

Synthesis and Study of Heterometallic Co–Bi Compounds Based on Ethylenediaminetetraacetic Acid. Crystal and Molecular Structures of $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2[\text{Bi}_2(\mu\text{-Edta})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$ (DH₂ is dimethylglyoxime)

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Abstract—Compounds of the $[\text{Co}(\text{DH})_2\text{A}_2](\text{BiEdta}) \cdot 6\text{H}_2\text{O}$ type (where DH is the monodeprotonated dimethylglyoxime $^-\text{ON}=\text{C}(\text{CH}_3)-(\text{CH}_3)\text{C}=\text{NOH}$; A is the *o*-, *m*-, or *p*-toluidine; and Edta is the ethylenediaminetetraacetate(4⁻) ion) were synthesized and studied. The composition and structures of the complexes were determined from their UV and ¹H NMR spectra and from X-ray diffraction data. The isomer $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2[\text{Bi}_2(\mu\text{-Edta})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$ was structurally characterized using X-ray diffraction analysis. The crystals are triclinic: $a = 12.153(2)$ Å, $b = 12.824(3)$ Å, $c = 16.215(3)$ Å, $\alpha = 67.73(3)^\circ$, $\beta = 86.18(3)^\circ$, $\gamma = 66.96(3)^\circ$, space group $P\bar{1}$, $\rho(\text{calcd}) = 1.719$ g/cm³, $Z = 4$. The structure is composed of complex binuclear $[\text{Bi}_2(\mu\text{-Edta})_2(\text{H}_2\text{O})_2]^{2-}$ anions, $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]^+$ cations, and molecules of crystallization water. The Edta⁴⁻ anion chelates with the Bi atom in a hexadentate manner (N₂O₄); the fifth O atom functions as a bridging ligand. The bismuth coordination polyhedron can be regarded as a strongly distorted antiprism. In the octahedral cation, the Co(III) atom coordinates four N atoms of two DH ligands (average Co–N 1.897 Å) and two N atoms of two *o*-toluidine molecules (Co–N 2.023 Å). Thermolysis of the complexes studied was found to proceed in several successive steps, namely, the deaquation, deamination, and pyrolysis of the ligands.

In the last few years, heterometallic coordination compounds with different organic and inorganic ligands have been under extensive study. They are of interest because of their practical applications in quantum optics and electronics and the important role they play in the technology of superconducting materials. Compounds of this class are very convenient as model systems for the study of the magnetic, optical, catalytic, electric, and structural properties of chemical compounds [1–3].

Earlier, the heterometallic compounds $[\text{Cu}(\text{H}_2\text{O})_6][\text{Bi}(\text{Edta})_2] \cdot 3\text{H}_2\text{O}$ [4] and $[\text{Co}(\text{NH}_3)_5(\text{NCS})]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$ [5] were synthesized and investigated using X-ray diffraction analysis. The Cu–Bi-containing compound was found to give a perovskite-like Bi₂CuO₄ phase as a pyrolysis product [4].

In this study, we report data on the synthesis, compositions, and some properties of coordination compounds of the $[\text{Co}(\text{DH})_2\text{A}_2][\text{Bi}(\text{Edta})] \cdot 6\text{H}_2\text{O}$ type (where DH is the monodeprotonated dimethylglyoxime— $^-\text{ON}=\text{C}(\text{CH}_3)-(\text{CH}_3)\text{C}=\text{NOH}$; A is the *ortho*- (**I**), *meta*- (**II**), or *para*-toluidine (**III**); and Edta is the ethylenediaminetetraacetate(4⁻) ion). The crystal and molecular

structures of $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2[\text{Bi}_2(\mu\text{-Edta})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$ (**I**) were also determined.

EXPERIMENTAL

Synthesis of $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (IV**).** A mixture of CoSO₄ · 7H₂O (2.81 g, 0.01 mol) and dimethylglyoxime (2.32 g, 0.02 mol) was ground in a porcelain mortar, transferred to a flask, and, after the addition of methanol (40 ml) and water (20 ml), stirred for a while. *o*-Toluidine (3.22 ml) was added dropwise, and an intense flow of air was passed through the resulting solution for 4 to 5 h. The brown crystals that formed were washed with ether and dried in air.

Sulfates **V** and **VI** were obtained analogously from *m*- and *p*-toluidines, respectively.

Synthesis of $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2[\text{Bi}_2(\mu\text{-Edta})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$ (I**).** $[\text{Bi}(\text{HEdta})] \cdot 2\text{H}_2\text{O}$ (0.9964 g, 0.002 mol) was dissolved in 30 ml of hot water and neutralized with BaCO₃ (0.1970 g, 0.001 mol) to give a solution of Ba(BiEdta)₂. A solution of $[\text{Co}(\text{DH})_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (1.1210 g, 0.001 mol) in 20 ml of water was added, BaSO₄ was filtered off, and the reaction mixture was allowed to stand

