Synthesis and crystal structure of poly[[di-μ₃-tetra-thioantimonato-tris[(cyclam)cobalt(II)]] acetonitrile disolvate dihydrate] (cyclam = 1,4,8,11-tetraaza-cyclotetradecane)

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Reaction of Co(ClO₄)₂·6H₂O with cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) and Na₃SbS₄·9H₂O (Schlippesches salt) in a mixture of acetonitrile and water leads to the formation of crystals of the title compound with the composition \([\text{[Co}_3\text{(SbS}_4\text{)}_2\text{(C}_{10}\text{H}_{24}\text{N}_4\text{)}_3\text{]}\text{/C}_2\text{CH}_3\text{CN/C}_2\text{H}_2\text{O}}_n\) or \(\text{[[(Co-cyclam) }_3\text{(SbS}_4\text{)}_2\text{]}\text{/C}_2\text{H}_2\text{O}}_n\). The crystal structure of the title compound consists of three crystallographically independent \([\text{Co-cyclam}]^{2+}\) cations, which are located on centers of inversion, one \([\text{SbS}_4\text{]}^{3−}\) anion, one water and one acetonitrile molecule that occupy general positions. The acetonitrile molecule is disordered over two orientations and was refined using a split model. The \(\text{Co}^{II}\) cations are coordinated by four \(\text{N}\) atoms of the cyclam ligand and two \(\text{trans-S}\) atoms of the tetrathioantimonate anion within slightly distorted octahedra. The unique \([\text{SbS}_4\text{]}^{3−}\) anion is coordinated to all three crystallographically independent \(\text{Co}^{II}\) cations and this unit, with its symmetry-related counterparts, forms rings composed of six \(\text{Co-cyclam}\) cations and six tetrathioantimonate anions that are further condensed into layers. These layers are perfectly stacked onto each other so that channels are formed in which acetonitrile solvate molecules that are hydrogen bonded to the anions are embedded. The water solvate molecules are located between the layers and are connected to the cyclam ligands and the \([\text{SbS}_4\text{]}^{3−}\) anions via intermolecular \(\text{N—H⋅⋅⋅O}\) and \(\text{O—H⋅⋅⋅S}\) hydrogen bonding.

1. Chemical context

Inorganic–organic chalcogenidometallates are an important class of compounds and many such compounds have been reported in the literature (Sheldrick & Wachhold, 1988; Bensch et al., 1997; Dehnen & Melullis, 2007; Wang et al., 2016; Zhou, 2016; Zhu & Dai, 2017; Nie et al., 2017). A large part of this family of compounds consists of thioantimonates, which exhibit a variety of coordination numbers that can lead to networks of different dimensionality (Jia et al., 2004; Powell et al., 2005; Spetzler et al., 2004; Zhang et al., 2007; Liu & Zhou, 2011; Engelke et al., 2004; Puls et al., 2006). Moreover, some of them have potential for applications, for example in the field of superionic conductors (Zhou et al., 2019) or as photoconductive materials (Pienack et al., 2008a). For these reasons, we have explored such compounds over many years (Schaefer et al., 2003; Stähler et al., 2001; Schur et al., 1998, 2001; Kiebach et al., 2004; Spetzler et al., 2004; Lührmann et al., 2008; Pienack et al., 2008b). In the beginning, we synthesized new thioantimonates using elemental antimony, sulfur and amine molecules under solvothermal conditions but later we found that
many of these compounds are also available under solvothermal conditions if Schlippeesch salt (Na₅SbS₄·9H₂O) or NaSbS₃ are used as reactants (Anderer et al., 2014, 2016; Daneker et al., 2020). In this case, different SbS₃ species are present in solution, because Schlippeesch salt is unstable and forms different reactive species such as [SbS₃O]₃⁻, HS⁻, [S₂O₃]²⁻ or [SbS₄]³⁻ anions (Rammelsberg, 1841; Long & Bowen, 1970; Mosselmanns et al., 2000; Planer-Friedrich & Scheinost, 2011; Planer-Friedrich & Wilson, 2012; Anderer et al., 2014). In addition, a variety of complex redox and condensation reactions occur, generating polymeric thioantimonate(III) anions, which are found in the structures of the reaction products. To prevent the reduction of Sb⁵⁺ to Sb³⁺, a different synthesis strategy is required and the reaction temperature must be reduced to slow down the decomposition of Schlippeesch salt. Using an aqueous solution of Na₅SbS₄·9H₂O and adding a solution of late transition-metal cations leads to immediate precipitation of sulfides or hydroxides, even when chelating amine molecules are added. To solve the problem we developed a two-solution strategy: an organic solution contains the transition-metal cations and the chelating amine molecule and a second solution comprises Schlippeesch salt. In the organic solution, the transition-metal complex is already generated in situ and mixing the two solutions leads to nucleation and successive growth of the product. A challenge is the integration of transition-metal cations into a thioantimonate(V) network, despite the [SbS₃]¹⁻ anion offering four possible binding sites. In the course of this project we became interested in cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane), which is a tetradentate ligand. This means that in an octahedral coordination of a transition-metal cation, two coordination sites are provided to which thioantimonate(V) anions can coordinate, which, depending on the nature of the anion, can lead to the formation of the desired thioantimonate(V) networks.

