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Crystal structure of the Ba^{II}-based Co^{II}-containing one-dimensional coordination polymer poly[[aqua- $\{\mu_4$ -2,2'-[(4,10-dimethyl-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methyldiene)]bis(4-oxo-4H-pyran-3-olato)}perchloratocobaltbarium] perchlorate]

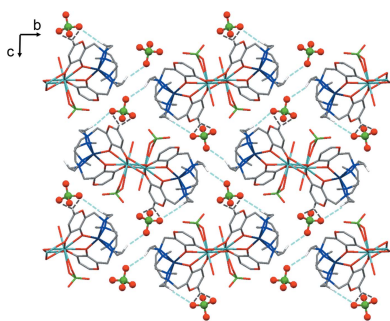
Paola Paoli,^a Eleonora Macedi,^{a*} Patrizia Rossi,^a Luca Giorgi,^b Mauro Formica^b and Vieri Fusi^b^aDepartment of Industrial Engineering, University of Firenze, via Santa Marta 3, I-50139 Firenze, Italy, and ^bDepartment of Pure and Applied Sciences, Lab of Supramolecular Chemistry, University of Urbino, via della Stazione, 4, I-61029 Urbino, Italy. *Correspondence e-mail: eleonora.macedi@unifi.it

The title compound, $\{[\text{Ba}\{\text{Co}(\text{H}_2\text{L1})\}(\text{ClO}_4)(\text{H}_2\text{O})]\text{ClO}_4\}_n$, **L1** = 4,10-bis[(3-hydroxy-4-pyran-2-yl)methyl]-1,7-dimethyl-1,4,7,10-tetraazacyclododecane, is a one-dimensional coordination polymer. The asymmetric unit consists of a $\{\text{Ba}\{\text{Co}(\text{H}_2\text{L1})\}(\text{ClO}_4)(\text{H}_2\text{O})\}^+$ cationic fragment and a non-coordinating ClO_4^- anion. In the neutral $[\text{Co}(\text{H}_2\text{L1})]$ moiety, the cobalt ion is hexacoordinated in a trigonal-prismatic fashion by the surrounding N_4O_2 donor set. The Ba^{2+} ion is nine-coordinated and exhibits a distorted $[\text{BaO}_9]$ monocapped square-antiprismatic geometry, the six oxygen atoms coming from three distinct $[\text{Co}(\text{H}_2\text{L1})]$ moieties, while the remaining three vertices are occupied by the oxygen atoms of a bidentate perchlorate anion and a water molecule. A barium- μ_2 -oxygen motif develops along the *a* axis, connecting symmetry-related dinuclear $\text{Ba}^{\text{II}}\text{-Co}^{\text{II}}$ cationic fragments in a wave-like chain, forming a one-dimensional metal coordination polymer. Non-coordinating ClO_4^- anions are located in the space between the chains. Weak $\text{C-H}\cdots\text{O}$ hydrogen bonds involving both coordinating and non-coordinating perchlorate anions build the whole crystal architecture. To our knowledge, this is the first example of a macrocyclic ligand forming a Ba^{II} -based one-dimensional coordination polymer, containing Co^{II} ions surrounded by a N_4O_2 donor set.

1. Chemical context

Metal coordination polymers (CPs) have witnessed continuous growth, owing to their fascinating structural diversity in terms of architecture and topology and also their numerous potential applications, such as gas storage (Banerjee *et al.*, 2016; Fracaroli *et al.*, 2014; Sumida *et al.*, 2012; Suh *et al.*, 2012), chemical sensing (Campbell *et al.*, 2015; Hu *et al.*, 2014; Wang *et al.*, 2013; Kreno *et al.*, 2012), catalysis (Chughtai *et al.*, 2015; Mo *et al.*, 2014; Yoon *et al.*, 2012; Liu, Xuan *et al.*, 2010) and so forth. Recently, the interest in alkaline-earth metal ion-based CPs has been growing due to their unusual advantages such as low toxicity, wide distribution and low cost, which are of benefit for applications in the field of materials science (Raja *et al.*, 2014; Foo *et al.*, 2012, 2013; Xiao *et al.*, 2012).

According to a Cambridge Structural Database (CSD, Version 5.38, May 2017; Groom *et al.*, 2016) search, alkaline-