Table 1. Elemental analysis data for complexes I–VI

	Compound	Content (found/calculated), %					
		Co	Bi	N	C	H	H ₂ O
I	[Co(DH) ₂ (<i>o</i> -NH ₂ C ₆ H ₄ CH ₃) ₂](BiEdta) · 6H ₂ O	5.4/5.32	19.3/18.85	9.53/10.11	35.07/34.67	5.09/5.09	
II	[Co(DH) ₂ (<i>m</i> -NH ₂ C ₆ H ₄ CH ₃) ₂](BiEdta) · 6H ₂ O	5.4/5.32	19.0/18.85	10.05/10.11	34.92/34.67	5.31/5.09	
III	[Co(DH) ₂ (<i>p</i> -NH ₂ C ₆ H ₄ CH ₃) ₂](BiEdta) · 6H ₂ O	5.3/5.32	19.2/18.85	10.17/10.11	35.15/34.67	5.17/5.09	
IV	[Co(DH) ₂ (<i>o</i> -NH ₂ C ₆ H ₄ CH ₃) ₂] ₂ SO ₄ · H ₂ O	10.0/10.51		15.36/14.99			1.55/1.61
V	[Co(DH) ₂ (<i>m</i> -NH ₂ C ₆ H ₄ CH ₃) ₂] ₂ SO ₄ · 5H ₂ O	9.7/9.88		14.33/14.09			7.45/7.55
VI	[Co(DH) ₂ (<i>p</i> -NH ₂ C ₆ H ₄ CH ₃) ₂] ₂ SO ₄ · 5H ₂ O	9.5/9.88		14.52/14.09			7.29/7.55

for several days. The dark brown crystals that formed were filtered off, washed with ethanol and ether, and dried in air to a constant weight.

Complexes **II** and **III** were obtained analogously from sulfates **V** and **VI**, respectively. The compounds obtained are finely crystalline substances stable in air which are soluble in water, poorly soluble in alcohols, and insoluble in acetone and ether. Elemental analysis data for complexes I–VI are given in Table 1.

Table 2. Crystallographic parameters of complex I

Parameter	Value
Empirical formula	C ₃₂ H ₅₆ BiCoN ₈ O ₁₈
<i>M</i>	1108.76
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Unit cell parameters	
<i>a</i> , Å	12.153(2)
<i>b</i> , Å	12.824(3)
<i>c</i> , Å	16.215(3)
α , deg	67.73(3)
β , deg	86.18(3)
γ , deg	66.96(3)
<i>V</i> , Å ³	2142.1(7)
<i>Z</i> ; ρ (calcd), g/cm ³	2; 1.719
μ_{Mo} , mm ⁻¹	4.571
θ range, deg	3.39–30.10
<i>hkl</i> ranges	$-16 \leq h \leq 17$, $-16 \leq k \leq 17$, $-15 \leq l \leq 21$
No. of measured reflections	23720
No. of reflections in the least-squares refinement/no. of refined parameters	10865/550
GOOF	0.975
Final <i>R</i> factor [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0562, <i>wR</i> ₂ = 0.1365
<i>R</i> factor for all the data array	<i>R</i> ₁ = 0.0764, <i>wR</i> ₂ = 0.1466
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$, e/Å ³	3.144 and 2.321

X-ray diffraction analysis. All measurements for a piece of brown crystal **I** (0.30 × 0.15 × 0.02 mm) were carried out at 293 K on a Kuma KM4CCD diffractometer using monochromated MoK α radiation. The crystal was positioned at a distance of 60 mm from the CCD chamber. Reflections of 931 frames in seven sets were collected for $\varphi = 0^\circ, 45^\circ, 90^\circ, 135^\circ, 180^\circ, 225^\circ,$ and 270° . The ω angle between the frames was 0.75° . Reflections from each frame were recorded within 20 s. All data processing was performed with the use of the Kuma Diffraction program package (Wroclaw, Poland).

The structure was solved by the direct methods. The non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms of the water molecules were objectively located from electron density difference maps, and the other H atoms were located geometrically. For the hydrogen atoms, only their thermal parameters were refined using the rider model.

All calculations were performed with the SHELXS86 [6] and SHELXL93 [7] program packages.

Selected crystallographic parameters and a summary of the structure refinement are present in Table 2. The coordinates and thermal parameters of the basic atoms are listed in Table 3, and the bond lengths and angles are given in Table 4.

UV spectra of aqueous solutions of the complexes were recorded on a Specord M40 spectrophotometer. ¹H NMR spectra of the compounds in D₂O were recorded on a Bruker AC-80 spectrometer. Chemical shifts are referred to TMS as the external standard.

Derivatograms were recorded on a Paulik-Paulik-Erdey derivatograph in the range 20–800°C.

RESULTS AND DISCUSSION

Thermal decomposition of complexes **I–III** proceeds in three steps. The derivatogram of complex **I** shows a broad endothermic peak in the range 50–150°C which corresponds to a loss of twelve water molecules (calcd.: 9.75%; found: 9.5%). When heated to 170–230°C, complex **I** loses the *o*-toluidine molecules (calcd.: 19.33%; found: 20.0%), and it decomposes completely at 235–470°C. Apparently, the final product

