A cuboidal \([\text{Cu}_4(\text{SO}_4)_4]\) structure supported by \(\beta\)-picoline ligands

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The solid-state structure of the cobalt–\(\beta\)-picoline–sulfate complex tetra-\(\mu_3\)-sulfato-tetrakis[bis(3-methylpyridine)cobalt(II)], \([\text{Co}_4(\text{SO}_4)_4(\text{C}_8\text{H}_7\text{N})_8]\), is reported. The tetrameric cobalt cluster contains a cuboidal core comprised of four cobalt(II) cations and four sulfate anions at alternate cube vertices. The cobalt corners are each capped with two \(\beta\)-picoline ligands. The sulfate anions adopt a rare [3.2110] bridging motif, and the cuboidal cluster is unprecedented in coordination chemistry.

1. Chemical context

For the past few years, our lab has examined the solid-state structures of first-row transition-metal–pyridine–sulfate complexes (Park et al., 2019; Pham et al., 2018; Roy et al., 2018). Despite the first such compound being reported in 1886 (Jørgensen, 1886; Manke, 2021), the structures of only two had been described in the literature when we started exploring this class of compounds. A series of these structures including Fe, Co, Ni, and Zn, showed one-dimensional coordination polymers exhibiting sulfate dianions bridging in \(\mu_3\)-sulfato-\(\kappa^2\text{O:O'}\) modes. Interestingly, by modifying growth conditions, cobalt demonstrated two additional crystalline forms with variation in the bridging mode of sulfate ions that was not observed for the other metals. We have also explored the structural chemistry of such complexes with substituted pyridines, including \(\gamma\)-picoline, which showed similar structural chemistry to that observed with the pyridine ligand (Pham et al., 2019). When we looked at the reaction of cobalt sulfate with \(\beta\)-picoline, a unique structure was obtained, a tetramer exhibiting an unprecedented cuboidal \([\text{Cu}_4(\text{SO}_4)_4]\) core, described herein.
2. Structural commentary

The asymmetric unit of the title compound contains one cobalt cation, one sulfate anion, and two \( \beta \)-picoline ligands (Fig. 1). When grown out, the cobalt center demonstrates a pseudo-octahedral coordination environment. This consists of two \( \beta \)-picoline nitrogen atoms, two oxygen atoms of a chelating sulfate ligand, one oxygen atom of a second sulfate anion, which bridges to another metal, and one terminal oxygen atom of a third sulfate ligand. The grown-out structure forms a tetramer of \((\beta\text{-pic})_2\text{CoSO}_4\) units, demonstrating a cuboidal core in which four vertices are occupied by cobalt cations, and the other four vertices are occupied by sulfate anions (Fig. 2). The sulfate anions all bridge three Co\(^{2+}\) cations, demonstrating [3.2110] bridging by Harris notation (Fig. 3). Harris notation is written as \([X\text{-}YYYY]\) where \(X\) is the number of metals that a ligand bridges, and the \(Y\)s are the number of metals connected to each donor atom in the ligand (Papatriantafyllopoulou et al., 2009). The [3.2110] bridging motif is rare in sulfates and has only been observed in 1D coordination polymers of copper (Li et al., 2008) and lanthanide/iron mixed-metal 3D coordination polymers (He et al., 2017). There are two C—H···O interactions between the ortho hydrogens of one \( \beta \)-picoline ligand and the oxygens of two sulfate ions (Table 1). This results in a plane-to-plane angle between the CoN\(_3\)O plane and the pyridine ring of 16.25 (9)°. These interactions are not present in the second unique picoline ligand, giving a larger plane-to-plane angle of 26.95 (9)°.

3. Supramolecular features

The crystal packing for the compound is shown in Fig. 4. The are weak C—H···O interactions between the trans-hydrogen atom of one picoline ligand and one of the terminal sulfate oxygens of a neighboring cuboid \([C3\cdots H3\cdots O2^h]\), symmetry code: (ii) \(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} - z\), Table 1). This interaction might

| & \( D - H \) & \( H \cdots A \) & \( D \cdots A \) & \( D - H \cdots A \) |
|---|---|---|---|---|
| C1—H1···O4\(^i\) & 0.93 & 2.53 & 3.116 (4) & 121 |
| C3—H3···O2\(^a\) & 0.93 & 2.46 & 3.135 (4) & 129 |
| C5—H5···O1 & 0.93 & 2.49 & 3.070 (4) & 121 |

Symmetry codes: (i) \(y, -x + 1, -z + 1\); (ii) \(x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}\).
assists in the interdigitation of the cuboids in the structure. No significant \( \pi-\pi \) interactions are observed.

