

Synthesis and Structure of $\{\mu\text{-Oxalato-Bis[ethylenediaminetetraacetato-}$ $\text{bismuthato(III)}\}$ pentaamminethiocyanatocobalt(III) Dodecahydrate, $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot$ $12\text{H}_2\text{O}$

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Abstract—A heterometallic complex of cobalt(III) and bismuth(III), $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$, was synthesized and studied by X-ray diffraction analysis. The crystals are monoclinic, $a = 12.792(3)$ Å, $b = 9.792(2)$ Å, $c = 22.945(5)$ Å, $\beta = 92.92(3)^\circ$, $\rho_{\text{calcd}} = 1.970$ g/cm³, space group $P2_1/c$, $Z = 4$. The complex has an isle structure composed of $[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})]^{4-}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ complex ions and molecules of crystallization water. The Edta^{4-} ligand functions as a hexadentate chelating ($2N + 4O$) agent, while the oxalate ion acts as a bridging ligand. The thiocyanate ion is coordinated to cobalt(III) through the N atom, while the cation interacts with the anion via the Bi–S contact (3.571 Å). Hence, the coordination polyhedron of Bi can be regarded as a tricapped trigonal prism. It was shown that thermolysis of the complex proceeds in several stages, viz., the deaquation, deamination, and pyrolysis of its ligands.

In recent years, solutions and crystals of bismuth(III) complexonates have been extensively studied. Such an interest in these compounds is explained by the possibility of using them both as precursors of bimetallic oxide ceramics with desired electric properties, prepared by low-temperature pyrolysis [1, 2], and as analytical reagents. Compounds with ethylenediaminetetraacetic acid are particularly attractive because the ligand and its sodium salts are available and form stable complexes with the bismuth(III) ion in a solution.

There are a large number of papers concerned with the X-ray study of bismuth(III) ethylenediaminetetraacetates [1, 3–14]. The mobile coordination sphere of bismuth makes it possible to change its coordination number and polyhedron.

In this work, experimental data on the synthesis and study of the composition, structure, and some properties of the coordination compound $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$ are reported. Thiocyanate and oxalate ions were chosen as ligands, for they are well known as the ligands bridging two metal atoms.

EXPERIMENTAL

Synthesis of $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$. An aqueous solution of $\text{K}_2\text{C}_2\text{O}_4$ (10 ml, 0.17 g, 0.001 mol) was added to an aqueous solution containing $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{SO}_4$ (0.60 g, 0.002 mol) and $\text{K}[\text{Bi}(\text{Edta})]$ (1.07 g, 0.002 mol). The solution of $\text{K}[\text{Bi}(\text{Edta})]$ was prepared by the reaction of $[\text{Bi}(\text{HEdta})] \cdot 2\text{H}_2\text{O}$ [9] with an equivalent amount of K_2CO_3 . When the reaction mixture was allowed to stand for several days, orange crystals precipitated from it. The obtained crystals were then filtered off, washed with ethanol and ether, and dried in air to a constant weight. The substance obtained is soluble in water but insoluble in alcohols, acetone, or ether. It can be recrystallized from water without compositional changes.

For $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$
anal. calcd. Co, 6.92; Bi, 24.54; C, 16.93; H, 4.62; N, 13.16.
(%):

Found (%): Co, 6.4; Bi, 23.7; C, 16.56; H, 4.41; N, 13.37.

IR (cm⁻¹): 2105 ($\nu(\text{CN})_{\text{NCS}}$), 1585 ($\nu_{\text{as}}(\text{COO})$), 1375 ($\nu_{\text{s}}(\text{COO})$), 1065, 1030 ($\nu(\text{CN})_{\text{Edta}}$), 805 ($\nu(\text{CS})$).