Table 3. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) of basic atoms ($U_{\text{equiv}} = 1/3 \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}, \text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}, \text{\AA}^2$
Bi	1400(1)	344(1)	565(1)	27(1)	C(3a)	973(6)	2311(6)	–1517(4)	32(1)
Co(1)	5000	5000	5000	21(1)	C(4a)	154(6)	1663(6)	–1506(4)	30(1)
Co(2)	5000	0	5000	22(1)	C(5a)	2693(6)	1518(7)	1473(4)	35(2)
O(1a)	–639(5)	2158(5)	–2130(4)	48(1)	C(6a)	2713(7)	377(7)	2247(5)	39(2)
O(2a)	334(4)	688(4)	–832(3)	34(1)	C(7a)	531(7)	2647(7)	1206(5)	43(2)
O(3a)	3331(5)	35(5)	2937(3)	48(1)	C(8a)	–587(6)	2807(7)	725(5)	40(2)
O(4a)	2089(5)	–156(5)	2117(3)	50(1)	C(9a)	2951(6)	621(6)	–1052(5)	35(2)
O(5a)	1547(6)	3620(7)	735(5)	74(2)	C(10a)	3810(6)	–357(6)	–233(5)	37(2)
O(6a)	–440(4)	2080(5)	319(4)	46(1)	C(1b)	2632(6)	1164(6)	4332(4)	31(1)
O(7a)	4757(5)	–1077(5)	–372(4)	56(2)	C(2b)	1454(7)	2130(6)	3859(6)	47(2)
O(8a)	3476(4)	–400(4)	529(3)	37(1)	C(3b)	2829(6)	–140(6)	4848(4)	28(1)
O(1b)	3533(4)	2519(4)	3944(3)	37(1)	C(4b)	1852(7)	–593(7)	4967(6)	44(2)
O(2b)	4308(4)	–2019(4)	5639(3)	33(1)	C(5b)	6434(8)	–232(8)	3450(5)	45(2)
O(1c)	6051(4)	6771(4)	4475(3)	30(1)	C(6b)	6354(11)	819(10)	2795(6)	66(3)
O(2c)	3648(4)	4557(4)	3904(3)	32(1)	C(7b)	5279(12)	1810(11)	2405(8)	82(3)
O(1w)	2282(5)	–1728(5)	233(4)	49(1)	C(8b)	7510(11)	907(12)	2447(8)	76(3)
O(2w)	3486(7)	4887(5)	–487(6)	98(3)	C(9b)	8532(13)	–95(12)	2806(7)	78(3)
O(3w)	1332(10)	5276(9)	–1506(7)	113(3)	C(10b)	8619(11)	–1201(15)	3464(10)	97(4)
O(4w)	4991(8)	–3516(7)	296(5)	91(2)	C(11b)	7619(10)	–1300(13)	3767(8)	81(4)
O(5w)	1304(6)	5285(6)	3023(5)	76(2)	C(1c)	5057(5)	6685(5)	3361(4)	26(1)
O(6w)	1911(5)	7911(5)	3540(4)	50(1)	C(2c)	5434(8)	7586(7)	2632(5)	41(2)
N(1a)	1626(5)	2054(5)	825(4)	30(1)	C(3c)	4366(6)	6060(6)	3198(4)	29(1)
N(2a)	1987(5)	1582(4)	–815(3)	26(1)	C(4c)	3853(8)	6339(7)	2291(5)	46(2)
N(1b)	3589(4)	1357(4)	4360(3)	27(1)	C(5c)	7175(6)	4020(5)	4043(5)	35(2)
N(2b)	3939(5)	–819(4)	5179(3)	25(1)	C(6c)	8118(7)	4347(7)	4060(6)	51(2)
N(3b)	5452(5)	–450(5)	3920(3)	26(1)	C(7c)	8590(9)	4368(9)	4847(8)	67(3)
N(1c)	5393(4)	6307(4)	4206(3)	24(1)	C(8c)	8711(9)	4621(7)	3250(7)	61(2)
N(2c)	4238(4)	5243(4)	3924(3)	24(1)	C(9c)	8320(9)	4543(8)	2529(8)	67(3)
N(3c)	6489(4)	3724(4)	4790(3)	25(1)	C(10c)	7367(10)	4230(8)	2481(7)	70(3)
C(1a)	1736(6)	2980(6)	–48(5)	36(2)	C(11c)	6816(9)	3971(7)	3236(5)	59(3)
C(2a)	2501(6)	2363(6)	–625(5)	31(1)					

of its pyrolysis is a mixture of the corresponding bismuth and cobalt oxides.

The UV spectra of compounds **I–III** contain an absorption band at 245–250 nm corresponding to the Co(DH)₂ group when the two other ligands in the octahedral complex are *trans* to each other. The band at 365–380 nm was assigned to the corresponding toluenes.

The ¹H NMR spectra of complexes **I–III** differ in signal intensity and chemical shifts. The signal from the methyl protons of the dimethylglyoximate ion coordinated by Co(III) is shifted downfield compared to the analogous signal in the spectrum of free dimethylglyoxime (δ 1.48 ppm (D₂O)). This shift is due to the elec-

tron density redistribution from the ligand to the metal atom in the formation of the Co←N bond. The spectra of the Co(III) *trans*-dimethylglyoximates studied contain only one resonance line characterizing the chemical shift of four magnetically equivalent CH₃ groups of two dimethylglyoximate residues; the position of this line varies from δ 2.15 to 2.34 ppm depending on the nature of the axial ligands.