In this context, we have reported on two new polymeric thioantimonates with the composition [(Cu-cyclam)$_2$(SbS$_3$)$_2$]·2H$_2$O and [(Zn-cyclam)$_2$(SbS$_3$)$_2$]·8H$_2$O (Daneker et al., 2021). In the crystal structure of the Cu compound, the copper cations are sixfold coordinated by the four N atoms of the cyclam ligand and two trans-sulfur atoms of the [SbS$_3$]¹⁻ anions within slightly distorted octahedra. The copper cations are linked by the anions into rings by corner-sharing SbS$_4$ and CuN$_3$S$_2$ units, which are condensed into layers. These layers are stacked in such a way that large pores are formed. Between the layers, water molecules are embedded. At first glance, the arrangement of the building blocks in the crystal structure of the Zn compound looks similar, but in this case the Zn$^{II}$ cation is disordered above and below the N$_4$ plane in a 1:1 ratio, which means that it is in a fivefold coordination of the four N atoms of the cyclam ligand and one S atom of the [SbS$_3$]¹⁻ anions in a square-pyramidal geometry. The structural difference between the Cu and Zn coordinations was reproduced by DFT calculations (Daneker et al., 2021). In the course of our systematic work we tried to prepare a similar compound with cobalt using the same synthetic approach. This led to crystals of the title compound, which were characterized by single-crystal X-ray diffraction.

2. Structural commentary

The asymmetric unit of the title compound consists of three crystallographically independent Co$^{III}$ cations and three independent cyclam ligands that are located on centers of inversion, as well as one [SbS$_3$]¹⁻ anion, one water and one acetonitrile molecule that occupy general positions (Fig. 1). The acetonitrile molecule is disordered over two orientations and was refined using a split model (see Refinement). The Co$^{III}$ cations are six-coordinate being bound to the four N atoms of the Co-ligand that are located in the equatorial plane and two trans-S atoms of two inversion-related tetrahioantimonate anions that occupy the apical positions (Fig. 2). The Co—N bond lengths are very similar for the three crystallographically independent Co$^{III}$ cations whereas significant differences are found for the Co—S bond lengths (Table 1). These changes, however, do not correlate with the Sb—S distances (Table 1). The angles around the Co centers prove that the octahedra are slightly distorted (see supporting information). The cyclam ligands are in the trans-III(S,S,R,R) configuration, which is the
most stable arrangement for the first row transition-metal cation-centered cyclam complexes (Bosnich et al., 1965).

The Sb—S bond lengths in the tetrathioantimonate anion (Table 1) are comparable and correspond to those observed in other compounds with this anion. From the S—Sb—S bond angles it is obvious that the tetrahedron is only slightly distorted (see supporting information). The [SbS$_4$]$^{3-}$ anion shows the rare tridentate coordination mode and is linked to each of the three crystallographically independent Co$^{II}$ cations and with inversion-related counterparts, forming rings composed of six [SbS$_4$]$^{3-}$ anions and six [Co(cyclam)]$^{2+}$ cations (Fig. 3). These rings are condensed into layers parallel to the $bc$ plane (Fig. 4). This layer topology is identical to that in

Table 1
Selected bond lengths (Å).

| Bond        | Length (Å) |
|-------------|------------|
| Sb1—S4     | 2.3195 (13) |
| Sb1—S1     | 2.3200 (12) |
| Sb1—S3     | 2.3221 (12) |
| Sb1—S2     | 2.3382 (11) |
| S1—Co1     | 2.7258 (12) |
| S2—Co2     | 2.6932 (11) |
| S3—Co3     | 2.7821 (12) |

Figure 2
Crystal structure of the title compound with a view of the coordination sphere of the three crystallographically independent Co cations.

Figure 3
Crystal structure of the title compound with a view of an 24-membered ring composed of six Co cations and six [SbS$_4$]$^{3-}$ anions.

Figure 4
Crystal structure of the title compound with a view of the Co$_3$(SbS$_4$)$_2$ network along the crystallographic $a$ axis. The cyclam ligands are not shown for clarity.
the angles are close to linearity and relatively short H—S contacts but at distances close to van der Waals contacts with angles ranging between about 110 and 125°.

4. Database survey

A search for structures of cobalt-centered cymal complexes in the Cambridge Structural Database (CSD version 5.42, last update November 2020; Groom et al., 2016) gave 152 hits, in four of which the cobalt cations are in an N₃S₄ coordination. In one of these structures (Refcode: NIMVIQ; Zeisler et al., 2013), a thioannate acts as anion but none of them contains thioantimonate anions. The same results are obtained if the search is expanded to any transition-metal cation. Therefore, only the Cu and Zn compounds mentioned above have been published (Danker et al., 2021).

However, 21 structures with CoII and tetrathioantimonate anions have been published and in two of these structures, the cobalt cations are linked to a tetrathioantimonate anion, viz. [Co(diethylenetriamine)₂][Co(tris(2-aminomethyl)amine)-SbS₄]₂·4H₂O (Engelke et al., 2008) and [Co(diethylenetriamine)₂][Co(tris(2-aminomethyl)amine)SnS₄]₂·0.5H₂O (Lichte, et al., 2009).