Table 1. Crystallographic parameters of the complex under study

| Parameter | Value |
|--|--|
| Molecular formula | C ₁₂ H ₃₉ BiCoN ₈ O ₁₆ S |
| Molecular mass | 851.48 |
| Temperature, K | 293(2) |
| $\lambda\text{MoK}\alpha$, Å | 0.71073 |
| Crystal system, space group | Monoclinic, <i>P2₁/c</i> |
| Unit cell parameters | |
| <i>a</i> , Å | 12.792(3) |
| <i>b</i> , Å | 9.792(2) |
| <i>c</i> , Å | 22.945(5) |
| β , deg | 92.92(3) |
| <i>V</i> , Å ³ | 2870(1) |
| <i>Z</i> , ρ calcd, g/cm ³ | 4, 1.970 |
| μ (MO), mm ⁻¹ | 6.854 |
| Crystal size, mm | 0.1 × 0.1 × 0.4 |
| θ range, deg | 4.12–28.28 |
| <i>hkl</i> ranges | –16 ≤ <i>h</i> ≤ 16, –10 ≤ <i>k</i> ≤ 13, –26 ≤ <i>l</i> ≤ 30 |
| No. of measured reflections | 14083 |
| No. of reflections refined by least squares/no. of parameters | 6740/352 |
| GOOF | 0.905 |
| Final <i>R</i> factor [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0565, <i>wR</i> ₂ = 0.1375 |
| <i>R</i> factor (all over the data set) | <i>R</i> ₁ = 0.0916, <i>wR</i> ₂ = 0.1499 |
| Residual peaks $\Delta\rho$ (max) and $\Delta\rho$ (min), e/Å ³ | 4.313 and –3.033 |

Table 2. Coordinates (×10⁴) and equivalent isotropic thermal parameters *U*_{equiv} (×10³) 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> | <i>U</i> _{equiv} , Å ² | Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{equiv} , Å ² |
|----------------|-----------|-----------|----------|--|-------|----------|----------|----------|--|
| Bi | 1674(1) | 3458(1) | 865(1) | 28(1) | N(2) | 3090(5) | 5218(6) | 1047(3) | 29(1) |
| Co | –811(1) | 8559(1) | 1591(1) | 27(1) | N(3) | –739(7) | 6596(6) | 1565(3) | 41(2) |
| S | –986(2) | 3895(2) | 1229(1) | 50(1) | N(4) | 438(6) | 8675(6) | 1129(3) | 39(2) |
| O(1) | 1371(5) | 1767(6) | 1712(3) | 42(2) | N(5) | –2074(6) | 8437(7) | 2031(3) | 38(2) |
| O(2) | 1714(6) | 1102(6) | 502(3) | 45(2) | N(6) | –844(6) | 10544(6) | 1628(3) | 35(2) |
| O(3) | 1633(4) | 4636(6) | 1820(2) | 35(1) | N(7) | 47(7) | 8578(7) | 2317(3) | 39(2) |
| O(4) | 2718(6) | 3637(6) | 66(3) | 43(2) | N(8) | –1666(7) | 8537(7) | 863(3) | 42(2) |
| O(5) | 2060(6) | –141(8) | 2040(4) | 79(3) | C(1) | 3237(7) | 1628(8) | 1776(4) | 40(2) |
| O(6) | 2598(5) | –779(6) | 339(3) | 56(2) | C(2) | 2123(7) | 1023(8) | 1847(4) | 33(2) |
| O(7) | 1804(6) | 6618(6) | 2279(3) | 48(2) | C(3) | 3537(8) | 1059(9) | 761(4) | 44(2) |
| O(8) | 3733(6) | 4932(8) | –464(3) | 75(3) | C(4) | 2532(8) | 402(9) | 524(4) | 40(2) |
| O(9) | 954(4) | 5699(5) | 480(2) | 35(1) | C(5) | 2680(7) | 6364(7) | 1394(4) | 32(2) |
| O(10) | –400(5) | 6712(5) | 21(2) | 33(1) | C(6) | 1975(7) | 5838(8) | 1872(3) | 31(2) |
| O(1 <i>w</i>) | –3604(7) | 3428(8) | 2278(4) | 87(3) | C(7) | 3438(8) | 5680(9) | 472(4) | 45(2) |
| O(2 <i>w</i>) | –845(7) | 1135(7) | 402(3) | 64(2) | C(8) | 3300(7) | 4667(11) | –11(4) | 45(2) |
| O(3 <i>w</i>) | –3506(7) | 6066(9) | 1624(4) | 74(2) | C(9) | 3961(7) | 4570(9) | 1406(4) | 40(2) |
| O(4 <i>w</i>) | –4762(10) | 8416(10) | 1979(6) | 125(5) | C(10) | 4252(7) | 3184(8) | 1182(4) | 37(2) |
| O(5 <i>w</i>) | –3574(9) | 10715(11) | 1653(6) | 132(4) | C(11) | 156(7) | 5693(7) | 148(3) | 31(2) |
| O(6 <i>w</i>) | –3663(15) | 1870(13) | 600(8) | 204(9) | C(12) | –845(7) | 5481(7) | 1429(3) | 31(2) |
| N(1) | 3354(5) | 2220(7) | 1181(3) | 33(2) | | | | | |