It is known that in Co(III) *trans*-dimethylglyoximates containing two identical axial ligands, e.g., in [Co(DH)₂(NH₃)₃]NO₃ [8], H[CoCl₂(DH)₂] [9], and [Co(DH)₂(Thio)₂]NO₃ (Thio is thiourea) [10], two dimethylglyoximate residues are coplanar and linked by two equivalent intramolecular hydrogen bonds (the

Table 4. Bond lengths and angles in structure **I**

[(Edta)Bi(H ₂ O)] ₂ ²⁻				[Co(DH) ₂ (<i>o</i> -NH ₂ C ₆ H ₄ CH ₃) ₂] ⁺			
Bond	<i>d</i> , Å	Angle	ω, deg	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Bi–O(8a)	2.328(5)	C(4a)O(2a)Bi	117.5(4)	Co(1)–N(1b)	1.892(5)	C(3b)–C(4b)	1.486(9)
Bi–N(1a)	2.500(5)	C(6a)O(4a)Bi	118.5(5)	Co(1)–N(2b)	1.904(5)	C(8b)–C(9b)	1.34(2)
Bi–O(4a)	2.466(5)	C(8a)O(6a)Bi	120.7(4)	Co(1)–N(3b)	2.023(5)	C(5b)–C(11b)	1.49(2)
Bi–O(2a)*	2.812(4)	C(10a)O(8a)Bi	113.7(4)	Co(2)–N(1c)	1.898(5)	C(6b)–C(8b)	1.51(2)
Bi–O(6a)	2.380(5)	C(7a)N(1a)C(5a)	110.1(5)	Co(2)–N(2c)	1.892(5)	C(9b)–C(10b)	1.38(2)
Bi–N(2a)	2.453(5)	C(7a)N(1a)C(1a)	109.1(5)	Co(2)–N(3c)	2.023(5)	N(1c)–C(1c)	1.303(8)
Bi–O(2a)	2.497(4)	C(5a)N(1a)C(1a)	112.1(5)	O(1b)–N(1b)	1.359(6)	N(3c)–C(5c)	1.439(8)
Bi–O(1w)	2.697(5)	C(7a)N(1a)Bi	107.5(4)	O(2b)–N(2b)	1.327(6)	N(2c)–C(3c)	1.295(8)
N(1a)–C(7a)	1.478(9)	C(5a)N(1a)Bi	108.1(4)	O(1c)–N(1c)	1.342(6)	C(1c)–C(3c)	1.460(9)
N(1a)–C(1a)	1.502(9)	C(1a)N(1a)Bi	109.9(4)	O(2c)–N(2c)	1.344(6)	C(1c)–C(2c)	1.500(9)
N(2a)–C(9a)	1.487(8)	C(3a)N(2a)C(9a)	111.3(5)	N(1b)–C(1b)	1.287(8)	C(5c)–C(6c)	1.37(1)
N(1a)–C(5a)	1.481(8)	C(3a)N(2a)C(2a)	112.3(5)	N(3b)–C(5b)	1.436(9)	C(6c)–C(8c)	1.45(1)
N(2a)–C(3a)	1.472(8)	C(9a)N(2a)C(2a)	109.6(5)	N(2b)–C(3b)	1.300(8)	C(8c)–C(9c)	1.34(1)
N(2a)–C(2a)	1.496(8)	C(3a)N(2a)Bi	111.1(4)	C(1b)–C(3b)	1.486(9)	C(10c)–C(11c)	1.35(1)
O(1a)–C(4a)	1.232(8)	C(9a)N(2a)Bi	101.7(4)	C(1b)–C(2b)	1.487(9)	C(3c)–C(4c)	1.494(9)
O(3a)–C(6a)	1.221(8)	C(2a)N(2a)Bi	110.3(4)	C(5b)–C(6b)	1.34(1)	C(5c)–C(11c)	1.44(1)
O(5a)–C(8a)	1.227(9)	C(2a)C(1a)N(1a)	111.1(5)	C(6b)–C(7b)	1.39(2)	C(6c)–C(7c)	1.45(1)
O(7a)–C(10a)	1.232(8)	C(1a)C(2a)N(2a)	110.8(5)	C(10b)–C(11b)	1.31(2)	C(9c)–C(10c)	1.38(2)
O(2a)–C(4a)	1.276(8)	N(2a)C(3a)C(4a)	113.8(5)	Angle	ω, deg	Angle	ω, deg
O(4a)–C(6a)	1.274(9)	O(1a)C(4a)O(2a)	126.0(6)	N(2c)Co(2)N(1c)**	98.6(2)	N(2b)C(3b)C(1b)	112.2(5)
O(6a)–C(8a)	1.285(8)	O(1a)C(4a)C(3a)	117.6(6)	N(2c)Co(2)N(1c)	81.4(2)	N(2b)C(3b)C(4b)	124.8(6)
O(8a)–C(10a)	1.263(9)	O(2a)C(4a)C(3a)	116.4(5)	N(2c)Co(2)N(3c)**	91.1(2)	C(1b)C(3b)C(4b)	123.0(6)
C(1a)–C(2a)	1.494(9)	N(1a)C(5a)C(6a)	111.1(6)	N(1c)Co(2)N(3c)**	87.9(2)	C(6b)C(5b)N(3b)	125.3(9)
C(5a)–C(6a)	1.516(10)	O(3a)C(6a)O(4a)	125.3(7)	N(2c)Co(2)N(3c)	88.9(2)	C(6b)C(5b)C(11b)	120.5(9)
C(9a)–C(10a)	1.524(10)	O(3a)C(6a)C(5a)	117.9(7)	N(1c)Co(2)N(3c)	92.1(2)	N(3b)C(5b)C(11b)	114.2(8)
C(3a)–C(4a)	1.522(9)	O(4a)C(6a)C(5a)	116.9(6)	N(1b)Co(1)N(2b)	80.9(2)	C(5b)C(6b)C(7b)	124(1)
C(7a)–C(8a)	1.516(10)	N(1a)C(7a)C(8a)	111.2(5)	N(1b)Co(1)N(2b)***	99.1(2)	C(5b)C(6b)C(8b)	117(1)
		O(5a)C(8a)O(6a)	125.1(7)	N(1b)Co(1)N(3b)	92.0(2)	C(7b)C(6b)C(8b)	119(1)
		O(5a)C(8a)C(7a)	118.6(7)	N(1b)**Co(1)N(3b)	88.0(2)	C(9b)C(8b)C(6b)	117(1)
		O(6a)C(8a)C(7a)	116.3(6)	N(2b)Co(1)N(3b)	86.3(2)	C(8b)C(9b)C(10b)	126(1)
		N(2a)C(9a)C(10a)	111.2(5)	N(2b)**Co(1)N(3b)	93.7(2)	C(11b)C(10b)C(9b)	118(1)
		O(7a)C(10a)O(8a)	125.3(7)	C(1b)N(1b)O(1b)	118.7(5)	C(10b)C(11b)C(5b)	121(1)
		O(7a)C(10a)C(9a)	116.8(7)	C(1b)N(1b)Co(1)	117.9(4)	N(1c)C(1c)C(3c)	112.8(5)
		O(8a)C(10a)C(9a)	117.8(6)	O(1b)N(1b)Co(1)	123.4(4)	N(1c)C(1c)C(2c)	123.1(6)
				C(3b)N(2b)O(2b)	121.6(5)	C(3c)C(1c)C(2c)	123.9(6)
				C(3b)N(2b)Co(1)	116.8(4)	N(2c)C(3c)C(1c)	113.0(5)
				O(2b)N(2b)Co(1)	121.7(4)	N(2c)C(3c)C(4c)	123.4(6)
				C(5b)N(3b)Co(1)	119.6(4)	C(1c)C(3c)C(4c)	123.6(6)
				C(1c)N(1c)O(1c)	120.8(5)	C(6c)C(5c)C(11c)	119.6(8)
				C(1c)N(1c)Co(2)	116.1(4)	C(6c)C(5c)N(3c)	124.2(7)
				O(1c)N(1c)Co(2)	123.0(4)	C(11c)C(5c)N(3c)	116.2(7)
				C(3c)N(2c)O(2c)	121.4(5)	C(5c)C(6c)C(8c)	117.3(9)
				C(3c)N(2c)Co(2)	116.6(4)	C(5c)C(6c)C(7c)	124.1(8)
				O(2c)N(2c)Co(2)	121.9(4)	C(8c)C(6c)C(7c)	118.5(9)
				C(5c)N(3c)Co(2)	122.7(4)	C(9c)C(8c)C(6c)	119(1)
				N(1b)C(1b)C(3b)	112.1(6)	C(8c)C(9c)C(10c)	125(1)
				N(1b)C(1b)C(2b)	124.5(6)	C(11c)C(10c)C(9c)	115(1)
				C(b3)C(1b)C(2b)	123.4(6)	C(10c)C(11c)C(5c)	123(1)