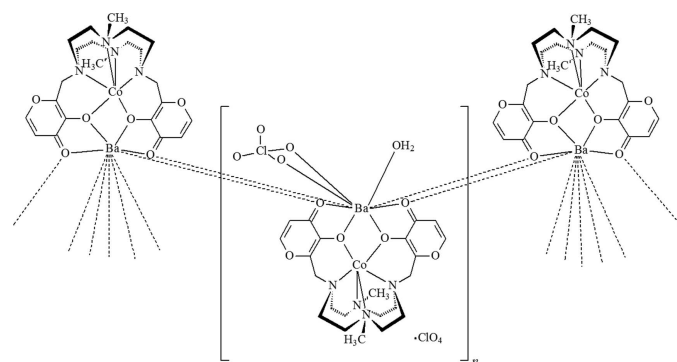
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earth metal-based CPs are less common compared to the reported transition metal and rare-earth metal CPs (Cai *et al.*, 2017). Indeed, the study of alkaline-earth–metal systems is limited by challenges in the synthesis (Lian *et al.*, 2016; Douvali *et al.*, 2015; Mali *et al.*, 2015; Chakraborty *et al.*, 2014; Zhang, Huang *et al.*, 2012; Liu, Tsao *et al.*, 2010), the main reason being the variable coordination numbers (the most preferred coordination numbers are six for magnesium, six to eight for calcium, and six to twelve for strontium and barium), which lead to uncontrolled coordination geometries around the metal centre (Cai *et al.*, 2016; Feng *et al.*, 2015; Shi *et al.*, 2015; Zheng *et al.*, 2015; Jia *et al.*, 2014; Zhang, Yuan *et al.*, 2013; Smith *et al.*, 2013; Zhai *et al.*, 2013; Zhang, Guo *et al.*, 2013; Deng *et al.*, 2012; Foo *et al.*, 2012; Xiao *et al.*, 2012; Xie *et al.*, 2012; Zhang, Luo *et al.*, 2012; Jing *et al.*, 2010; Zhang *et al.*, 2010; Li *et al.*, 2009).

Besides, the ability of a system to bind alkaline-earth metal ions in aqueous solution is highly desirable and can be achieved thanks to the presence of oxygenated ligands and the preorganization of the receptor, which satisfies the need for a high coordination number without specific coordination requirements.

Ligand **L1** {4,10-bis[(3-hydroxy-4-pyron-2-yl)methyl]-1,7-dimethyl-1,4,7,10-tetraazacyclododecane} is a Maltol-based macrocycle (Amatori *et al.*, 2012) and is able to form discrete heteropolynuclear complexes. It has already proved to be able to form a Co^{II} species (Borgogelli *et al.*, 2013) that is able to bind hard metal ions such as Ln^{III} (Ln = Gd, Eu) and Na(I). In the case of Ln^{III} ions, heterotrimeric Co^{II}–Ln^{III}–Co^{II} systems form, where the Co^{II} cation preorganizes the system and two Co^{II} species are involved in the coordination of one Ln^{III} ion (Benelli *et al.*, 2013; Rossi *et al.*, 2017). In the case of the alkaline ion, a heterodinuclear complex forms, involving only one Co^{II} species (Borgogelli *et al.*, 2013).

Herein we present a Ba^{II}–Co^{II} heterodinuclear metal coordination compound of **L1**, where a one-dimensional wave-like infinite array of barium ions bridges the [Co(H₂L1)] moieties through a barium–μ₂-oxygen motif. This is the first time that **L1** has proven able to form a coordination polymer and, to our knowledge, this is the first example of a macrocyclic ligand forming a Ba^{II}-based 1D-CP containing Co^{II} ions surrounded by an N₄O₂ donor set.



2. Structural commentary

The title compound is the Ba^{II}-based Co^{II}-containing 1D-CP of **L1** of formula {[Ba[Co(H₂L1)](ClO₄)(H₂O)]·ClO₄]_n and crystallizes in the monoclinic system in space group *P*2₁/*n*, with a {Ba[Co(H₂L1)](ClO₄)(H₂O)]⁺ cationic fragment (Fig. 1) and a (ClO₄)[−] anion in the asymmetric unit.

In the neutral [Co(H₂L1)] moiety, the Co²⁺ ion is hexacoordinated and exhibits a distorted trigonal–prismatic geometry (Muetterties & Guggenberger, 1974), where the cobalt ion is surrounded by four nitrogen atoms of the macrocyclic base and two deprotonated hydroxyl oxygen atoms provided by both maltolate rings of the ligand. In the distorted trigonal prism, the O1,N2,N3/O4,N1,N4 atoms define the two triangular faces, which are parallel within 12.51 (11)° (Fig. 2). The cobalt ion is displaced 1.0971 (5) Å above the mean plane described by the four nitrogen atoms of the tetraazamacrocycle [maximum deviation of 0.068 (4) Å for N3] and falls, together with the Co–N(CH₃) and Co–O bond distances (Table 1), in the expected range for Co–[12]aneN₄ complexes where the cobalt ion is hexacoordinated with a N₄O₂ donor set (Fig. 3, left). The Co–N(Maltol) bond distances, instead, are longer (Table 1) than the Co–N(CH₃) ones and longer with respect to those reported for other Co–**L1** complexes [Co–N(Maltol): range 2.26–2.44; Co–N(CH₃): range: 2.13–2.19; Benelli *et al.*, 2013; Borgogelli *et al.*, 2013; Rossi *et al.*, 2017].