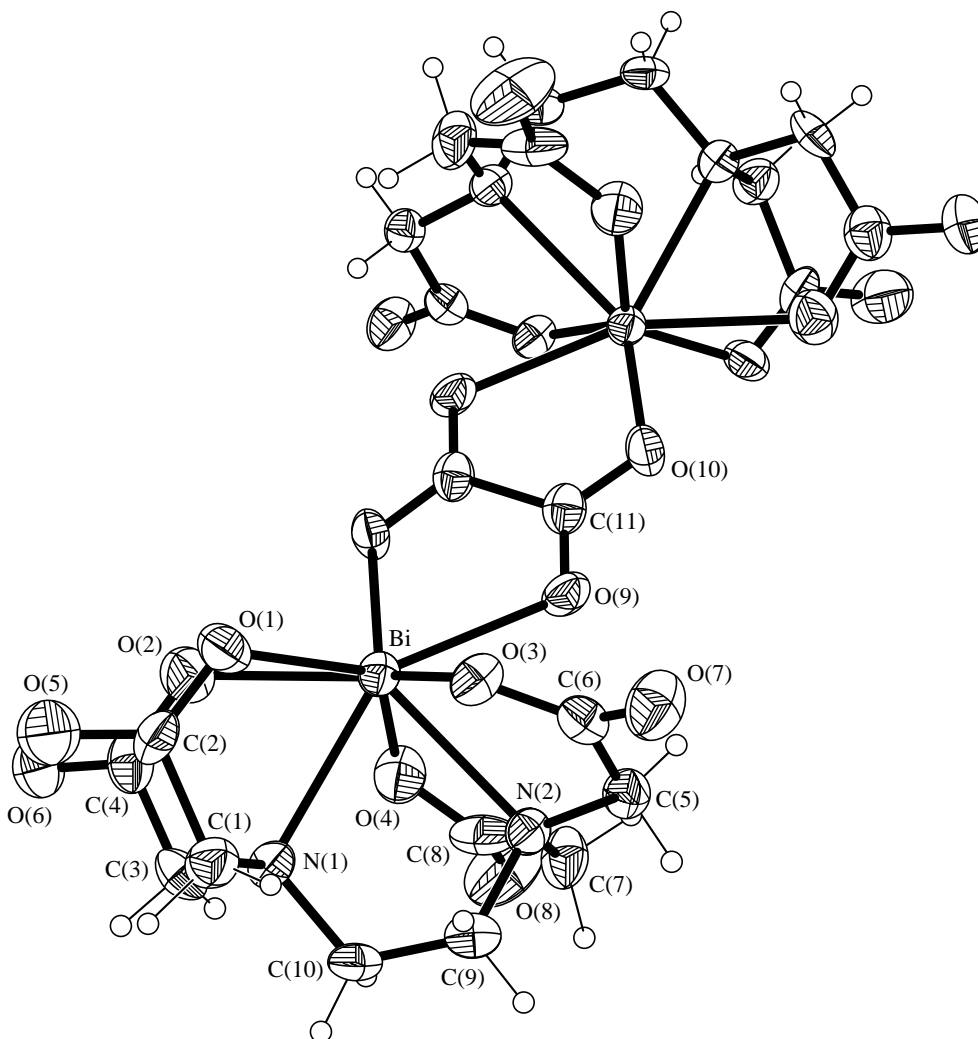


Fig. 1. Structure of the complex $[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})]^{4-}$ anion.

X-ray diffraction analysis. All crystallographic data were obtained at room temperature from an orange crystal of prismatic habitus ($0.1 \times 0.1 \times 0.4$ mm) on a Kuma KM4CCD diffractometer (monochromated MoK_α radiation). The crystal was positioned at a distance of 60 mm from the CCD chamber. Reflections of 449 frames in four sets were collected. The ω angle between the frames was 0.75° . Reflections from each frame were recorded within 18 s. Intensity data were corrected for the Lorentz and polarization effects. Absorption correction was not applied. All data processing was performed with the use of the Kuma Diffraction program package (Wroclaw, Poland).