5. Synthesis and crystallization

**Synthesis of Na₃SbS₄·9H₂O**

Na₃SbS₄·9H₂O was synthesized by adding 16.6 g (0.213 mol) of Na₂S·9H₂O (technical grade, purchased from Acros Organics) to 58 mL of demineralized water. This solution was heated to 323 K for 1 h. Afterwards, 19.6 g (0.058 mol) of Sb₂S₃ (98%, purchased from Alfa Aesar) were added and the reaction mixture was heated to 343 K for 6 h. The reaction mixture was filtered and the filtrate was stored overnight, leading to the formation of slightly yellow crystals, which were filtered off, washed with small amounts of water and dried under vacuum (yield about 30% based on Sb₂S₃).

**Synthesis of the title compound**

16 mg (0.044 mmol) of Co(ClO₄)₂·6H₂O (purchased from Alfa Aesar) and 16 mg (0.08 mmol) of cyclam (purchased from Strem Chemicals) were dissolved in 2 mL of acetonitrile (purchased from Merck). To this solution, a solution of 50 mg (0.14 mmol) of Na₃SbS₄·9H₂O dissolved in 1 mL of H₂O was added. Within 3d a few colorless crystals of the title compound were obtained, which were always contaminated with an additional and unknown phase that is amorphous to X-rays. This additional phase is also present if the reaction conditions are varied slightly. Therefore, one of the colorless crystals was selected for structure determination.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. The C- and N-bound H atoms were

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**Table 2**

Hydrogen-bond geometry (Å, °).

| D—H···A   | D—H   | H···A   | D···A   | D—H···A   |
|-----------|--------|---------|---------|-----------|
| N1—H1···S2i | 1.00   | 2.48    | 3.442 (4) | 161       |
| C1—H1B···S4iv | 0.99   | 2.95    | 3.858 (5) | 152       |
| N2—H2···S4 | 1.00   | 2.49    | 3.448 (4) | 159       |
| N11—H11···O1vi | 1.00   | 2.23    | 3.151 (6) | 153       |
| N12—H12···S3v | 1.00   | 2.43    | 3.378 (4) | 157       |
| N21—H21···O1 | 1.00   | 2.08    | 2.920 (6) | 141       |
| N22—H22···S1 | 1.00   | 2.35    | 3.290 (4) | 156       |
| O1—H1C···S2iv | 0.84   | 2.49    | 3.276 (4) | 157       |
| O1—H1D···Siv | 0.84   | 2.46    | 3.280 (4) | 166       |
| C32—H32B···S4 | 0.98   | 2.81    | 3.71 (4)  | 154       |
| C32—H32F···S4 | 0.98   | 2.88    | 3.85 (5)  | 172       |

Symmetry codes: (i) −x+1, −y, −z+2; (ii) −x+2, −y, −z+2; (iii) −x+1, −y, −z+1; (iv) −x+1, −y+1, −z+1; (v) −x+2, −y, −z+1.

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Figure 5

Crystal structure of the title compound with a view in the a-axis direction with intermolecular hydrogen bonding shown as dashed lines. The disorder of the acetonitrile molecules is omitted for clarity.
Table 3
Experimental details.

| Crystal data | Chemical formula | [Co3(SbS4)2(C10H24N4)3]·2C2H3N·2H2O |
| Crystal system, space group | Triclinic, P1 | |
| Temperature (K) | 200 | |
| a, b, c (Å) | 8.7292 (3), 12.9680 (5), 13.8936 (5) | |
| α, β, γ (°) | 66.218 (3), 77.035 (3), 83.321 (3) | |
| V (Å³) | 1401.93 (9) | |
| Z | 1 | |
| Crystal size (mm) | 0.15 x 0.20 x 0.22 | |
| Data collection | Stoe IPDS2 | |
| Absorption correction | Numerical (X-RED and X-SHAPE) | |
| Tmin, Tmax | 0.649, 0.774 | |
| No. of measured, independent and observed | 15304, 6098, 5078 | |
| Rint | 0.030 | |
| sin θ/λ (Å⁻¹) | 0.639 | |

Refinement
R[F² > 2σ(F²)], wR(F²), S | 0.047, 0.126, 1.06 | |
| No. of reflections | 6008 | |
| No. of parameters | 321 | |
| No. of restraints | 87 | |
| H-atom treatment | H-atom parameters constrained | |
| Δρmax, Δρmin (e Å⁻³) | 0.81, -1.56 | |

Computer programs: X-AREA (Stoe, 2008), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), DIAMOND (Brandenburg, 1999) and publCIF (Westrip, 2010).

located in the difference map but were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{iso}(H) = 1.2U_{eq}(C,N)$ (1.5 for methyl H atoms) using a riding model. The O-bound H atoms were located in the difference map, their bond lengths were set to ideal values and finally they were refined isotropically with $U_{iso}(H) = 1.5U_{eq}(O)$ using a riding model. The acetonitrile molecule is disordered over two orientations and was refined using a split model (ratio: 1:1) with restraints for the geometry and the components of the anisotropic displacement parameters.