Table 2
Experimental details.

| Parameter                  | Value          |
|----------------------------|----------------|
| Chemical formula           | \([\text{Co}_4(\text{SO}_4)_4(\text{C}_6\text{H}_7\text{N})_8]\) |
| Density                    | 1.3649 g/cm\(^3\) |
| Crystal system, space group| Tetragonal, \( \text{P} \bar{4}2_1 \) |
| Temperature (K)            | 298            |
| \(a\), \(c\) (Å)           | 15.6121 (16), 11.8359 (13) |
| \(V\) (Å\(^3\))            | 2884.9 (7)     |
| \(Z\)                      | 2              |
| Radiation type             | Mo Kα          |
| \(\mu\) (mm\(^{-1}\))      | 1.35           |
| Crystal size (mm)          | 0.24 \(\times\) 0.22 \(\times\) 0.20 |

Data collection

| Diffractometer            | Bruker D8 Venture CMOS |
|---------------------------|------------------------|
| Absorption correction     | Multi-scan (SADABS, Bruker, 2018) |
| \(T_{\text{min}}\) - \(T_{\text{max}}\) | 0.517, 0.562 |
| No. of measured, independent and observed | 54595, 2744, 2624 |
| \(R_{\text{int}}\)        | 0.037                  |
| \(\sin \theta/\lambda_{\text{max}}\) (Å\(^{-1}\)) | 0.611 |

Refinement

| \(R(F^2 > 2\sigma(F^2))\), \(wR(F^2)\) | 0.019, 0.046, 1.14 |
| No. of reflections         | 2744 |
| No. of parameters          | 184 |
| H-atoms treatment          | H-atoms parameters constrained |
| \(\Delta \rho_{\text{max}},\Delta \rho_{\text{min}}\) (e Å\(^{-3}\)) | 0.16, -0.20 |
| Absolute structure         | Flack \(x\) determined using 1117 quotients \([I(\bar{I})-\langle I(\bar{I})\rangle]/[\langle I(\bar{I})\rangle+\langle I(\bar{I})\rangle]\) (Parsons et al., 2013) |
| Absolute structure parameter | 0.087 (4) |

Database survey

The reported structures demonstrating sulfate ions with [3.2110] bridging modes are with copper (DOHKIV, DOHKIB: Li et al., 2008) or mixtures of lanthanides with iron (He et al., 2017), including dysprosium (DADNOO), erbium (DADPEG), europium (DADNII), gadolinium (DADNUU) and samarium (DADPAC). The prior structures of metal–pyridine sulfate complexes include three variations with pyridine (QIBFOZ: Pham et al., 2018; QOXJAR, QOXJEV: Park et al., 2019) and one with \( \gamma \)-picoline (ROFIL: Pham et al., 2019), all of which demonstrate 1D coordination polymers that are structurally quite different than the cuboidal compound reported here.

Synthesis and crystallization

32 mg of \( \text{CoSO}_4\cdot7\text{H}_2\text{O} \) were dissolved in 2.0 mL of 3-methylpyridine (Aldrich) and heated at 343 K for 24 h. Dark-pink crystals suitable for X-ray analysis were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed in calculated positions [C—H = 0.93 Å \((sp^2)\) and 0.96 Å \((sp^3)\)]. Isotropic displacement parameters were set to \(1.2U_{eqC}(sp^2)\) or \(1.5U_{eqC}(sp^3)\).

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Figure 4
The crystal packing of the title compound shown along the \(c\) axis. H atoms have been omitted for clarity.
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A cuboidal \([\text{Cu}_4(\text{SO}_4)_4]\) structure supported by \(\beta\)-picoline ligands

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Computing details
Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov et al., 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

[Tetra-\(\mu_3\)-sulfato-tetrakis(3-methylpyridine)cobalt(II)]

Crystal data

\([\text{Co}_4(\text{SO}_4)_4(\text{C}_6\text{H}_7\text{N})_8]\)

\(M_r = 1364.96\)

Tetragonal, \(P\bar{4}2_1\)  

\(a = 15.6121\) (16) \(\text{Å}\)  