The conformation of the [12]aneN₄ macrocycle is the usual [3333]C-corners one (Meurant, 1987) with the *trans* nitrogen distances in agreement with those reported in the CSD for this conformation type, but the N2···N4 distance being longer than the N1···N3 one by 0.26 Å (Table 1), as found only in

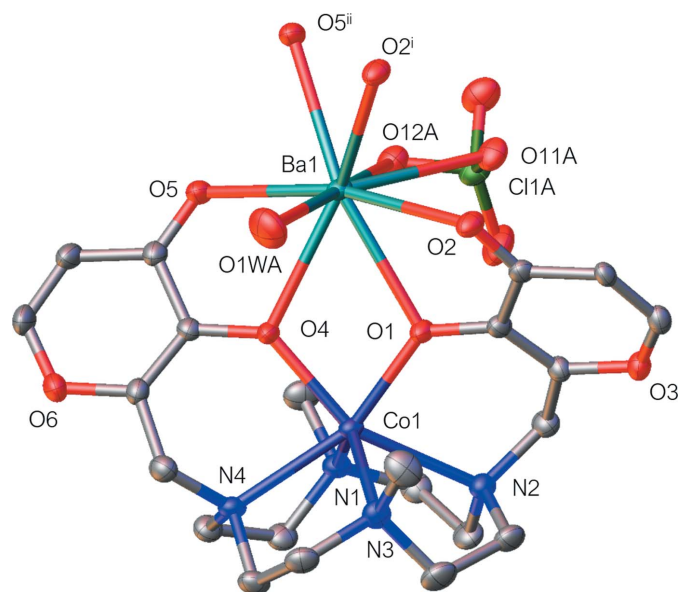


Figure 1

The molecular structure of the {Ba[Co(H₂L1)](ClO₄)(H₂O)]⁺ cationic fragment, with the atom labelling and 30% probability displacement ellipsoids. Only one component of the disordered perchlorate anion and water molecule is shown. H atoms have been omitted for clarity. Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$.

Table 1
Selected bond lengths and angles (Å, °).

| | |
|---------------------------------------|---|
| Co1—N1 | 2.199 (3) |
| Co1—N2 | 2.414 (3) |
| Co1—N3 | 2.220 (4) |
| Co1—N4 | 2.344 (3) |
| Co1—O1 | 2.044 (3) |
| Co1—O4 | 2.075 (3) |
| Ba1—O1 | 2.688 (3) |
| Ba1—O2 | 2.861 (3) |
| Ba1—O4 | 2.690 (3) |
| Ba1—O5 | 2.814 (3) |
| Ba1—O1W | 2.774 (14)/2.75 (2)/2.972 (15) ^a |
| Ba1—O11 | 2.853 (19)/3.154 (13) ^b |
| Ba1—O12 | 2.955 (18)/2.863 (12) ^b |
| N1···N3 | 3.903 (5) |
| N2···N4 | 4.164 (5) |
| Ba1···Ba1 ⁱ | 4.9123 (4) |
| Ba1···O2 ⁱ | 2.860 (3) |
| O2···O2 ⁱ | 2.932 (4) |
| Ba1···Ba1 ⁱⁱ | 4.8443 (4) |
| Ba1···O5 ⁱⁱ | 2.900 (3) |
| O5···O5 ⁱⁱ | 3.033 (4) |
| Ba1 ⁱ ···Ba1 ⁱⁱ | 8.8965 (4) |
| | |
| Ba1—O1—Co1 | 113.82 (12) |
| Ba1—O4—Co1 | 112.64 (11) |
| Ba1—O2—Ba1 ⁱ | 118.34 (10) |
| Ba1—O5—Ba1 ⁱⁱ | 115.92 (10) |

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$. Notes: (a) the values refer to O1W/A/B/C atoms, respectively; (b) the values refer to the A/B oxygen atoms, respectively, of the disordered perchlorate anion (see *Refinement* section).

36% of cases. This is probably due to the fact that the Maltol units linked to atoms N2 and N4 are involved in chelate six-membered rings, which stiffen the system and force those nitrogen atoms to move farther apart.

The two maltolate rings are almost orthogonal to each other (dihedral angle between ring mean planes about 71°); both rings form similar angles (about 55°) with the mean plane N1,N2,N3,N4. The dimensions of the binding area defined by the four oxygen donor atoms of the ligand, as roughly estimated by the distances separating the opposite O1···O5 and O2···O4 atoms, are quite similar (about 4.5 Å).

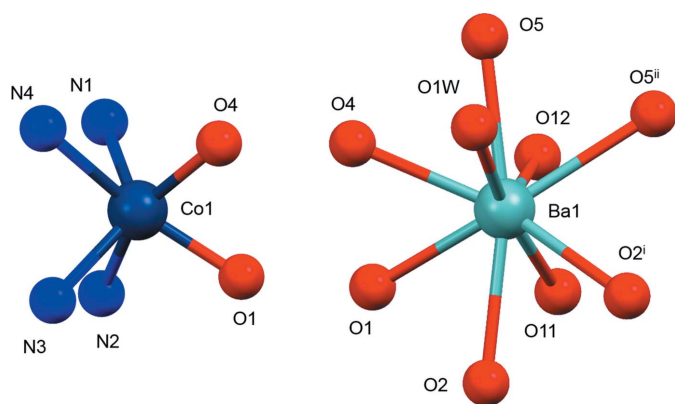


Figure 2
Coordination polyhedra around cobalt (left) and barium (right) ions. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$.]