The structure was solved by the direct method with the use of the SHELXS97 program [15]. Non-hydrogen atoms were refined by the least-squares method in the anisotropic approximation. Hydrogen atoms were located geometrically with the refinement of their thermal factors only.

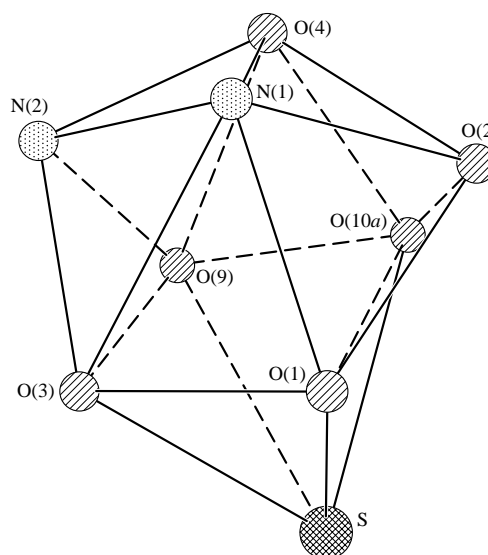


Fig. 2. Coordination polyhedron of the bismuth atom.

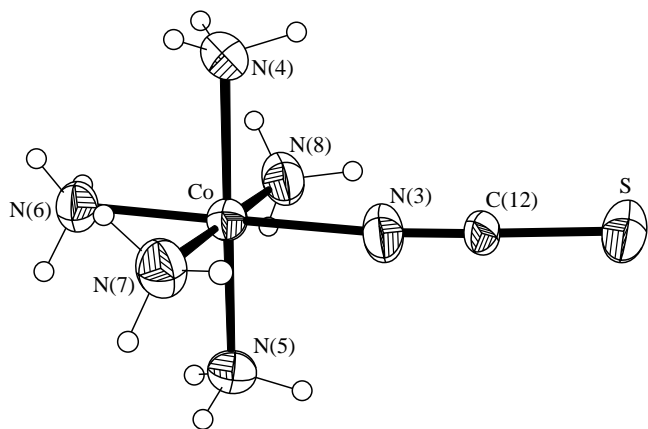


Fig. 3. Structure of the complex $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ cation.

Experimental and structure refinement data are given in Table 1. The coordinates of basic atoms are listed in Table 2.

Derivatograms were recorded in air on a Paulik–Paulik–Erdely derivatograph in the 20–800°C temperature range at heating rates of 5 and 2.5 K/min.

RESULTS AND DISCUSSION

Thermal decomposition of the complex occurs in three stages. In the 50–120°C range, the derivatogram shows a broad endothermic peak corresponding to the loss of 12 molecules of crystallization water (found: 12.5%, calcd.: 12.7%). On further heating, at 160–250°C, the complex loses ammonia molecules (found: 11.0%, calcd.: 10.0%) and it decomposes completely at 250–490°C. Apparently, the final product of pyrolysis is a mixture of bismuth and cobalt oxides.

The crystal is built from the $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ cations, binuclear centrosymmetric $[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})]^{4-}$ anions, and molecules of crystallization water, which are combined by hydrogen bonds to form a framework structure.