\(c = 11.8359\) (13) \(\text{Å}\)  

\(V = 2884.9\) (7) \(\text{Å}^3\)

\(Z = 2\)

\(F(000) = 1400\)

\(D_x = 1.571 \text{ Mg m}^{-3}\)

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

Cell parameters from 9496 reflections

\(\theta = 2.9–25.7^\circ\)

\(\mu = 1.35 \text{ mm}^{-1}\)

\(T = 298 \text{ K}\)

BLOCK, pink  

0.24 \times 0.22 \times 0.20 \text{ mm}

Data collection

Bruker D8 Venture CMOS
diffractometer

\(\phi\) and \(\omega\) scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2018)

\(T_{\text{min}} = 0.517, T_{\text{max}} = 0.562\)

54595 measured reflections

2744 independent reflections

2624 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.037\)

\(\theta_{\text{max}} = 25.7^\circ, \theta_{\text{min}} = 2.9^\circ\)

\(h = -19\rightarrow19\)

\(k = -19\rightarrow19\)

\(l = -14\rightarrow14\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.019\)

\(wR(F^2) = 0.046\)

\(S = 1.14\)

2744 reflections

184 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\(w = 1/[\sigma^2(F^2) + (0.0165P)^2 + 1.2064P]\)

where \(P = (F^2 + 2F_c^2)/3\)

\((\Delta\sigma)_{\text{max}} = 0.001\)

\(\Delta\rho_{\text{max}} = 0.16 \text{ e} \text{Å}^{-3}\)

\(\Delta\rho_{\text{min}} = -0.20 \text{ e} \text{Å}^{-3}\)

Extinction correction: *SHELXL-2018/3* (Sheldrick 2015b), \(F_c^2 = kF_c[1+0.001xF_c^2\lambda^2/\sin(2\theta)]^{-1/4}\)

Extinction coefficient: 0.0049 (4)

Absolute structure: Flack \(x\) determined using 1117 quotients \([(I^-)-(I^+)/[(I^+)+(I^-)]\] (Parsons et al., 2013)

Absolute structure parameter: 0.007 (4)
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)

| Atom | x       | y       | z       | Uiso* | Ueq  |
|------|---------|---------|---------|-------|------|
| Co1  | 0.64636 (2) | 0.49053 (2) | 0.41389 (3) | 0.02066 (11) |
| S1   | 0.52522 (4) | 0.64004 (4) | 0.35520 (5) | 0.02043 (15) |
| O1   | 0.58168 (12) | 0.57205 (12) | 0.30908 (15) | 0.0267 (4) |
| O2   | 0.49144 (15) | 0.69145 (13) | 0.26473 (17) | 0.0370 (5) |
| O3   | 0.45605 (11) | 0.59894 (11) | 0.42553 (16) | 0.0240 (4) |
| O4   | 0.57034 (12) | 0.69234 (11) | 0.43961 (15) | 0.0258 (4) |
| N1   | 0.75982 (14) | 0.57112 (15) | 0.4121 (2) | 0.0319 (5) |
| N2   | 0.70169 (16) | 0.42286 (15) | 0.2775 (2) | 0.0293 (5) |
| C1   | 0.82170 (19) | 0.5691 (2) | 0.4896 (3) | 0.0400 (7) |
| H1   | 0.813680 | 0.534627 | 0.552786 | 0.048* |
| C2   | 0.8976 (2) | 0.6156 (2) | 0.4819 (3) | 0.0489 (8) |
| C3   | 0.9084 (2) | 0.6660 (2) | 0.3863 (3) | 0.0546 (10) |
| H3   | 0.958296 | 0.697697 | 0.376688 | 0.065* |
| C4   | 0.8451 (2) | 0.6690 (2) | 0.3064 (3) | 0.0541 (10) |
| H4   | 0.851466 | 0.702977 | 0.242445 | 0.065* |
| C5   | 0.7719 (2) | 0.6210 (2) | 0.3218 (3) | 0.0434 (8) |
| H5   | 0.729157 | 0.623471 | 0.267110 | 0.052* |
| C6   | 0.9650 (3) | 0.6110 (3) | 0.5724 (4) | 0.0829 (15) |
| H6A  | 0.946445 | 0.572676 | 0.630913 | 0.124* |
| H6B  | 0.973938 | 0.667009 | 0.603611 | 0.124* |
| H6C  | 1.017567 | 0.590328 | 0.540358 | 0.124* |
| C7   | 0.6638 (2) | 0.4183 (2) | 0.1768 (3) | 0.0340 (7) |
| H7   | 0.611734 | 0.446338 | 0.167140 | 0.041* |
| C8   | 0.6978 (2) | 0.3738 (2) | 0.0853 (3) | 0.0422 (7) |
| C9   | 0.7741 (2) | 0.3311 (2) | 0.1032 (3) | 0.0499 (9) |
| H9   | 0.798504 | 0.299413 | 0.045000 | 0.060* |
| C10  | 0.8143 (2) | 0.3351 (2) | 0.2062 (3) | 0.0490 (9) |
| H10  | 0.865907 | 0.306837 | 0.218114 | 0.059* |
| C11  | 0.7766 (2) | 0.3817 (2) | 0.2914 (3) | 0.0386 (8) |
| H11  | 0.803962 | 0.384829 | 0.361126 | 0.046* |
| C12  | 0.6512 (3) | 0.3707 (3) | −0.0255 (3) | 0.0732 (12) |
| H12A | 0.590895 | 0.377919 | −0.012705 | 0.110* |
| H12B | 0.661205 | 0.316328 | −0.061099 | 0.110* |
| H12C | 0.671634 | 0.415746 | −0.073630 | 0.110* |