Acknowledgements

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Synthesis and crystal structure of poly[[di-μ₃-tetrathioantimonato-tris-[(cyclam)cobalt(II)]] acetonitrile disolvate dihydrate] (cyclam = 1,4,8,11-tetrazacyclotetradecane)

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Computing details

Data collection: X-AREA (Stoe, 2008); cell refinement: X-AREA (Stoe, 2008); data reduction: X-AREA (Stoe, 2008); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: publCIF (Westrip, 2010).

Poly[[di-μ₃-tetrathioantimonato-tris[(cyclam)cobalt(II)]] acetonitrile disolvate dihydrate]

Crystal data

\[ \text{[Co}_3\text{(SbS}_4\text{)}_2\text{(C}_{10}\text{H}_{24}\text{N}_4\text{)}_3\text{]}·2\text{C}_2\text{H}_3\text{N}·2\text{H}_2\text{O} \]

Mr = 1395.90
Triclinic, \( P_{\text{1}} \)

\( a = 8.7292 \ (3) \ \text{Å} \)
\( b = 12.9680 \ (5) \ \text{Å} \)
\( c = 13.8936 \ (5) \ \text{Å} \)
\( \alpha = 66.218 \ (3)^{\circ} \)
\( \beta = 77.035 \ (3)^{\circ} \)
\( \gamma = 83.321 \ (3)^{\circ} \)
\( V = 1401.93 \ (9) \ \text{Å}^3 \)

Z = 1

\( F(000) = 711 \)

\( D_\text{c} = 1.653 \ \text{Mg m}^{-3} \)

Mo Kα radiation, \( \lambda = 0.71073 \ \text{Å} \)

Cell parameters from 15304 reflections

\( \theta = 1.6^{\circ} - 27.0^{\circ} \)

\( \mu = 2.16 \ \text{mm}^{-1} \)

\( T = 200 \ \text{K} \)

Block, red

0.15 x 0.10 x 0.07 mm

Data collection

Stoe IPDS-2

diffraction metr

ω scans

Absorption correction: numerical

(X-Red and X-Shape; Stoe, 2008)

\( T_{\text{min}} = 0.649, \ T_{\text{max}} = 0.774 \)

15304 measured reflections

6098 independent reflections

5078 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.030 \)

\( \theta_{\text{max}} = 27.0^{\circ}, \ \theta_{\text{min}} = 1.6^{\circ} \)

\( h = -11→11 \)

\( k = -16→16 \)

\( l = -17→17 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.047 \)

\( wR(F^2) = 0.126 \)

\( S = 1.06 \)

6098 reflections

321 parameters

87 restraints

Hydrogen site location: mixed

H-atom parameters constrained

\( w = 1/\left[\sigma^2(F^2) + (0.084P)^2 + 0.1597P \right] \)