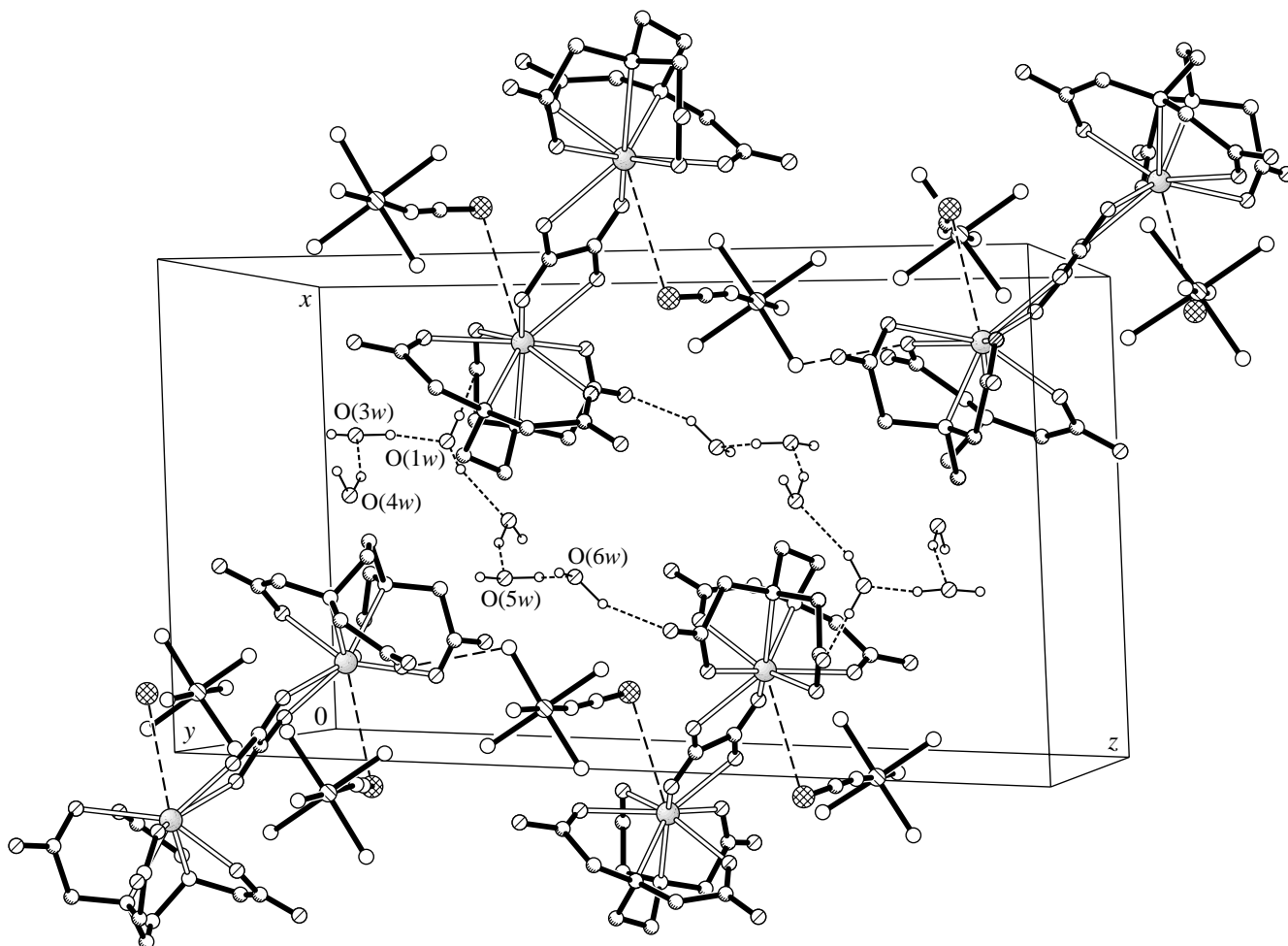


Fig. 4. Fragment of the crystal structure.

Table 3. Atomic deviations (Å) from the basic planes and dihedral angles (deg) of chelate cycles in the structure*

| <i>E</i> BiN(1)N(2) | | <i>G</i> (1) BiN(1)O(1) | | <i>G</i> (2) BiN(1)O(2) | | <i>G</i> (3) BiN(2)O(3) | | <i>G</i> (4) BiN(2)O(4) | |
|------------------------|-------|----------------------------|-------|----------------------------|-------|----------------------------|-------|----------------------------|-------|
| C(9) | +0.45 | C(1) | +0.45 | C(3) | +0.57 | C(5) | +0.79 | C(7) | +0.53 |
| C(10) | -0.26 | C(2) | -0.14 | C(4) | +0.23 | C(6) | +0.53 | C(8) | +0.34 |
| | | O(5) | -0.69 | O(6) | +0.26 | O(7) | +0.83 | O(8) | +0.57 |
| ψ | 28 | φ ₁ | 11 | φ ₂ | 20 | φ ₃ | 33 | φ ₄ | 22 |

* ψ is the angle between the NBiN and CBiC planes in the *E* cycle, and φ_{*i*} is the dihedral angle along the N···O_(COO) direction in the *G*(*i*) cycles.

