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# Novel Co(III)/Co(II) mixed valence compound $[Co(bapen)Br_2]_2[CoBr_4]$ (bapen = *N,N′*-bis(3-aminopropyl)ethane-1,2-diamine): Synthesis, crystal structure and magnetic properties

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Green crystals of Co(III)/Co(II) mixed valence compound $[Co(bapen)Br_2]_2[CoBr_4]$ (bapen = *N,N′*-bis(3-aminopropyl)ethane-1,2-diamine) were isolated from the aqueous system $CoBr_2$ − bapen − HBr, crystallographically studied and characterized by elemental analysis and IR spectroscopy. Its ionic crystal structure is built up of $[Co(bapen)Br_2]^+$ cations and $[CoBr_4]^{2-}$ anions. The Co(III) central atoms within the complex cations are hexacoordinated (donor set *trans*-$N_4Br_2$) with bromido ligands placed in the axial positions. The Co(II) atoms exhibit distorted tetrahedral coordination. Beside ionic forces weak N—H···Br intermolecular hydrogen bonding interactions contribute to the stability of the structure. Temperature variable magnetic measurements confirm the $S = 3/2$ behavior with the zero-field splitting of an intermediate strength: $D/hc = 8.7\ cm^{-1}$.

## 1. Introduction

Since the discovery of single-molecule magnetism in 1993 [1], the field of molecular magnetism has been developing fast. Currently, mononuclear Co(II) complexes are among the most studied materials in this area due to their single-molecule magnet (SMM) behaviour [2–7]. Although syntheses of Co(II) complexes under aerobic conditions are widely used, Co(II) ions often undergo oxidation to Co(III) during syntheses [8,9]. In some cases the oxidation can be only partial, leading to Co(III)/Co(II) mixed-valence compounds [10,11]. In this work, within our broader study of magnetic materials based on high-spin tetrahedral Co(II) complexes, we report synthesis, crystal structure and magnetic properties of a novel Co(III)/Co(II) mixed-valence compound $[Co(bapen)Br_2]_2[CoBr_4]$ (**1**).

## 2. Experimental

### 2.1. Methods

Elemental analysis (C, H, N) was performed on a CHNOS Elemental Analyzer vario MICRO (Elementar Analysensysteme GmbH) using silver boats, and the results were found to be in good agreement with the calculated values (See Supplementary material). Infrared spectrum was collected on a Nicolet 6700 FT-IR spectrophotometer from Thermo Scientific equipped with a diamond crystal Smart Orbit™ in the range 4000–400 $cm^{-1}$. X-ray experiment was carried out on a four-circle κ-axis Xcalibur2 diffractometer equipped with a CCD detector Sapphire2 (Oxford Diffraction) and Oxford Cryosystems Desktop Cooler at 173(2) K. The CrysAlis software package [12] was used for data collection and reduction. For absorption correction was used the analytical method [13]. The structures were solved by the SIR2004 program [14] incorporated in the WinGX program package [15]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure SHELXL-2014 [16] on $F^2$. The molecular graphics were created by Diamond 3.2k software [17]. The magnetic data was taken for a polycrystalline sample with the SQUID magnetometer (MPMS-XL7, Quantum Design) in the RSO mode of

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detection.

### 2.2. *Synthesis of bis(bis(3-aminopropyl)ethane-1,2-diaminedibromidocobalt(III)) tetrabromido cobaltate(II) (**1**)*

All starting materials were used as received from commercial sources. Cobalt(II) bromide (0.219 g; 1 mmol) was dissolved in 20 $cm^3$ of distilled water. Ligand bapen (0.19 $cm^3$; 1 mmol) was slowly added into the solution under constant stirring, followed by dropwise addition of concentrated HBr (48%, 5 $cm^3$). Dark green solution was stirred at room temperature for one hour and was left aside for crystallization in air afterwards. After one week green parallelepipeds separated from the solution and were collected by filtration. The yield based on $CoBr_2$ was 0.257 g (66%).

## 3. Results and discussion

### 3.1. *Synthesis*

Title compound in the single crystal form was prepared by reaction of $CoBr_2$, bapen and concentrated HBr in water under aerobic conditions. As the consequence of complex equilibria in the solution partial oxidation of Co(II) atoms occurred leading to the formation of $[Co(bapen)Br_2]^+$ complex cations and $[CoBr_4]^{2-}$ complex anions. We note that our attempts to isolate analogous chlorido and iodido ligand containing compounds from the aqueous systems $CoX_2$ − bapen − HX (conc.) (X = Cl, I) were unsuccessful. To our knowledge compound $[Co(en)_2Cl_2]_2[CoCl_4]$ (en = ethane-1,2-diamine) is the only Co(III)/Co(II) mixed-valence compound with similar composition that has been structurally described in literature yet [18].

### 3.2. *IR spectroscopy*

The most characteristic absorption bands present in the IR spectrum of the $[Co(bapen)Br_2]_2[CoBr_4]$ compound can be assigned upon the IR study of similar complexes $[Co(bapen)Br_2]Br$ and $[Co(bapen)Br_2]ClO_4$ [19]. The absorption bands observed in 3290–3124 $cm^{-1}$ region are attributable to ν(N–H) stretching vibrations of the bapen ligand (3295, 3176 $cm^{-1}$ in $[Co(bapen)Br_2]Br$; 3277, 3208, 3187 $cm^{-1}$ in $[Co(bapen)Br_2]ClO_4$). Furthermore, three strong to medium absorption bands around 879, 871 and 811 $cm^{-1}$ can be ascribed to $\rho(CH_2)$ rocking vibrations (874, 818 $cm^{-1}$ in $[Co(bapen)Br_2]Br$; 877, 818 $cm^{-1}$ in $[Co(bapen)Br_2]ClO_4$), and confirm the *trans*-coordination mode of the bapen ligand. Positions of further absorption bands present in IR spectrum are gathered in Supplementary data section.