\( \Delta \rho_{\text{max}} = 0.81 \ \text{e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -1.56 \ \text{e Å}^{-3} \)
### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|  | x         | y         | z         | U_iso* / U_eq | Occ. (<1) |
|---|-----------|-----------|-----------|---------------|-----------|
| Sb1 | 0.73888 (3) | 0.19084 (2) | 0.69041 (2) | 0.03283 (12) |
| S1 | 0.64905 (15) | 0.01167 (10) | 0.80137 (9) | 0.0414 (3) |
| S2 | 0.51359 (13) | 0.30840 (9) | 0.67415 (9) | 0.0380 (3) |
| S3 | 0.86596 (14) | 0.19636 (10) | 0.52265 (9) | 0.0416 (3) |
| S4 | 0.90553 (14) | 0.24527 (12) | 0.76901 (10) | 0.0461 (3) |
| Co1 | 0.500000 | 0.000000 | 1.000000 | 0.0350 (2) |
| N1 | 0.6290 (4) | −0.1388 (3) | 1.0629 (3) | 0.0392 (8) |
| H1 | 0.583701 | −0.171109 | 1.141506 | 0.047* |
| C1 | 0.7871 (6) | −0.1025 (5) | 1.0528 (4) | 0.0461 (11) |
| H1A | 0.847663 | −0.085872 | 0.979114 | 0.055* |
| H1B | 0.843932 | −0.162998 | 1.103578 | 0.055* |
| C2 | 0.7700 (6) | 0.0016 (5) | 1.0773 (4) | 0.0465 (11) |
| H2A | 0.720658 | −0.016978 | 1.153611 | 0.056* |
| H2B | 0.874555 | 0.032869 | 1.063722 | 0.056* |
| N2 | 0.6701 (5) | 0.0849 (3) | 1.0071 (3) | 0.0391 (8) |
| H2 | 0.736736 | 0.114228 | 0.933522 | 0.047* |
| C3 | 0.6268 (7) | 0.1831 (4) | 1.0369 (4) | 0.0465 (11) |
| H3A | 0.723689 | 0.218535 | 1.033103 | 0.056* |
| H3B | 0.567730 | 0.157340 | 1.111845 | 0.056* |
| C4 | 0.5275 (7) | 0.2697 (4) | 0.9642 (4) | 0.0502 (12) |
| H4A | 0.584251 | 0.290889 | 0.889012 | 0.060* |
| H4B | 0.515488 | 0.338203 | 0.980459 | 0.060* |
| C5 | 0.3653 (6) | 0.2311 (4) | 0.9738 (4) | 0.0462 (11) |
| H5A | 0.309991 | 0.205729 | 1.049576 | 0.055* |
| H5B | 0.304013 | 0.295721 | 0.930767 | 0.055* |
| Co2 | 0.500000 | 0.500000 | 0.500000 | 0.0342 (2) |
| N11 | 0.3450 (4) | 0.4238 (3) | 0.4693 (3) | 0.0375 (8) |
| H11 | 0.350102 | 0.342674 | 0.518595 | 0.045* |
| C11 | 0.1850 (5) | 0.4666 (4) | 0.5023 (4) | 0.0422 (10) |
| H11A | 0.105455 | 0.411439 | 0.515475 | 0.051* |
| H11B | 0.160604 | 0.538662 | 0.445200 | 0.051* |
| C12 | 0.1825 (5) | 0.4840 (4) | 0.6041 (4) | 0.0422 (10) |
| H12A | 0.083455 | 0.523577 | 0.622556 | 0.051* |
| H12B | 0.188964 | 0.410337 | 0.664261 | 0.051* |
| N12 | 0.3180 (4) | 0.5518 (3) | 0.5857 (3) | 0.0370 (8) |
| Atom | x       | y       | z       | Biso   |
|------|---------|---------|---------|--------|
| H12  | 0.291146| 0.630110| 0.537533| 0.044* |
| C13  | 0.3355 (6)| 0.5600 (4)| 0.6854 (4)| 0.0433 (10)|
| H13A | 0.348209 | 0.483093 | 0.739725 | 0.052* |
| H13B | 0.238416 | 0.594863 | 0.713526 | 0.052* |
| C14  | 0.4744 (7) | 0.6285 (5) | 0.6695 (5) | 0.0500 (12)|
| H14A | 0.471829 | 0.639111 | 0.736564 | 0.060* |
| H14B | 0.464296 | 0.703873 | 0.612383 | 0.060* |
| C15  | 0.6317 (6) | 0.5751 (4) | 0.6397 (4) | 0.0435 (10)|
| H15A | 0.717003 | 0.616669 | 0.643320 | 0.052* |
| H15B | 0.637578 | 0.496295 | 0.691914 | 0.052* |
| Co3  | 1.000000 | 0.000000 | 0.500000 | 0.0441 (2)|
| N21  | 0.8192 (5) | −0.0196 (3) | 0.4448 (3) | 0.0409 (9)|
| H21  | 0.851395 | −0.081969 | 0.418885 | 0.049* |
| C21  | 0.6910 (6) | −0.0636 (5) | 0.5384 (5) | 0.0480 (11)|
| H21A | 0.610940 | −0.097814 | 0.520863 | 0.058* |
| H21B | 0.639594 | −0.001829 | 0.559812 | 0.058* |
| C22  | 0.7616 (6) | −0.1511 (4) | 0.6284 (4) | 0.0484 (12)|
| H22A | 0.680551 | −0.178519 | 0.694862 | 0.058* |
| H22B | 0.805027 | −0.216022 | 0.609610 | 0.058* |
| N22  | 0.8886 (5) | −0.0960 (3) | 0.6442 (3) | 0.0401 (9)|
| H22  | 0.833782 | −0.042725 | 0.677357 | 0.048* |
| C23  | 0.9780 (7) | −0.1761 (4) | 0.7226 (4) | 0.0477 (12)|
| H23A | 1.027418 | −0.235259 | 0.696736 | 0.057* |
| H23B | 0.904885 | −0.213090 | 0.791464 | 0.057* |
| C24  | 1.1039 (7) | −0.1201 (5) | 0.7413 (4) | 0.0549 (13)|
| H24A | 1.148426 | −0.175116 | 0.802670 | 0.066* |
| H24B | 1.055165 | −0.056814 | 0.761253 | 0.066* |
| C25  | 1.2359 (6) | −0.0757 (5) | 0.6455 (4) | 0.0496 (12)|
| H25A | 1.320806 | −0.049907 | 0.666612 | 0.060* |
| H25B | 1.279912 | −0.137189 | 0.621601 | 0.060* |
| O1   | 0.7600 (5) | −0.1823 (3) | 0.3619 (3) | 0.0554 (9)|
| H1C  | 0.704099 | −0.205901 | 0.333522 | 0.08 (2)* |
| H1D  | 0.850839 | −0.202701 | 0.339072 | 0.10 (3)* |
| N31  | 0.748 (3) | 0.4588 (19) | 1.0545 (11) | 0.116 (7) |
| C31  | 0.815 (5) | 0.457 (4) | 0.9743 (13) | 0.101 (7) |
| C32  | 0.908 (4) | 0.469 (4) | 0.8707 (12) | 0.090 (7) |
| H32A | 0.899961 | 0.547550 | 0.820009 | 0.135* |
| H32B | 0.869880 | 0.419111 | 0.844728 | 0.135* |
| H32C | 1.018580 | 0.449588 | 0.876821 | 0.135* |
| N31' | 0.814 (3) | 0.4114 (18) | 1.0734 (10) | 0.112 (7) |
| C31' | 0.833 (5) | 0.452 (4) | 0.9817 (11) | 0.093 (7) |
| C32' | 0.854 (5) | 0.488 (4) | 0.8670 (12) | 0.122 (12) |
| H32D | 0.943593 | 0.537807 | 0.831978 | 0.183* |
| H32E | 0.758528 | 0.529186 | 0.843259 | 0.183* |
| H32F | 0.873030 | 0.422251 | 0.847836 | 0.183* |

