Prismatic crystals were formed in 15 days, and a single crystal for X-ray diffraction analysis was selected.

X-ray diffraction analysis

Reflection arrays were obtained at 293 K on an Xcalibur R Oxford Diffraction diffractometer (Cu$K\alpha$ radiation, λ = 1.54184 Å, ω-scan method, a graphite monochromator). Experimental data were collected using the CrysAlisPro software [7]. Absorption was taken into account by the “multi-scan” method in the CrysAlisPro software package. Structure I was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms (SHELXL-97) [8]. The positions of hydrogen atoms were determined geometrically and refined with fixed isotropic displacement parameters Uiso = nUeqv, where n = 1.5 for hydroxyl groups and 1.2 for the other groups, and Ueqv is the equivalent isotropic displacement parameter of corresponding carbon atoms. Molecular graphics was based on the XP program included in the SHELXTL-Plus program package [9]. The crystallographic characteristics of complex I and details of the diffraction experiment are presented in Table 1.

Table 1: Crystal data and structure refinement parameters for I

Empirical Formula	**$C_6H_{12}CoN_3O_3$, $C_7H_4O_3$, $0.5(C_4N_2O_2)$**
Formula weight	423.25
Crystal system	monoclinic
Space group	P21/n
a, Å	12.4429(13)
b, Å	8.9370(9)
c, Å	17.9020(15)
α, deg	90
β, deg	99.698(9)
γ, deg	90
V, $Å^3$	1962.3(3)
Z	4
D_x, gcm^{-3}	1.433
$\mu(CuK_\alpha)$, mm^{-1}	7.253
T, K	293
Scan θ range, deg	4.0, 76.1
Range *h,k,l*	-15/14 ; -11/10 ; -22/16;
Total data	9171
Independent data	4017
R_{int}	0.044
Observed data [$F^2 \geq 2\sigma(F^2)$]	2557
Goodness-of-fit (F^2)	1.03
R_1, $wR_2(I>2\sigma(I))$	0.0822, 0.2653
$\Delta\rho_{min/max}$, $eÅ^{-3}$	-0.43, 0.51

3. Results and Discussion

The asymmetric unit of the compound I with the formula $[Co(C_2H_7NO)_2(C_2N_6NO)]$ $(C_7H_5O_3)\cdot(C_2H_7NO)$ (Fig. 1) consists of one discrete $[Co(EtaH)_2(Eta)]^+$ cation and one 4-hydroxybenzoate anion and one EtaH molecules. The $[Co(EtaH)_2(Eta)]^+$ cation contains two neutral and one deprotonated monoethanolamine ligands. Both the monoethanolamine molecules and monoethanolaminate anion act as bidentate ligands through the amine nitrogen and ethanol oxygen atoms and form five-membered chelate rings. The $CoNC_2O$ five-membered chelate rings have the *gauche* conformation. In the $[Co(EtaH)_2(Eta)]^+$ cation the NH_2 and OH groups are disordered over two positions, with a ratio of their occupancies close to 0.5:0.5. The coordination polyhedron of the Co(II) cation is a distorted octahedron defined by an N_3O_3 coordination set.

The distortion is indicated by bond angles O5—Co—N4 [176.9(4)°], O6—Co—N2 [176.5(4)°], O7—Co—N3 [176.6(4)°], O5′—Co—N3′ [178.1(5)°], O6′—Co—N4′ [177.8(4)°] and O7′—Co—N2′ [177.3(4)°]. The Co—N, Co—N′ and Co—O, Co—O′ bond distances are in the range of 1.932(10)-1.946(10), 1.925(11)-1.965(11) and 1.904(9)-1.926(8), 1.899(7)-1.912(9)Å, respectively (Table 2). Co–N bonds are systematically longer than Co–O, which makes it possible, along with the rather reliable location of the hydrogen atoms, to distinguish reliably the OH and NH_2 groups in monoethanolamine. The *cis* angles of the coordination octahedron range from 86.6(4) and 93.7(5)°, while the *trans* angles are in the range of 176.5(4)-178.1(5)°.

The carboxylate group of 4-hydroxybenzoate anion retorts a small angle of 9.42 (7)° with respect to the phenyl ring and two C—O bonds of the carboxylate group tend to be average (1.247(10)Å and 1.241(10) Å) for the elimination of the proton.