### 3.3. *Crystal structure*

The mixed valence Co(III)/Co(II) ion-pair crystal structure of the title compound consists of two crystallographically independent *trans*-$[Co(bapen)Br_2]^+$ cations and tetrahedral $[CoBr_4]^{2-}$ anions (Fig. 1). Crystal data and structure refinement, as well as selected geometric parameters are included in Tables 1 and 2. In both complex cations the Co(III) central atoms are hexacoordinated by four nitrogen atoms of the ligand bapen placed in the equatorial plane and two bromido ligands in the axial positions. Best to our knowledge the *trans*-$[Co(bapen)Br_2]^+$ complex cation has not been structurally characterized in literature yet. However, similar *trans*-$[Co(bapen)Cl_2]^+$ complex cation was already found in $[Co(bapen)Cl_2]NO_3$ [20].

While the nitrogen atoms of the secondary amine groups become centres of asymmetry upon coordination of the bapen ligand, there are two possible enantiomeric forms of the *trans*-

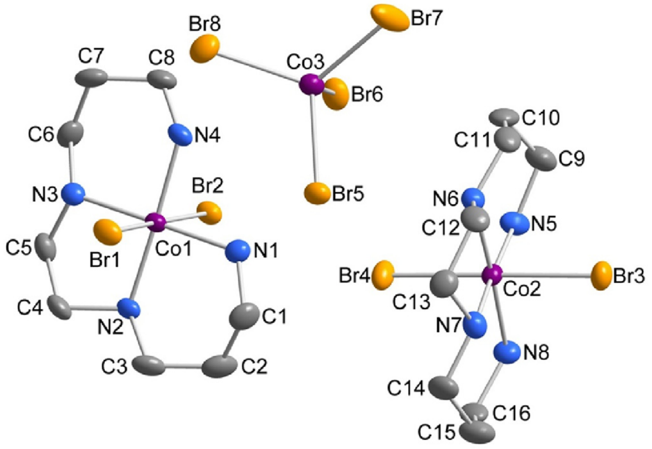

**Fig. 1.** Molecular structure of the title compound including atom numbering scheme. The thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted in the sake of clarity.

**Table 1**
Crystal data and structure refinement parameters.

| | |
|---|---|
| Empirical formula | $C_{16}H_{44}N_8Br_8Co_3$ |
| Formula weight | 1164.66 |
| Temperature [K] | 173 (2) |
| Wavelength [Å] | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions [Å,°] | a = 10.0404 (2)<br>b = 17.9950 (4)<br>c = 18.7720 (4)<br>β = 91.392 (2) |
| Absorption coefficient [$mm^{-1}$] | 10.900 |
| Crystal dimensions [mm] | 0.24 × 0.11 × 0.07 |
| Unit cell volume [$Å^3$] | 3390.67 (12) |
| Z | 4 |
| F (000) | 2228 |
| Density (calc.) [g $cm^{-3}$] | 2.282 |
| $2\theta$ range for data collection | 3.040–25.998 |
| Data/restraints/parameters | 6663/0/316 |
| $R_{int}$ | 0.0512 |
| Goodness-of-fit on $F^2$ | 1.0430 |
| Final R (observed) | 0.0445 |
| Final R (all data) | 0.0654 |
| Final wR (observed) | 0.1089 |

**Table 2**
Selected geometric parameters [Å,°].

| | | | |
|---|---|---|---|
| Co1–N1 | 1.992 (5) | N1–Co1–N2 | 94.6 (2) |
| Co1–N2 | 1.978 (5) | N2–Co1–N3 | 85.1 (2) |
| Co1–N3 | 1.987 (5) | N3–Co1–N4 | 92.0 (2) |
| Co1–N4 | 1.966 (5) | N1–Co1–N3 | 178.9 (2) |
| Co1–Br1 | 2.4143 (10) | N2–Co1–N4 | 176.7 (2) |
| Co1–Br2 | 2.4101 (10) | Br1–Co1–Br2 | 177.0 (4) |
| Co2–N5 | 1.977 (5) | N5–Co2–N6 | 93.8 (2) |
| Co2–N6 | 1.987 (5) | N6–Co2–N7 | 85.1 (2) |
| Co2–N7 | 1.997 (5) | N7–Co2–N8 | 92.9 (2) |
| Co2–N8 | 1.980 (5) | N5–Co2–N7 | 176.2 (2) |
| Co2–Br3 | 2.3853 (9) | N6–Co2–N8 | 177.0 (2) |
| Co2–Br4 | 2.4093 (9) | Br3–Co2–Br4 | 177.7 (4) |
| Co3–Br5 | 2.4336 (10) | Br5–Co3–Br6 | 104.38 (4) |
| Co3–Br6 | 2.4118 (11) | Br5–Co3–Br7 | 112.23 (4) |
| Co3–Br7 | 2.3849 (11) | Br5–Co3–Br8 | 106.17 (4) |
| Co3–Br8 | 2.4200 (11) | Br6–Co3–Br7 | 107.68 (4) |
| | | Br6–Co3–Br8 | 113.57 (4) |
| | | Br7–Co3–Br8 | 112.59 (5) |