* Symmetry operation code: $-x, -y, -z$.** Symmetry operation code: $-x + 1, -y + 1, -z + 1$.*** Symmetry operation code: $-x + 1, -y, -z + 1$.

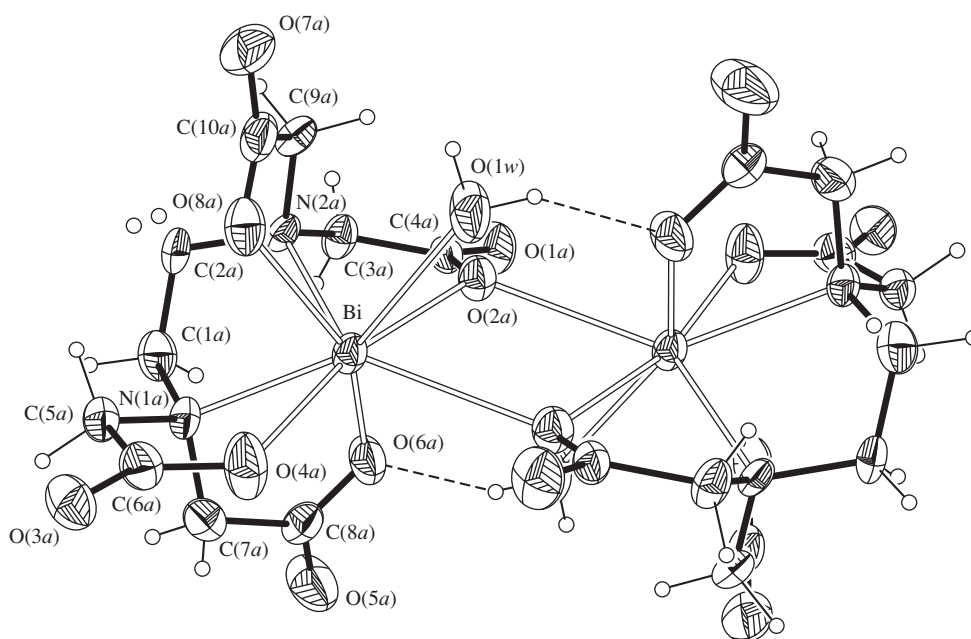


Fig. 1. Structure of the complex $[\text{Bi}(\text{Edta})(\text{H}_2\text{O})]_2^{2-}$ anion in compound **I**.