Table 2
Hydrogen-bond geometry (Å, °).

| D—H··· | D—H | H···A | D···A | D—H···A |
|-----------------------------|------|-----------|---------------------|-------------|
| C8—H8A···O21 | 0.99 | 2.91/2.62 | 3.877 (12)/3.60 (3) | 165.3/172.3 |
| C3—H3A···O22 ⁱⁱⁱ | 0.99 | 2.65/2.48 | 3.577 (11)/3.46 (3) | 155.7/166.7 |
| C8—H8B···O13 ^{iv} | 0.99 | 2.49/2.59 | 3.46 (2)/3.524 (15) | 168.5/156.6 |
| C22—H22···O21 ^v | 0.95 | 2.62/2.66 | 3.482 (11)/3.51 (3) | 151.4/149.2 |
| C22—H22···O23 ^v | 0.95 | 2.57/2.54 | 3.455 (11)/3.39 (4) | 155.1/149.9 |

Symmetry codes: (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x - 1, y, z$. Note: the first and second values for each entry refer to the A and B oxygen atoms, respectively, of the disordered perchlorate anion (see *Refinement* section).

The Ba²⁺ ion is nine-coordinated and exhibits a distorted [BaO₉] monocapped square-antiprismatic geometry (Guggenberger & Muetterties, 1976), Fig. 2, where the barium cation is surrounded by six oxygen atoms from three distinct [Co(H₂L1)] moieties {four from two maltolate groups of a moiety and two from the carbonyl groups belonging to two distinct symmetry-related moieties, O2ⁱ and O5ⁱⁱ [symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$]}, an oxygen atom of a disordered water molecule and two oxygen atoms of a disordered perchlorate anion, the latter acting as a bidentate ligand (Fig. 1). In the distorted monocapped square antiprism, the O5 oxygen atom caps the O5ⁱⁱ, O4, O1W, O12 face (Fig. 2, right). All bond distances (Table 1) are in agreement with data found in the CSD.

The Ba²⁺ and Co²⁺ cations are located 3.9799 (7) Å apart from each other, the line connecting them being normal to the mean plane described by the four nitrogen atoms of the macrocycle [angle value: 87.59 (7)°; Fig. 1]. As for the bridged Co—O—Ba moiety (Fig. 3, right), while the Ba—O and Co—O bond distances and the Ba···Co distance are in agreement with those found in the CSD, the corresponding Ba—O—Co angles (Table 1) are outside the observed range (89.5–111.4°).

3. Supramolecular features

The title compound forms wave-like chains with a repeating unit comprising a dinuclear Ba^{II}–Co^{II} cationic fragment with associated coordinating water molecules and perchlorate ions (Fig. 4). Non-coordinating ClO₄[−] anions are located in the space between the chains.

A barium-μ₂-oxygen motif develops along the *a* axis, the angle between the two mean planes formed by atoms Ba, O2,

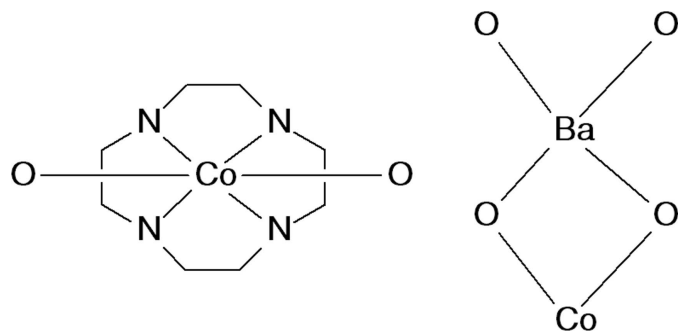
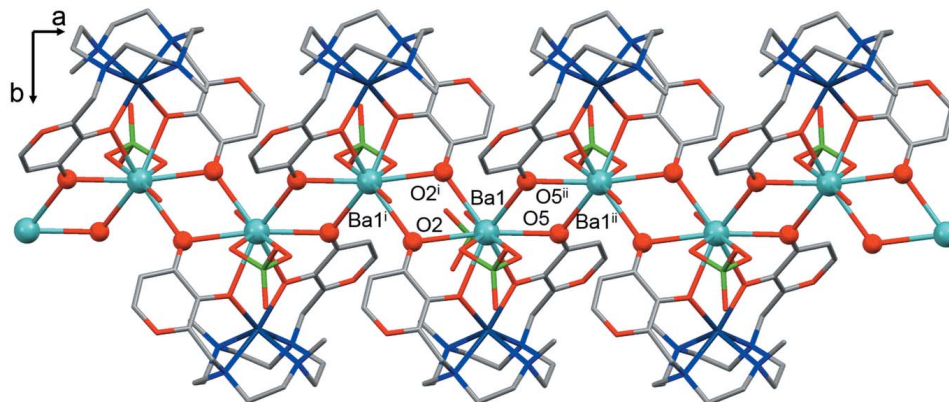


Figure 3
Fragments searched in the CSD.