Atomic displacement parameters (Å²)

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| Co1  | 0.01998 (17) | 0.02203 (18) | 0.01997 (16) | 0.00207 (14) | 0.00180 (15) | 0.00176 (14) |
### Geometric parameters (Å, °)

|       | 2.7458 (7) | 2.0441 (19) | 2.2037 (19) | 2.1274 (18) | 2.1229 (18) | 2.173 (2) | 2.114 (2) | 1.4839 (19) | 1.438 (2) | 1.5069 (18) | 1.491 (2) | 1.332 (4) | 1.336 (4) | 1.333 (4) | 1.345 (4) | 0.9300 | 1.392 (4) | 1.389 (5) | 1.503 (5) | 0.9300 |
|-------|------------|-------------|-------------|-------------|-------------|-----------|-----------|-------------|-----------|-------------|-----------|-----------|-----------|-----------|-----------|-------|-----------|-----------|-----------|-------|
| S1    |            |             |             |             |             | 2.215 (2) | 2.114 (2) | C7—H7       | 1.391 (4) | 1.5069 (18) | 1.491 (2) | 1.332 (4) | 1.336 (4) | 1.333 (4) | 1.345 (4) | 0.9300 | 1.392 (4) | 1.389 (5) | 1.503 (5) | 0.9300 |
| O1    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| O2    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| O3    |            |             |             |             |             |           |           |             |           |             |           |           |           |           | C8—C12   |       |           |           |           |       |
| N1    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| N2    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| N3    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C1    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C2    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C3    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C4    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C5    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C6    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C7    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C8    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |
| C9    |            |             |             |             |             |           |           |             |           |             |           |           |           |           |           |       |           |           |           |       |