*Estimated standard deviations or uncertainties of the last digits are given in parentheses.
### Atomic displacement parameters (Å²)

|      | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Sb1  | 0.03142 (17) | 0.03401 (17) | 0.02939 (17) | -0.00144 (10) | -0.00454 (10) | -0.00920 (11) |
| S1   | 0.0463 (6) | 0.0347 (5) | 0.0360 (6) | -0.0044 (4) | 0.0013 (5) | -0.0103 (5) |
| S2   | 0.0336 (5) | 0.0376 (5) | 0.0357 (6) | 0.0022 (4) | -0.0059 (4) | -0.0085 (4) |
| S3   | 0.0441 (6) | 0.0424 (6) | 0.0312 (5) | 0.0026 (5) | -0.0021 (4) | -0.0111 (5) |
| S4   | 0.0384 (6) | 0.0608 (7) | 0.0406 (6) | -0.0107 (5) | -0.0073 (5) | -0.0189 (6) |
| Co1  | 0.0331 (4) | 0.0364 (4) | 0.0342 (4) | -0.0022 (3) | -0.0069 (3) | -0.0119 (3) |
| N1   | 0.0383 (19) | 0.041 (2) | 0.0338 (19) | 0.0015 (16) | -0.0068 (15) | -0.0103 (16) |
| C1   | 0.036 (2) | 0.055 (3) | 0.044 (3) | 0.002 (2) | -0.0090 (19) | -0.016 (2) |
| C2   | 0.038 (2) | 0.061 (3) | 0.039 (3) | -0.008 (2) | -0.0099 (19) | -0.016 (2) |
| N2   | 0.040 (2) | 0.045 (2) | 0.0311 (18) | -0.0077 (16) | -0.0064 (15) | -0.0122 (16) |
| C3   | 0.060 (3) | 0.043 (3) | 0.041 (3) | -0.014 (2) | -0.007 (2) | -0.018 (2) |
| C4   | 0.065 (3) | 0.040 (2) | 0.040 (3) | -0.010 (2) | 0.000 (2) | -0.013 (2) |
| C5   | 0.053 (3) | 0.038 (2) | 0.038 (2) | 0.003 (2) | -0.001 (2) | -0.011 (2) |
| Co2  | 0.0295 (4) | 0.0378 (4) | 0.0331 (4) | -0.0022 (3) | -0.0049 (3) | -0.0118 (3) |
| N11  | 0.0363 (19) | 0.0381 (19) | 0.0348 (19) | -0.0025 (15) | -0.0086 (15) | -0.0095 (16) |
| C11  | 0.032 (2) | 0.047 (3) | 0.044 (3) | -0.0011 (18) | -0.0105 (19) | -0.013 (2) |
| C12  | 0.030 (2) | 0.042 (2) | 0.043 (3) | -0.0043 (17) | -0.0024 (18) | -0.006 (2) |
| N12  | 0.0352 (18) | 0.0370 (18) | 0.0337 (19) | 0.0011 (15) | -0.0061 (15) | -0.0093 (15) |
| C13  | 0.044 (2) | 0.048 (3) | 0.035 (2) | 0.003 (2) | -0.0039 (19) | -0.016 (2) |
| C14  | 0.057 (3) | 0.050 (3) | 0.046 (3) | -0.004 (2) | -0.008 (2) | -0.022 (2) |
| C15  | 0.049 (3) | 0.043 (2) | 0.043 (3) | -0.003 (2) | -0.015 (2) | -0.017 (2) |
| Co3  | 0.0412 (5) | 0.0448 (5) | 0.0438 (5) | -0.0033 (4) | -0.0067 (4) | -0.0149 (4) |
| N21  | 0.0363 (19) | 0.042 (2) | 0.046 (2) | 0.0010 (16) | -0.0086 (16) | -0.0195 (18) |
| C21  | 0.035 (2) | 0.055 (3) | 0.058 (3) | -0.004 (2) | -0.006 (2) | -0.027 (3) |
| C22  | 0.046 (3) | 0.044 (3) | 0.052 (3) | -0.009 (2) | 0.003 (2) | -0.020 (2) |
| N22  | 0.042 (2) | 0.0364 (19) | 0.037 (2) | -0.0024 (16) | -0.0023 (16) | -0.0117 (16) |
| C23  | 0.056 (3) | 0.039 (2) | 0.037 (2) | 0.003 (2) | -0.002 (2) | -0.009 (2) |
| C24  | 0.067 (3) | 0.060 (3) | 0.042 (3) | 0.011 (3) | -0.020 (3) | -0.022 (2) |
| C25  | 0.044 (3) | 0.058 (3) | 0.051 (3) | 0.007 (2) | -0.019 (2) | -0.023 (2) |
| O1   | 0.054 (2) | 0.060 (2) | 0.061 (2) | -0.0025 (18) | -0.0136 (19) | -0.031 (2) |
| N31  | 0.150 (16) | 0.126 (13) | 0.073 (4) | -0.026 (10) | 0.011 (6) | -0.052 (5) |
| C31  | 0.141 (15) | 0.097 (11) | 0.071 (4) | -0.041 (10) | 0.014 (6) | -0.045 (5) |
| C32  | 0.117 (15) | 0.094 (14) | 0.066 (4) | -0.033 (11) | 0.002 (6) | -0.041 (7) |
| N31′ | 0.162 (19) | 0.106 (13) | 0.070 (3) | -0.046 (12) | -0.019 (5) | -0.026 (5) |
| C31′ | 0.114 (13) | 0.100 (13) | 0.070 (3) | -0.052 (11) | -0.017 (5) | -0.026 (5) |
| C32′ | 0.18 (3) | 0.12 (2) | 0.070 (3) | -0.07 (2) | -0.020 (6) | -0.026 (5) |