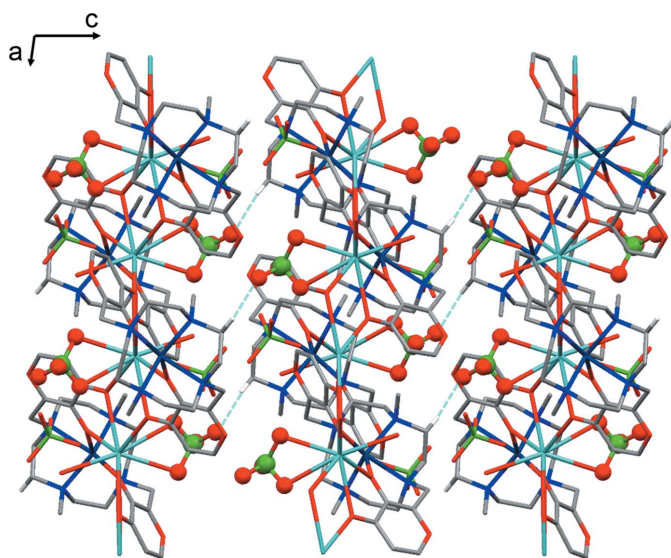

Figure 4

Wave-like one-dimensional Ba^{II}-based coordination polymer that develops along the *a* axis. The oxygen and barium atoms belonging to the barium- μ_2 -oxygen motif are depicted in ball and stick mode. Only one component of the disordered perchlorate anion and water molecule is shown. H atoms and the non-coordinating ClO₄⁻ anions have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$.]

Baⁱ and O2ⁱ and atoms Ba, O5, Baⁱⁱ and O5ⁱⁱ is about 40° [symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 2, -y, -z$], Fig. 4. The Ba–O bond distances, the O···O and Ba···Ba distances and the Ba–O–Ba angle values within each plane and the Baⁱ···Baⁱⁱ distance (Table 1) are in agreement with data reported in the CSD.

Weak C–H···O hydrogen bonds (Desiraju & Steiner, 1999) involving both coordinating and non-coordinating perchlorate anions build the whole crystal architecture (Table 2). Distinct 1D-CPs are held together by weak C–H···O interactions between the coordinating perchlorate anions belonging to a CP and methylene hydrogen atoms belonging to the adjacent CPs (Fig. 5).

The non-coordinating perchlorate anion connects, *via* a net of weak hydrogen bonds, three {Ba[Co(H₂L1)](ClO₄)(H₂O)}⁺

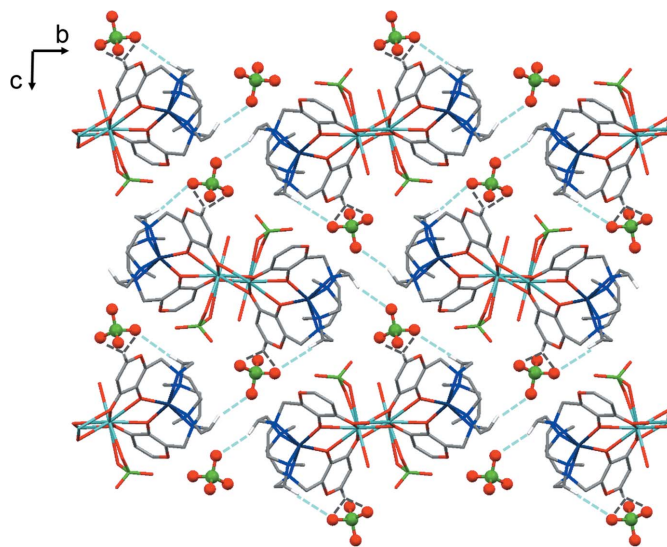

Figure 5

Adjacent CPs connected *via* hydrogen bonds involving the coordinating ClO₄⁻ anions as viewed along the *b* axis. The coordinating ClO₄⁻ anions are depicted in ball and stick mode. Hydrogen bonds are depicted as light-blue dotted lines. Only H atoms involved in the C–H···O interactions and only one component of the disordered perchlorate anion and water molecule are shown.

cationic fragments belonging to two different 1D-CPs wave-like disposed along the *b* axis (Fig. 6).