$\text{O}\cdots\text{O}$ distances 2.48–2.52 Å). The magnetic equivalence of the CH_3 groups in the DH residues indicates that the complex cation has a *trans*-structure, which is consistent with the X-ray diffraction data.

In the ^1H NMR spectra of complexes **I–III**, signals from the $\text{NCH}_2\text{CH}_2\text{N}$ ethylene protons appear at δ 3.58–3.70 ppm, while the corresponding signals from the methylene protons in the CH_2COO groups are shifted downfield (δ 4.09–4.58 ppm) and split. The nonequivalence of the acetato groups of Edta^{4-} in solution suggests different types of their coordination to the bismuth(III) atom, which is in agreement with the X-ray diffraction data for complex **I**.

The crystal of **I** is built from doubly charged binuclear $[(\text{Edta})\text{Bi}(\text{H}_2\text{O})]_2^{2-}$ anions, $[\text{Co}(\text{DH})_2(\text{o-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]^+$ cations, and molecules of crystallization water in the ratio 1 : 2 : 5. All the components of the system are united through hydrogen bonds into a three-dimensional framework.

The structure of the doubly charged centrosymmetric complex $[\text{Bi}(\text{Edta})(\text{H}_2\text{O})]_2^{2-}$ anion is displayed in Fig. 1. The Edta^{4-} ligand is coordinated by the bismuth atom in a hexadentate fashion (N_2O_4) to form one ethylenediamine and four glycine rings. These chelate rings are significantly nonplanar; their conformations are characterized by the dihedral φ and ψ angles (Table 5). The Bi–N and Bi–O interatomic distances are 2.453(5)–2.500(5) Å and 2.328(5)–2.497(4) Å, respectively. The O(2a) and O(2a)* atoms of the acetato groups in two Edta^{4-} anions act as bridging ligands (Bi–O(2a) 2.497(4), Bi–O(2a)* 2.812(4) Å).

Thus, the dentate number of Edta^{4-} is seven and its coordination type is G^{100001} (as designated in [11]). The bismuth coordination number is extended to eight by the O(1w) of the water molecule (Bi–O(1w) 2.697(5) Å). The Bi coordination polyhedron can be interpreted as a strongly distorted square antiprism (Fig. 2). Two moieties of the dimer are additionally linked by an intramolecular O(1w)–H \cdots O(6a)* hydrogen bond of the coordinated water molecule (Table 6).

Table 5. Atom deviations from the basic planes and angles between the chelate fragments in structure **I**

Ring	Plane	$\varphi(\psi)^*$, deg	Atom	Deviation, Å
<i>E</i>	BiN(1a)N(2a)	28	C(1a)	–0.28
			C(2a)	+0.42
<i>G</i> (1)	BiN(1a)O(4a)	29	C(5a)	+0.85
			C(6a)	+0.57
			O(3a)	+0.91
			C(7a)	+0.81
<i>G</i> (2)	BiN(1a)O(6a)	24	C(8a)	+0.49
			O(5a)	+0.70
			C(4a)	–0.57
			C(3a)	–0.72
<i>G</i> (3)	BiN(2a)O(2a)	30	C(1a)	–1.03
			C(10a)	–0.73
			C(9a)	–0.98
			O(7a)	–1.32
<i>G</i> (4)	BiN(2a)O(8a)	40		

* ψ is the angle between the NBiN and CBiC planes in the *E* ring, and φ is the dihedral angle along the N \cdots O direction in the *G* rings.

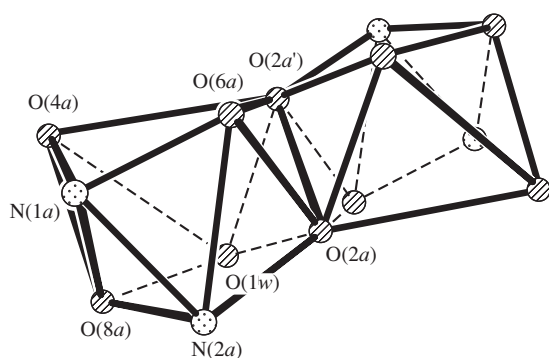


Fig. 2. Coordination polyhedron of the bismuth atom in the dimeric anion of structure **I**.

It has been shown in [12] that complexes containing the [Bi(Edta)] or [Bi(HEdta)] units are mostly structured as polymeric chains or layers, with one or two bismuth-noncoordinated carboxy O atoms of Edta⁴⁻ (HEdta³⁻) acting as bridging ligands (coordination type H⁰¹⁰⁰⁰¹ or O²⁰⁰⁰⁰¹ [11]). For example, polymeric chains were found in [Co(NH₃)₄(Ala)₂][Bi(Edta)(H₂O)] · 5H₂O [12], [Co(NH₃)₄(C₂O₄)](Bi(Edta)) · 3H₂O [12], Bi(HEdta) [13], [Ca(H₂O)₇][Bi(Edta)]₂ · 2H₂O (**VII**) [14], [Cu(H₂O)₆][Bi(Edta)]₂ · 3H₂O [4], [Co(H₂O)₆][Bi(Edta)]₂ · 3H₂O [15], [Ni(H₂O)₆][Bi(Edta)]₂ · 3H₂O [15], and (CN₃H₆)[Bi(Edta)(H₂O)] [12] and laminated structures

were found in Na[Bi(Edta)] · 3H₂O [16, 17], [Bi(HEdta)] · 2H₂O [18, 19], and (NH₄)[Bi(Edta)(H₂O)] [13].