### Geometric parameters (Å, °)

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| Sb1—S4 | 2.3195 (13) | N12—H12 | 1.0000 |
| Sb1—S1 | 2.3200 (12) | C13—C14 | 1.510 (8) |
| Sb1—S3 | 2.3221 (12) | C13—H13A | 0.9900 |
| Sb1—S2 | 2.3382 (11) | C13—H13B | 0.9900 |
| S1—Co1 | 2.7258 (12) | C14—C15 | 1.514 (7) |
| S2—Co2 | 2.6932 (11) | C14—H14A | 0.9900 |

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S3—Co3  2.7821 (12)  C14—H14B  0.9900
Co1—N2i  1.990 (4)  C15—H15A  0.9900
Co1—N2  1.990 (4)  C15—H15B  0.9900
Co1—N1  1.993 (4)  Co3—N22  1.976 (4)
Co1—N1i  1.993 (4)  Co3—N22iii  1.976 (4)
N1—C1  1.468 (6)  Co3—N21  1.985 (4)
N1—C5i  1.470 (7)  Co3—N21iii  1.985 (4)
N1—H1  1.0000  N21—C21  1.472 (7)
C1—C2  1.504 (8)  N21—C25iii  1.488 (6)
C1—H1A  0.9900  N21—H21  1.0000
C1—H1B  0.9900  C21—C22  1.506 (8)
C2—N2  1.481 (6)  C21—H21A  0.9900
C2—H2A  0.9900  C21—H21B  0.9900
C2—H2B  0.9900  C22—N22  1.486 (7)
N2—C3  1.476 (6)  C22—H22A  0.9900
N2—H2  1.0000  C22—H22B  0.9900
C3—C4  1.511 (8)  N22—C23  1.468 (6)
C3—H3A  0.9900  N22—H22  1.0000
C3—H3B  0.9900  C23—C24  1.506 (9)
C4—C5  1.517 (8)  C23—H23A  0.9900
C4—H4A  0.9900  C23—H23B  0.9900
C4—H4B  0.9900  C24—C25  1.510 (8)
C5—H5A  0.9900  C24—H24A  0.9900
C5—H5B  0.9900  C24—H24B  0.9900
Co2—N11a  1.975 (4)  C25—H25A  0.9900
Co2—N11  1.975 (4)  C25—H25B  0.9900
Co2—N12  1.985 (4)  O1—H1C  0.8400
Co2—N12a  1.985 (4)  O1—H1D  0.8400
N11—C15a  1.475 (6)  N31—C31  1.145 (15)
N11—C11  1.486 (6)  C31—C32  1.442 (17)
N11—H11  1.0000  C32—H32A  0.9800
C11—C12  1.514 (7)  C32—H32B  0.9800
C11—H11A  0.9900  C32—H32C  0.9800
C11—H11B  0.9900  N31′—C31′  1.145 (15)
C12—N12  1.470 (6)  C31′—C32′  1.442 (16)
C12—H12A  0.9900  C32′—H32D  0.9800
C12—H12B  0.9900  C32′—H32E  0.9800
N12—C13  1.474 (6)  C32′—H32F  0.9800