4. Database survey

Five structures containing **L1** were found in a search of the CSD (Version 5.38, May 2017; Groom *et al.*, 2016), three of them containing Co^{II}: a hetero-trinuclear Gd^{III}–Co^{II}–Gd^{III} dimer, a hetero-dinuclear Na^I–Co^{II} complex and a Co^{II} complex (Benelli *et al.*, 2013; Amatori *et al.*, 2012; Borgogelli *et al.*, 2013). In addition, our group recently published the


Figure 6

Crystal packing of the title compound as viewed along the *a* axis. The non-coordinating ClO₄⁻ anions are depicted in ball and stick mode. Hydrogen bonds involving the non-coordinating ClO₄⁻ anion and two {Ba[Co(H₂L1)](ClO₄)(H₂O)}⁺ cationic fragments on the same plane are depicted in light-blue dotted lines. Hydrogen bonds involving the non-coordinating ClO₄⁻ anion and a {Ba[Co(H₂L1)](ClO₄)(H₂O)}⁺ cationic fragment out of plane (symmetry operation $x - 1, y, z$) are depicted in grey dotted lines. Only H atoms involved in the C–H···O interactions and only one component of the disordered perchlorate anion and water molecule are shown.

corresponding hetero-trinuclear Eu–Co–Eu dimer (Rossi *et al.*, 2017).

A general search for structures containing both Co^{II} and Ba^{II} ions revealed 61 hits, 20 of which are polymeric structures formed by organic ligands containing both oxygen and nitrogen donor atoms and only two being 1D-CPs. It is noteworthy that none of the 20 structures contains either macrocyclic ligands or an N₄O₂ donor set around the Co^{II} ion. In eight out of those 20 polymeric structures, the Ba^{II} and Co^{II} ions are bridged by oxygen atoms and ten out of 20 show oxygen-bridged Ba^{II} ions (only eight forming an infinite chain). Finally, only six out of the 20 polymeric structures contain both oxygen-bridged Ba^{II} ions and oxygen-bridged Ba^{II} and Co^{II} ions.

All these data suggest that structures containing both oxygen-bridged Ba^{II} ions and oxygen-bridged Ba^{II} and Co^{II} ions are not common and that no Ba^{II}-based 1D-CPs formed by macrocyclic ligands and containing Co^{II} ions surrounded by an N₄O₂ donor set are present in the CSD.

5. Synthesis and crystallization

Compound **L1** was obtained following the synthetic procedure previously reported (Amatori *et al.*, 2012).

To obtain the Ba^{II}-based Co^{II}-containing 1D-CP of **L1**, {[Ba[Co(H₂L1)](ClO₄)(H₂O)]·ClO₄]_n, 0.1 mmol of CoCl₂·6H₂O in water (10 mL) were added to an aqueous solution (20 mL) containing 0.1 mmol of L1·3HClO₄·H₂O. The solution was adjusted to pH 7 with 0.1 M N(CH₃)₄OH and then 0.05 mmol of BaCl₂·2H₂O were added. The solution was saturated with NaClO₄. The Ba^{II}–Co^{II} 1D-CP of **L1** quickly precipitated as a microcrystalline pink solid. Crystals suitable for X-ray analysis were instead obtained by slow evaporation of a more diluted aqueous solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms of the macrocycle were positioned geometrically and refined as riding with C–H = 0.95–0.99 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C-methyl) and = 1.2*U*_{eq}(C) for other H atoms. Both perchlorate anions are disordered, all oxygen and chlorine atoms were set in double positions [anion 1: Cl1A/B, O11A/B, O12A/B, O13A/B, O14A/B, occupancy factor: 0.40 (3) and 0.60 (3); anion 2: Cl2A/B, O21A/B, O22A/B, O23A/B, O24A/B, occupancy factor: 0.78 (3) and 0.22 (3)]. The water molecule is disordered over three positions [SUMP command was used, occupancies 0.49 (3), 0.27 (3) and 0.24 (3)], the hydrogen atoms were not found in the Fourier-difference map and they were not introduced in the refinement. All non-hydrogen atoms were anisotropically refined: as for the disordered perchlorate anions, the SIMU instruction was used to restrain the anisotropic displacement parameters of the disordered atoms, while the ISOR instruction was used to model the disordered water oxygen atoms.

Table 3
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | [BaCo(C ₂₂ H ₂₈ N ₄ O ₆)(ClO ₄)(H ₂ O)]·ClO ₄ |
| <i>M</i> _r | 857.67 |
| Crystal system, space group | Monoclinic, <i>P</i> ₂ ₁ / <i>n</i> |
| Temperature (K) | 120 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 8.8965 (2), 18.0995 (4), 19.0103 (6) |
| β (°) | 94.572 (2) |
| <i>V</i> (Å ³) | 3051.34 (14) |
| <i>Z</i> | 4 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ^{−1}) | 2.08 |
| Crystal size (mm) | 0.45 × 0.38 × 0.27 |
| Data collection | |
| Diffractometer | Rigaku OD Xcalibur, Sapphire3 |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.884, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 15496, 6966, 5315 |
| <i>R</i> _{int} | 0.037 |
| (sin θ/λ) _{max} (Å ^{−1}) | 0.682 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.041, 0.103, 1.06 |
| No. of reflections | 6966 |
| No. of parameters | 519 |
| No. of restraints | 133 |
| H-atom treatment | H-atom parameters constrained |
| Δρ _{max} , Δρ _{min} (e Å ^{−3}) | 1.00, −0.72 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SIR2014* (Burla, 2015), *SHELXL2014/7* (Sheldrick, 2015).