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Supporting information

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| Bond | Distance (Å) | Bond | Distance (Å) | Distance (Å) |
|------|-------------|------|-------------|-------------|
| O1—Co1—N2 | 92.84 (9) | C3—C2—C6 | 121.5 (3) |
| O3i—Co1—S1i | 33.21 (5) | C2—C3—H3 | 120.2 |
| O3ii—Co1—S1i | 81.36 (5) | C4—C3—C2 | 119.7 (3) |
| O3i—Co1—O3i | 86.57 (8) | C4—C3—H3 | 120.2 |
| O3i—Co1—N1 | 173.44 (9) | C3—C4—H4 | 120.4 |
| O4i—Co1—S1i | 32.58 (5) | C3—C4—C5 | 119.3 (3) |
| O4i—Co1—O3ii | 83.94 (7) | C5—C4—H4 | 120.4 |
| O4i—Co1—O3i | 65.55 (7) | N1—C5—C4 | 122.6 (4) |
| O4—Co1—N1 | 90.16 (9) | N1—C5—H5 | 118.7 |
| N1—Co1—S1i | 95.20 (8) | C4—C5—H5 | 118.7 |
| N1—Co1—O3i | 93.61 (8) | C2—C6—H6A | 109.5 |
| N2—Co1—S1i | 136.90 (7) | C2—C6—H6B | 109.5 |
| N2—Co1—O3i | 170.11 (9) | C2—C6—H6C | 109.5 |
| N2—Co1—O3ii | 91.63 (8) | H6A—C6—H6B | 109.5 |
| N2—Co1—O4i | 104.59 (8) | H6A—C6—H6C | 109.5 |
| N2—Co1—N1 | 87.07 (9) | H6B—C6—H6C | 109.5 |
| O1—S1—Co1iii | 116.43 (7) | N2—C7—H7 | 118.2 |
| O1—S1—O3 | 108.92 (10) | N2—C7—C8 | 123.6 (3) |
| O1—S1—O4 | 109.93 (11) | C8—C7—H7 | 118.2 |
| O2—S1—Co1ii | 133.48 (9) | C7—C8—C12 | 120.8 (3) |
| O2—S1—O1 | 110.07 (11) | C9—C8—C7 | 116.8 (3) |
| O2—S1—O3 | 112.71 (12) | C9—C8—C12 | 122.4 (3) |
| O2—S1—O4 | 112.15 (12) | C8—C9—H9 | 119.7 |
| O3—S1—Co1iii | 53.22 (7) | C10—C9—C8 | 120.6 (3) |
| O4—S1—Co1ii | 50.06 (7) | C10—C9—H9 | 119.7 |
| O4—S1—O3 | 102.82 (11) | C9—C10—H10 | 120.6 |
| S1—O1—Co1 | 121.04 (10) | C9—C10—C11 | 118.7 (3) |
| Co1ii—O3—Co1iii | 124.11 (9) | C11—C10—H10 | 120.6 |
| S1—O3—Co1ii | 141.48 (12) | N2—C11—C10 | 122.3 (3) |
| S1—O3—Co1iii | 93.57 (9) | N2—C11—H11 | 118.9 |
| S1—O4—Co1ii | 97.36 (9) | C10—C11—H11 | 118.9 |
| C1—N1—Co1 | 124.8 (2) | C8—C12—H12A | 109.5 |
| C1—N1—C5 | 117.5 (3) | C8—C12—H12B | 109.5 |
| C5—N1—Co1 | 117.4 (2) | C8—C12—H12C | 109.5 |
| C7—N2—Co1 | 121.9 (2) | H12A—C12—H12B | 109.5 |
| C7—N2—C11 | 118.1 (3) | H12A—C12—H12C | 109.5 |
| C11—N2—Co1 | 120.0 (2) | H12B—C12—H12C | 109.5 |

| Bond | Distance (Å) |
|------|-------------|
| Co1ii—S1—O1—Co1 | -1.75 (15) |
| Co1ii—S1—O3—Co1ii | -168.6 (2) |
| Co1—N1—C1—C2 | 173.9 (3) |
| Co1—N1—C5—C4 | -174.0 (3) |
| Co1—N2—C7—C8 | -179.4 (2) |
| Co1—N2—C11—C10 | 178.4 (2) |
| O1—S1—O3—Co1iii | 109.34 (9) |
| O1—S1—O3—Co1ii | -59.3 (2) |
| O1—S1—O4—Co1iii | -108.29 (10) |
| O2—S1—O1—Co1 | 176.64 (13) |

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O2—S1—O3—Co1iii  −128.20 (11)  C6—C2—C3—C4 −179.4 (4)
O2—S1—O3—Co1ii  63.1 (2)  C7—N2—C11—C10 −0.6 (4)
O2—S1—O4—Co1iii  128.92 (11)  C7—C8—C9—C10 −1.5 (5)
O3—S1—O1—Co1 −59.31 (15)  C8—C9—C10—C11 0.6 (5)
O3—S1—O4—Co1iii  7.57 (11)  C9—C10—C11—N2 0.5 (5)
O4—S1—O1—Co1  52.63 (15)  C11—N2—C7—C8 −0.5 (4)
O4—S1—O3—Co1ii −175.90 (17)  C12—C8—C9—C10 −179.4 (3)

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

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| C1—H1···O4i | 0.93  | 2.53  | 3.116 (4) | 121 |
| C3—H3···O2iv | 0.93  | 2.46  | 3.135 (4) | 129 |
| C5—H5···O1  | 0.93  | 2.49  | 3.070 (4) | 121 |

Symmetry codes: (i) y, −x+1, −z+1; (iv) x+1/2, −y+3/2, −z+1/2.