Table 4. Bond lengths and angles

| Bond | <i>d</i> , Å | Bond | <i>d</i> , Å | Angle | ω, deg | Angle | ω, deg |
|-------------|--------------|--------------|--------------|------------------|----------|-----------------|----------|
| Bi–O(4) | 2.328(6) | Bi–O(2) | 2.454(6) | N(7)CoN(5) | 90.2(3) | N(8)CoN(5) | 90.0(3) |
| Bi–O(3) | 2.481(5) | Bi–N(2) | 2.520(6) | N(3)CoN(4) | 90.0(3) | N(6)CoN(4) | 89.2(3) |
| Bi–O(9) | 2.523(6) | Bi–N(1) | 2.540(7) | N(7)CoN(4) | 91.3(3) | N(8)CoN(4) | 88.5(3) |
| Bi–O(10*) | 2.545(6) | Bi–O(1) | 2.598(6) | N(5)CoN(4) | 178.5(3) | C(2)O(1)Bi | 114.8(5) |
| Co–N(3) | 1.925(6) | Co–N(6) | 1.946(6) | C(4)O(2)Bi | 122.2(6) | C(6)O(3)Bi | 119.6(5) |
| Co–N(7) | 1.947(7) | Co–N(8) | 1.950(8) | C(8)O(4)Bi | 122.2(6) | C(11)O(9)Bi | 119.0(5) |
| Co–N(5) | 1.953(7) | Co–N(4) | 1.966(8) | C(11)O(10)Bi* | 117.9(5) | C(10)N(1)C(1) | 110.9(7) |
| S–C(12) | 1.627(7) | O(1)–C(2) | 1.23(1) | C(10)N(1)C(3) | 109.4(7) | C(1)N(1)C(3) | 108.4(7) |
| O(2)–C(4) | 1.25(1) | O(3)–C(6) | 1.259(9) | C(10)N(1)Bi | 109.9(5) | C(1)N(1)Bi | 108.8(5) |
| O(4)–C(8) | 1.27(1) | O(5)–C(2) | 1.23(1) | C(3)N(1)Bi | 109.4(5) | C(7)N(2)C(5) | 112.0(6) |
| O(6)–C(4) | 1.24(1) | O(7)–C(6) | 1.23(1) | C(7)N(2)C(9) | 111.8(7) | C(5)N(2)C(9) | 107.4(6) |
| O(8)–C(8) | 1.23(1) | O(9)–C(11) | 1.241(9) | C(7)N(2)Bi | 107.9(5) | C(5)N(2)Bi | 109.5(5) |
| O(10)–C(11) | 1.251(9) | N(1)–C(1) | 1.50(1) | C(9)N(2)Bi | 108.1(5) | C(12)N(3)Co | 163.3(8) |
| N(1)–C(10) | 1.49(1) | N(2)–C(7) | 1.48(1) | N(1)C(1)C(2) | 112.1(7) | O(5)C(2)O(1) | 125.0(9) |
| N(1)–C(3) | 1.52(1) | N(2)–C(9) | 1.49(1) | O(5)C(2)C(1) | 117.9(8) | O(1)C(2)C(1) | 117.1(7) |
| N(2)–C(5) | 1.49(1) | C(1)–C(2) | 1.56(1) | C(4)C(3)N(1) | 113.0(7) | O(6)C(4)O(2) | 124.8(9) |
| N(3)–C(12) | 1.142(9) | C(5)–C(6) | 1.54(1) | O(6)C(4)C(3) | 116.7(8) | O(2)C(4)C(3) | 118.4(8) |
| C(3)–C(4) | 1.51(1) | C(9)–C(10) | 1.51(1) | N(2)C(5)C(6) | 111.3(6) | O(7)C(6)O(3) | 125.1(8) |
| C(7)–C(8) | 1.49(1) | C(11)–C(11)* | 1.56(2) | O(7)C(6)C(5) | 117.6(7) | O(3)C(6)C(5) | 117.3(7) |
| Angle | ω, deg | Angle | ω, deg | N(2)C(7)C(8) | 115.4(7) | O(8)C(8)O(4) | 125.3(1) |
| N(3)CoN(6) | 178.4(4) | N(3)CoN(7) | 90.6(3) | O(8)C(8)C(7) | 116.5(9) | O(4)C(8)C(7) | 118.1(8) |
| N(6)CoN(7) | 88.0(3) | N(3)CoN(8) | 89.3(3) | N(2)C(9)C(10) | 112.6(7) | N(1)C(10)C(9) | 111.6(7) |
| N(6)CoN(8) | 92.0(3) | N(7)CoN(8) | 179.8(4) | O(9)C(11)O(10) | 125.4(7) | O(9)C(11)C(11)* | 117.1(9) |
| N(3)CoN(5) | 89.8(3) | N(6)CoN(5) | 91.0(3) | O(10)C(11)C(11)* | 117.5(9) | N(3)C(12)S | 179.2(9) |