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supporting information

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Crystal structure of the Ba^{II}-based Co^{II}-containing one-dimensional coordination polymer poly[[aqua{ μ_4 -2,2'-[(4,10-dimethyl-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methyldiene)]bis(4-oxo-4*H*-pyran-3-olato)}perchloratocobaltbarium] perchlorate]

Paola Paoli, Eleonora Macedi, Patrizia Rossi, Luca Giorgi, Mauro Formica and Vieri Fusi

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SIR2014* (Burla, 2015); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *SHELXL2014/7* (Sheldrick, 2015); software used to prepare material for publication: *SHELXL2014/7* (Sheldrick, 2015).

Poly[[aqua{ μ_4 -2,2'-[(4,10-dimethyl-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methyldiene)]bis(4-oxo-4*H*-pyran-3-olato)}perchloratocobaltbarium] perchlorate]

Crystal data

[BaCo(C₂₂H₂₈N₄O₆)(ClO₄)(H₂O)]ClO₄

$M_r = 857.67$

Monoclinic, $P2_1/n$

$a = 8.8965$ (2) Å

$b = 18.0995$ (4) Å

$c = 19.0103$ (6) Å

$\beta = 94.572$ (2)°

$V = 3051.34$ (14) Å³

$Z = 4$

$F(000) = 1708$

$D_x = 1.867$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4989 reflections

$\theta = 2.2$ – 27.7 °

$\mu = 2.08$ mm⁻¹

$T = 120$ K

Prism, pink

$0.45 \times 0.38 \times 0.27$ mm

Data collection

Rigaku OD Xcalibur, Sapphire3
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.4547 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlisPro*; Rigaku OD, 2015) Empirical
absorption correction using spherical
harmonics, implemented in *SCALE3*
ABSPACK scaling algorithm.

$T_{\min} = 0.884$, $T_{\max} = 1.000$

15496 measured reflections

6966 independent reflections

5315 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 29.0$ °, $\theta_{\min} = 2.2$ °

$h = -12 \rightarrow 11$

$k = -22 \rightarrow 22$

$l = -22 \rightarrow 24$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.041$ $wR(F^2) = 0.103$ $S = 1.06$

6966 reflections

519 parameters

133 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 2.9358P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 1.00 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$ *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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|--------------|---------------|----------------------------------|-----------|
| Ba1 | 0.75388 (3) | 0.05421 (2) | 0.01055 (2) | 0.03237 (9) | |
| Co1 | 0.75301 (6) | 0.26481 (3) | 0.07072 (3) | 0.02836 (14) | |
| O1 | 0.6344 (3) | 0.19069 (15) | 0.00703 (16) | 0.0351 (7) | |
| N1 | 0.9308 (4) | 0.33476 (19) | 0.03199 (19) | 0.0336 (8) | |
| C1 | 0.5130 (6) | 0.3782 (3) | 0.1078 (3) | 0.0545 (14) | |
| H1A | 0.4189 | 0.3897 | 0.1300 | 0.065* | |
| H1B | 0.5870 | 0.4177 | 0.1210 | 0.065* | |
| O2 | 0.4340 (3) | 0.07423 (16) | -0.00434 (18) | 0.0400 (8) | |
| N2 | 0.6147 (4) | 0.35215 (19) | -0.00548 (19) | 0.0350 (8) | |
| C2 | 0.4817 (5) | 0.3772 (3) | 0.0300 (3) | 0.0461 (12) | |
| H2A | 0.3957 | 0.3438 | 0.0172 | 0.055* | |
| H2B | 0.4530 | 0.4275 | 0.0133 | 0.055* | |
| O3 | 0.3318 (3) | 0.26420 (17) | -0.11008 (16) | 0.0374 (7) | |
| N3 | 0.5736 (4) | 0.3060 (2) | 0.1354 (2) | 0.0389 (9) | |
| C3 | 0.7199 (5) | 0.4133 (3) | -0.0140 (3) | 0.0445 (11) | |
| H3A | 0.7282 | 0.4440 | 0.0292 | 0.053* | |
| H3B | 0.6818 | 0.4449 | -0.0541 | 0.053* | |
| O4 | 0.8695 (3) | 0.16663 (15) | 0.09010 (15) | 0.0340 (7) | |
| N4 | 0.8905 (4) | 0.30110 (18) | 0.17530 (19) | 0.0324 (8) | |
| C4 | 0.8729 (5) | 0.3827 (3) | -0.0275 (3) | 0.0434 (11) | |
| H4A | 0.8650 | 0.3537 | -0.0718 | 0.052* | |
| H4B | 0.9442 | 0.4239 | -0.0330 | 0.052* | |
| O5 | 1.0650 (3) | 0.05816 (16) | 0.05118 (17) | 0.0406 (8) | |
| C5 | 0.9983 (5) | 0.3822 (2) | 0.0890 (3) | 0.0422 (11) | |
| H5A | 0.9293 | 0.4240 | 0.0962 | 0.051* | |
| H5B | 1.0941 | 0.4029 | 0.0746 | 0.051* | |
| O6 | 1.1536 (4) | 0.16710 (18) | 0.23669 (17) | 0.0462 (8) | |
| C6 | 1.0284 (5) | 0.3412 (3) | 0.1570 (3) | 0.0414 (11) | |
| H6A | 1.1114 | 0.3055 | 0.1527 | 0.050* | |
| H6B | 1.0601 | 0.3764 | 0.1952 | 0.050* | |