In compound **VII**, one of the coordinated carboxy O atoms (O(1)) functions as a chelating and bridging ligand; it is bound, as in **I**, to form a doubly charged dimeric anion. The Bi–O(1) distances in **VII** (2.463 and 3.038 Å) are longer than the analogous distances in **I**. However, the Edta⁴⁻ ligand in compound **VII** unites the dimeric fragments into a polymer via the coordination of the free carboxy O atom. In this case, the dentate number of Edta⁴⁻ is eight. In contrast, the framework of compound **I** is built from the dimers held together only by H bonds.

Selected geometrical parameters of the complex [Bi(Edta)(H₂O)]₂²⁻ anions in compound **I** are given in Table 4. In Edta⁴⁻, the average C–O_{coord}, C–O_{noncoord}, C–N, C–C (glycine ring), and C–C (ethylenediamine ring) distances are 1.275, 1.228, 1.486, 1.520, and 1.494 Å, respectively.

The structure of one of the [Co(DH)₂(NH₂C₆H₄CH₃)₂]⁺ cations in complex **I** is shown in Fig. 3. The coordination octahedron of either cobalt atom includes four N atoms of two DH⁻ ligands in the equatorial plane (Co–N 1.892–1.904 Å) and two axial N atoms from two toluidine molecules (average Co–N 2.023 Å). The geometrical parameters of the coordination environment of Co(III) in **I** are typical of compounds of this type [20].

Table 6. Geometrical parameters of the expected hydrogen bonds in structure **I**

D–H...A	Distance, Å			D–H...A angle, deg	Symmetry operation for the A atom
	D–H	H...A	D...A		
O(1b)–H...O(2b)	0.92	1.61	2.518(7)	169	–x + 1, –y, –z + 1
O(2c)–H...O(1c)	0.90	1.60	2.488(6)	172	–x + 1, –y + 1, –z + 1
O(1w)–H...O(6a)	0.90	1.90	2.717(7)	150	–x, –y, –z
O(2w)–H(1w2)...O(5a)	0.90	1.90	2.70(1)	147	x, y, z
O(2w)–H(2w2)...O(4w)	0.95	1.98	2.93(1)	171	–x, –y, –z
O(3w)–H(1w3)...O(2w)	0.91	2.21	3.11(1)	168	x, y, z
O(3w)–H(2w3)...O(5w)	0.90	1.91	2.81(1)	173	–x, –y + 1, –z
O(4w)–H(1w4)...O(7a)	0.90	1.91	2.80(1)	169	x, y, z
O(4w)–H(2w4)...O(2w)	0.90	1.91	2.82(1)	173	x + 1, y – 1, z
O(5w)–H(1w5)...O(1a)	0.91	1.92	2.826(8)	174	–x, –y + 1, –z
O(5w)–H(2w5)...O(2c)	0.98	1.97	2.911(8)	162	x, y, z
O(6w)–H(1w6)...O(1a)	0.93	1.98	2.891(7)	168	–x, –y + 1, –z
O(6w)–H(2w6)...O(4a)	0.91	1.90	2.745(8)	153	x, y + 1, z
N(3a)–H(3b1)...O(1c)	0.90	2.21	3.108(6)	178	x, y – 1, z
N(3b)–H(3b2)...O(3a)	0.90	2.02	2.849(7)	152	x, y, z
N(3c)–H(3c1)...O(6w)	0.90	2.08	2.953(7)	163	–x + 1, –y + 1, –z + 1
N(3c)–H(3c2)...O(2b)	0.90	2.13	3.018(6)	167	–x + 1, –y, –z + 1

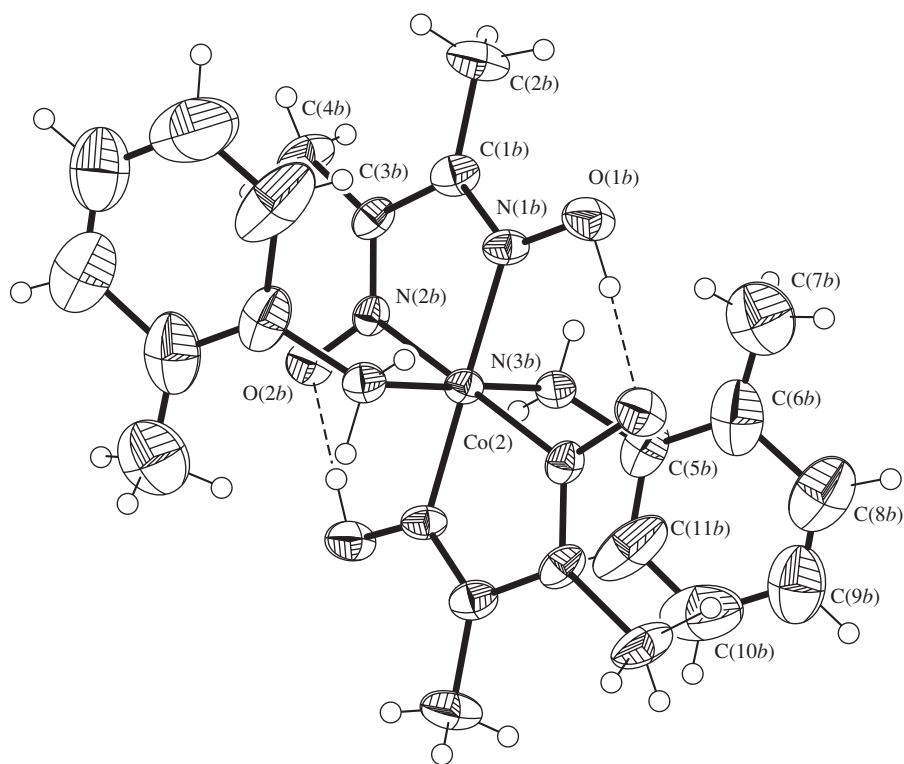


Fig. 3. Structure of the complex $[\text{Co}(\text{DH})_2(\text{o}\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2]^+$ cation in compound I.