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

The structure of the complex anion is shown in Fig. 1. Edta⁴⁻ functions as a hexadentate chelating ligand coordinated to the Bi atom through two nitrogen and four oxygen atoms of the four deprotonated car-

boxyl groups. The coordination sphere of Bi also includes the bridging oxalate anion attached in the 1,4-chelate manner to form an additional five-membered chelate cycle. The coordination polyhedron of bismuth

Table 5. Geometric parameters of the expected hydrogen bonds

| D–H...A | D–H, Å | D...A, Å | D...A, Å | D–H...A angle, deg | Symmetry operation for the A atom |
|-----------------|--------|----------|----------|--------------------|-----------------------------------|
| O(1w)–H...O(5) | 0.91 | 1.94 | 2.83 | 166 | $-x, y + 1/2, -z + 1/2$ |
| O(1w)–H...O(4w) | 0.91 | 1.92 | 2.76 | 155 | $-x - 1, y - 1/2, -z + 1/2$ |
| O(2w)–H...O(6) | 0.90 | 1.90 | 2.77 | 160 | $-x, -y, -z$ |
| O(2w)–H...O(10) | 0.94 | 1.93 | 2.84 | 166 | $-x, -y + 1, -z$ |
| O(3w)–H...O(8) | 0.92 | 1.93 | 2.84 | 167 | $-x, -y + 1, -z$ |
| O(3w)–H...O(1w) | 1.04 | 1.97 | 2.99 | 166 | x, y, z |
| O(4w)–H...O(5w) | 0.95 | 1.95 | 2.84 | 155 | x, y, z |
| O(4w)–H...O(3w) | 0.97 | 2.02 | 2.95 | 159 | x, y, z |
| O(5w)–H...O(6w) | 0.94 | 1.89 | 2.67 | 138 | $x, y + 1, z$ |
| O(5w)–H...O(1w) | 1.06 | 2.00 | 3.02 | 162 | $x, y + 1, z$ |
| O(6w)–H...O(6) | 0.97 | 1.91 | 2.82 | 154 | $-x, -y, -z$ |
| O(6w)–H...O(8) | 1.01 | 2.16 | 3.15 | 165 | $-x, -y + 1, -z$ |
| N(4)–H...O(9) | 0.89 | 2.45 | 3.35 | 172 | x, y, z |
| N(4)–H...O(5) | 0.89 | 2.22 | 3.09 | 168 | $x, y + 1, z$ |
| N(4)–H...O(2w) | 0.89 | 2.54 | 3.32 | 146 | $x, y + 1, z$ |
| N(5)–H...O(3w) | 0.89 | 2.21 | 3.07 | 164 | x, y, z |
| N(5)–H...O(5w) | 0.89 | 2.15 | 3.04 | 177 | x, y, z |
| N(5)–H...O(3) | 0.89 | 2.10 | 2.91 | 151 | $-x, y + 1/2, -z + 1/2$ |
| N(6)–H...O(7) | 0.89 | 2.15 | 3.04 | 173 | $-x, y + 1/2, -z + 1/2$ |
| N(6)–H...O(2w) | 0.89 | 2.17 | 2.87 | 135 | $x, y + 1, z$ |
| N(6)–H...O(1) | 0.89 | 2.18 | 3.07 | 177 | $x, y + 1, z$ |
| N(7)–H...O(3) | 0.89 | 2.30 | 3.17 | 166 | $-x, y + 1/2, -z + 1/2$ |
| N(7)–H...O(5) | 0.89 | 2.12 | 2.96 | 158 | $x, y + 1, z$ |
| N(7)–H...O(7) | 0.89 | 2.24 | 2.96 | 137 | x, y, z |
| N(8)–H...O(4) | 0.89 | 2.53 | 3.26 | 139 | $-x, -y + 1, -z$ |
| N(8)–H...O(10) | 0.89 | 2.56 | 3.14 | 123 | x, y, z |
| N(8)–H...O(2w) | 0.89 | 2.18 | 2.97 | 147 | $x, y + 1, z$ |
| N(8)–H...O(2) | 0.89 | 2.56 | 3.15 | 125 | $-x, -y + 1, -z$ |