S4—Sb1—S1  109.86 (5)  H12A—C12—H12B  108.4
S4—Sb1—S3  110.64 (5)  C12—N12—C13  111.3 (4)
S1—Sb1—S3  110.81 (5)  C12—N12—Co2  108.0 (3)
S4—Sb1—S2  110.32 (5)  C13—N12—Co2  119.6 (3)
S1—Sb1—S2  105.36 (4)  C12—N12—H12  105.6
S3—Sb1—S2  109.73 (4)  C13—N12—H12  105.6
Sb1—S1—Co1  112.07 (5)  Co2—N12—H12  105.6
Sb1—S2—Co2  122.01 (4)  N12—C13—C14  112.7 (4)
Sb1—S3—Co3  119.94 (5)  N12—C13—H13A  109.0
N2—Co1—N2 180.00 (19) C14—C13—H13A 109.0
N2—Co1—N1 93.50 (17) N12—C13—H13B 109.0
N2—Co1—N1 86.50 (17) C14—C13—H13B 109.0
N2—Co1—N1i 86.50 (17) H13A—C13—H13B 107.8
N2—Co1—N1i 93.50 (17) C13—C14—C15 113.7 (4)
N1—Co1—N1i 180.0 C13—C14—H14A 108.8
N2—Co1—S1 89.02 (12) C15—C14—H14A 108.8
N2—Co1—S1i 90.98 (12) C13—C14—H14B 108.8
N1—Co1—S1i 91.50 (12) H13A—C13—H13B 107.8
N2—Co1—S1 89.02 (12) C15—C14—H14B 108.8
N1—Co1—S1i 88.50 (12) N11ii—C15—C14 111.5 (4)
N1—Co1—S1 89.02 (12) N11ii—C15—H15A 109.3
N1—Co1—S1i 91.50 (12) C14—C15—H15A 109.3
N1—Co1—S1i 88.50 (12) N11ii—C15—H15B 109.3
S1—Co1—S1i 180.0 C14—C15—H15B 109.3
C1—N1—C5i 111.8 (4) H15A—C15—H15B 108.0
C1—N1—Co1 107.1 (3) N22—Co3—N22iii 180.00 (19)
C5—N1—Co1 119.1 (3) N22—Co3—N21 86.93 (17)
C1—N1—H1 106.0 N22iii—Co3—N21iii 93.07 (17)
C5—N1—H1 106.0 N22iii—Co3—N21iii 93.07 (17)
Co1—N1—H1i 106.0 N22—Co3—N21 86.93 (17)
N1—Co1—C2 108.2 (4) N21—Co3—N21iii 180.0
N1—Co1—H1A 110.1 N22—Co3—S3iii 87.74 (11)
C2—Co1—H1A 110.1 N22iii—Co3—S3iii 92.26 (11)
N1—Co1—C2i 110.1 N21—Co3—S3iii 87.89 (12)
C2—Co1—C2i 110.1 N21ii—Co3—S3iii 92.11 (12)
H1A—Co1—H1Bi 108.4 N22—Co3—S3ii 92.26 (11)
N2—Co1—C2 107.9 (4) N22iii—Co3—S3ii 92.11 (12)
N2—Co1—H2A 110.1 N21—Co3—S3ii 87.89 (12)
C1—Co1—H2A 110.1 N21ii—Co3—S3ii 92.11 (12)
N2—Co1—H2B 110.1 S3iii—Co3—S3 180.00 (5)
C1—Co1—H2Bi 110.1 C21—N21—C25iii 111.9 (4)
H2A—Co1—H2Bi 108.4 C21—N21—Co3 106.4 (3)
C3—Co1—C2 111.7 (4) C25iii—N21—Co3 119.8 (3)
C3—Co1—N1ii 118.9 (3) C21—N21—H21 105.9
C2—Co1—N1ii 110.1 C25iii—N21—H21 105.9
C3—Co1—N2 106.2 Co3—N21—H21 105.9
C2—Co1—N2 106.2 N21—C21—C22 107.7 (4)
Co1—Co1—N2 106.2 N21—C21—H21A 110.2
N2—Co1—C4 112.0 (4) C22—C21—H21A 110.2
N2—Co1—H3A 109.2 N21—C21—H21B 110.2
C4—Co1—H3A 109.2 C22—C21—H21B 110.2
N2—Co1—H3B 109.2 H21A—C21—H21B 108.5
C4—Co1—H3B 109.2 N22—C22—C21 107.0 (4)
H3A—Co1—H3B 107.9 N22—C22—H22A 110.3
C3—Co1—C5 114.6 (4) C21—C22—H22A 110.3
C3—Co1—H4A 108.6 N22—C22—H22B 110.3
C5—Co1—H4A 108.6 C21—C22—H22B 110.3
### Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H  | H···A | D···A    | D—H···A |
|------------------|------|-------|----------|---------|
| N1—H1···S2\( ii \) | 1.00 | 2.48  | 3.442 (4) | 161     |

Symmetry codes: (i) \(-x+1, -y, -z+2\); (ii) \(-x+1, -y+1, -z+1\); (iii) \(-x+2, -y, -z+1\).
|        | Bond Length (Å) | Bond Length (Å) | Bond Length (Å) | Bond Length (Å) |
|--------|----------------|----------------|----------------|----------------|
| C1—H1B···S4\textsuperscript{v} | 0.99 | 2.95 | 3.858 (5) | 152 |
| N2—H2···S4 | 1.00 | 2.49 | 3.448 (4) | 159 |
| N11—H11···O1\textsuperscript{v} | 1.00 | 2.23 | 3.151 (6) | 153 |
| N12—H12···S3\textsuperscript{a} | 1.00 | 2.43 | 3.378 (4) | 157 |
| N21—H21···O1 | 1.00 | 2.08 | 2.920 (6) | 141 |
| N22—H22···S1 | 1.00 | 2.35 | 3.290 (4) | 156 |
| O1—H1C···S2\textsuperscript{v} | 0.84 | 2.49 | 3.276 (4) | 157 |
| O1—H1D···S4\textsuperscript{iii} | 0.84 | 2.46 | 3.280 (4) | 166 |
| C32—H32B···S4 | 0.98 | 2.81 | 3.71 (4) | 154 |
| C32′—H32F···S4 | 0.98 | 2.88 | 3.85 (5) | 172 |

Symmetry codes: (i) −x+1, −y, −z+2; (ii) −x+1, −y+1, −z+1; (iii) −x+2, −y, −z+1; (iv) −x+2, −y, −z+2; (v) −x+1, −y, −z+1.