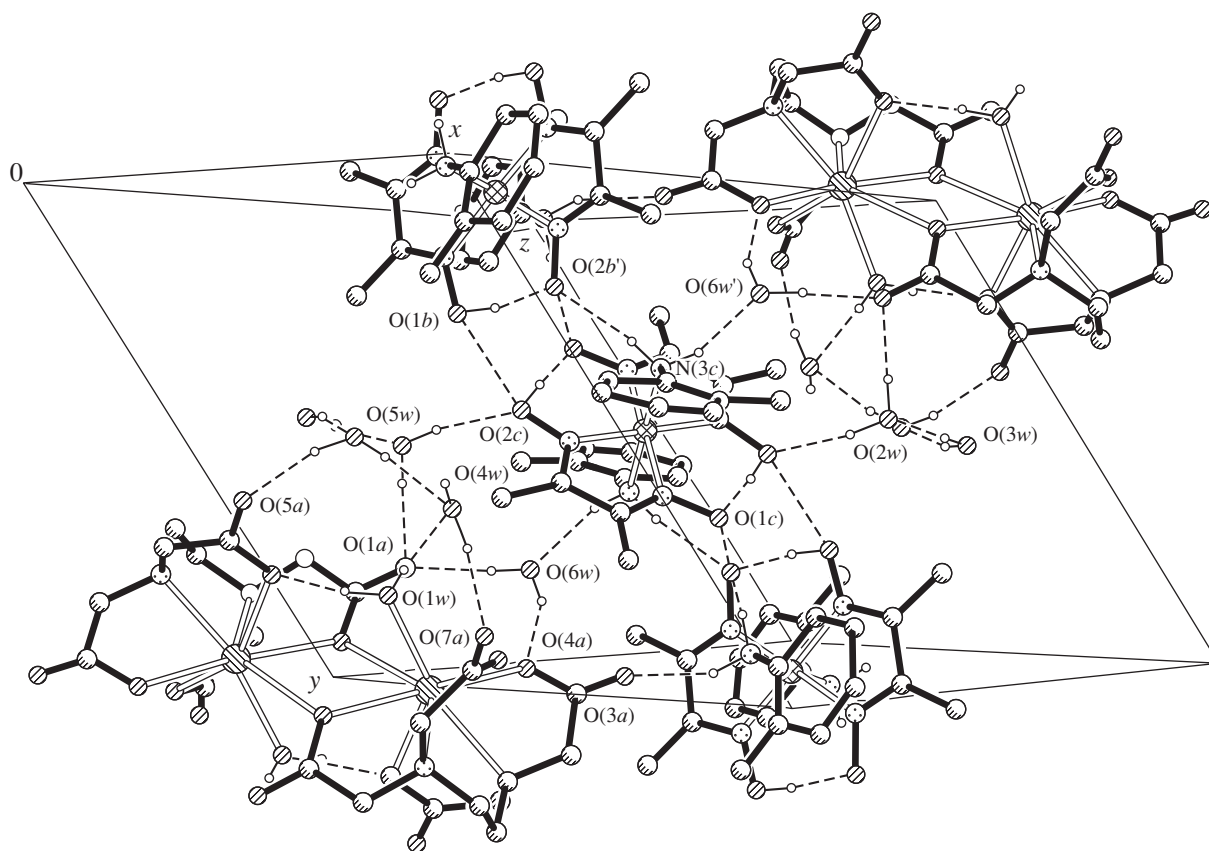


Fig. 4. Fragment of crystal structure I.

Two dimethylglyoxime residues are linked by the O–H...O hydrogen bonds (O...O 2.488–2.518 Å). Such a structure is not uncommon among [Co(DH)₂A₂]⁺ complexes (where A is aniline [20], Py [21], or Thio [22]). A possible intramolecular π – π interaction between five-membered chelate rings and aromatic (or π -delocalized as in thiourea) ligands has been noted in [23]. Such an interaction is observed for both complex cations in **I**.

In the DH residues, the average N–O, C–C, C–C(Me), and N–C distances are equal to 1.343, 1.473, 1.492, and 1.296 Å, respectively. The C–C, C–C(Me), and C–N bond lengths in the toluidine are 1.392, 1.417, and 1.438 Å, respectively.

Note that the complex cations are packed in a crystal such that the O(1*b*) and O(2*c*) atoms are spaced at 2.64 Å. This can suggest that the complex cations are united not only through the N(3*c*)–H...O(2*b*) hydrogen bonds but also through a bifurcate O–H...O hydrogen bond (Table 4).

The packing of complex **I** in crystal is shown in Fig. 4. The anionic and cationic sublattices of the crystal are linked by hydrogen bonds involving water molecules. The main geometrical parameters of the hydrogen bonds are given in Table 6.

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