can be treated as a bicapped trigonal prism with the N(1)O(1)O(3) and O(4)O(9)O(10a) atoms constituting its basis and the N(2) and O(2) atoms centering its square faces. The complex anion and the cation are spaced by the shortened Bi–S contact (3.571 Å). Taking this interaction into account, the coordination polyhedron of Bi, rather than the antiprism found in [5, 11], can be regarded as a tricapped trigonal prism [16] (Fig. 2) due to the additional chelate ring formed by the oxalate anion. The total dentate number of Edta^{4-} is equal to six.

Such a manner of coordination of ethylenediaminetetraacetate anion was not reported for the known bismuth complexes. In $\text{CN}_3\text{H}_6[\text{Bi}(\text{Edta})\text{H}_2\text{O}]$ [3], $\text{NH}_4[\text{Bi}(\text{Edta})] \cdot \text{H}_2\text{O}$ [4], $[\text{Bi}(\text{HEdta})]$ [4], and $\text{Na}[\text{Bi}(\text{Edta})] \cdot 3\text{H}_2\text{O}$ [5, 11], the HEdta acid (or its deprotonated forms) functions as a chelating and bridg-

ing ligand. The dentate number of the complexone can increase from six to seven or even ten. The hexadentate type (N_2O_4) of the ligand coordination is characteristic of cobalt [17], nickel [18], manganese [19], antimony [3], and aluminum [20] complexes and is designated in [21] as G^{000001} . According to the data presented in [21], this type is most frequently encountered in ethylenediaminetetraacetate complexes and was found to occur in 52 structures out of the 132 studied by X-ray diffraction analysis.

With such a coordination of Edta^{4-} , the coordination polyhedron of Bi includes four glycine and one ethylenediamine chelate cycles. Atomic deviations from the planar fragments in the structure of the complex anion and the corresponding dihedral angles are presented in Table 3. The average Bi–O_(COO), Bi–N, and Bi–O_(oxalate) distances are equal to 2.465(6), 2.530(6), and

2.534(6) Å, respectively. These and other distances (Table 4) are close to those found in other bismuth compounds with Edta^{4-} (with no regard to the bridging bonds involving the carboxyl groups of the ligand).

The average interatomic distances in the complex $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ cation (Fig. 3) are $\text{Co}-\text{N}_{(\text{NH}_3)}$ 1.952(7) Å, $\text{Co}-\text{N}_{(\text{NCS})}$ 1.925(6) Å, $\text{N}-\text{C}$ 1.142(9) Å, and $\text{C}-\text{S}$ 1.627(7) Å, and the $\text{CoN}(3)\text{C}(12)$ and $\text{N}(3)\text{C}(12)\text{S}$ bond angles are equal to $163.4(8)^\circ$ and $179.2(9)^\circ$, respectively.

A fragment of molecular packing in the crystal is shown in Fig. 4. As was noted above, there is a $\text{Bi}-\text{S}$ contact 3.571 Å long between the complex cation and the anion. The determining factor in the packing is a system of H bonds which involves all the components of $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2[(\text{Edta})\text{Bi}(\mu\text{-C}_2\text{O}_4)\text{Bi}(\text{Edta})] \cdot 12\text{H}_2\text{O}$.

The geometric parameters of hydrogen bonds are given in Table 5. In the structure, one can distinguish layers composed of the complex anions and cations linked by the H bonds. The layers are arranged perpendicular to the crystal y axis and are combined into a three-dimensional framework via the hydrogen bonds involving the $\text{O}(2w)$, $\text{O}(5w)$, and $\text{O}(6w)$ atoms of water.

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