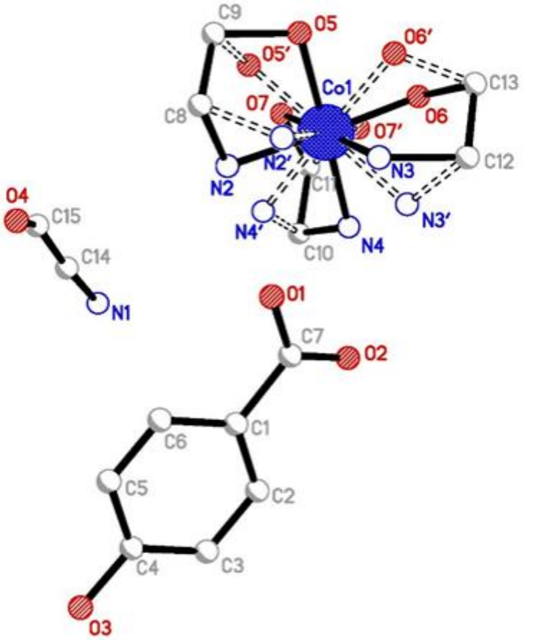

Fig 1: Crystallographically independent part of the unit cell in structure I.

Table 2: Selected bond lengths (*d*) and bond angles (ω) in compound I

Bond	*d*, Å	Angle	ω, deg
Co–O5	1.911(9)	O5–Co–O6	90.3(4)
Co–O6	1.904(9)	O5–Co–O7	91.2(4)
Co–O7	1.926(8)	O5–Co–N2	86.6(4)
Co–O5'	1.899(7)	O5–Co–N3	91.8(4)
Co–O6'	1.907(8)	O5–Co–N4	176.9(4)
Co–O7'	1.912(9)	O6–Co–N2	176.5(4)
Co–N2	1.946(10)	O6–Co–N4	89.5(4)
Co–N3	1.932(10)	O7–Co–N2	89.6(4)
Co–N4	1.943(10)	O7–Co–N3	176.6(4)
Co–N2'	1.965(11)	O5'–Co–O6'	91.8(3)
Co–N3'	1.958(11)	O5'–Co–O7'	91.3(4)
Co–N4'	1.925(11)	O5'–Co–N3'	178.1(5)
		O6'–Co–O7'	91.6(4)
		O6'–Co–N2'	90.0(4)
		O6'–Co–N3'	87.0(4)
		O6'–Co–N4'	177.8(4)
		N2–Co–N4	93.7(5)

A packing diagram with hydrogen bonding scheme is shown in Fig. 2. The packing of structural units in a crystal is determined by the system of O–H···O, N–H···O and C–H···O hydrogen bonds. The solvated EtaH molecule interacts via hydrogen bond with the coordinated EtaH molecule and the 4-hydroxybenzoate anion molecules and occupies the cavity formed by the $[Co(EtaH)_2(Eta)]^+$ moieties.

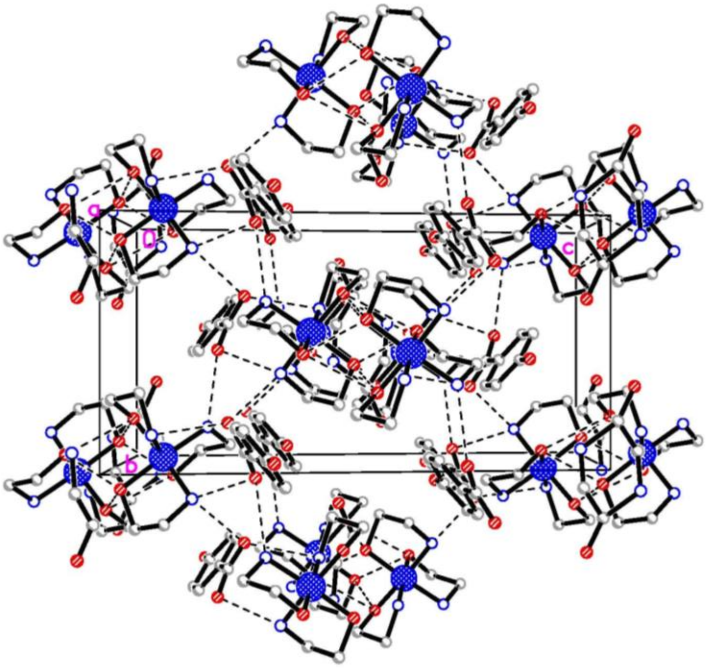

Fig 2: The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) networks.

4. Conclusions

Thus, instead of anticipated mixed-ligand metal complex coordination compound in the form of supramolecular complex has been obtained. Its molecular and crystal structure have been established by X-ray crystallography. The specific feature of the new complex is localization of the both potential ligands in outer coordination sphere which is very rare phenomenon in coordination chemistry.

5. Acknowledgments

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6. References

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