| | | | | | |
|------|-------------|-------------|--------------|-------------|----------|
| C7 | 0.7907 (5) | 0.3517 (3) | 0.2110 (3) | 0.0426 (11) | |
| H7A | 0.7868 | 0.4003 | 0.1870 | 0.051* | |
| H7B | 0.8308 | 0.3593 | 0.2606 | 0.051* | |
| C8 | 0.6351 (5) | 0.3191 (3) | 0.2090 (3) | 0.0442 (12) | |
| H8A | 0.6387 | 0.2719 | 0.2353 | 0.053* | |
| H8B | 0.5678 | 0.3533 | 0.2324 | 0.053* | |
| C9 | 0.4532 (6) | 0.2506 (3) | 0.1367 (3) | 0.0589 (15) | |
| H9A | 0.4106 | 0.2409 | 0.0885 | 0.088* | |
| H9B | 0.4947 | 0.2047 | 0.1576 | 0.088* | |
| H9C | 0.3738 | 0.2691 | 0.1650 | 0.088* | |
| C10 | 1.0466 (5) | 0.2848 (3) | 0.0060 (3) | 0.0500 (13) | |
| H10A | 1.0003 | 0.2536 | -0.0319 | 0.075* | |
| H10B | 1.1274 | 0.3143 | -0.0121 | 0.075* | |
| H10C | 1.0886 | 0.2536 | 0.0448 | 0.075* | |
| C11 | 0.5658 (5) | 0.3217 (2) | -0.0762 (2) | 0.0395 (10) | |
| H11A | 0.5112 | 0.3604 | -0.1049 | 0.047* | |
| H11B | 0.6556 | 0.3072 | -0.1006 | 0.047* | |
| C12 | 0.4661 (5) | 0.2566 (2) | -0.0707 (2) | 0.0318 (9) | |
| C13 | 0.5033 (4) | 0.1960 (2) | -0.0315 (2) | 0.0316 (9) | |
| C14 | 0.3993 (4) | 0.1344 (2) | -0.0339 (2) | 0.0325 (9) | |
| C15 | 0.2580 (4) | 0.1477 (2) | -0.0733 (2) | 0.0310 (9) | |
| H15 | 0.1815 | 0.1109 | -0.0739 | 0.037* | |
| C16 | 0.2308 (5) | 0.2098 (3) | -0.1090 (2) | 0.0367 (10) | |
| H16 | 0.1358 | 0.2158 | -0.1349 | 0.044* | |
| C17 | 0.9321 (5) | 0.2400 (2) | 0.2241 (2) | 0.0404 (11) | |
| H17A | 0.9863 | 0.2604 | 0.2673 | 0.048* | |
| H17B | 0.8390 | 0.2160 | 0.2380 | 0.048* | |
| C18 | 1.0276 (5) | 0.1841 (2) | 0.1936 (2) | 0.0354 (10) | |
| C19 | 0.9936 (4) | 0.1509 (2) | 0.1305 (2) | 0.0307 (9) | |
| C20 | 1.0956 (5) | 0.0936 (2) | 0.1072 (2) | 0.0364 (10) | |
| C21 | 1.2276 (5) | 0.0819 (3) | 0.1537 (3) | 0.0479 (12) | |
| H21 | 1.3017 | 0.0479 | 0.1404 | 0.058* | |
| C22 | 1.2496 (6) | 0.1168 (3) | 0.2147 (3) | 0.0536 (14) | |
| H22 | 1.3377 | 0.1056 | 0.2443 | 0.064* | |
| Cl1A | 0.800 (2) | 0.1249 (9) | -0.1620 (10) | 0.047 (2) | 0.40 (3) |
| O11A | 0.658 (2) | 0.0849 (10) | -0.1333 (10) | 0.047 (3) | 0.40 (3) |
| O12A | 0.9088 (18) | 0.1007 (11) | -0.1140 (9) | 0.052 (3) | 0.40 (3) |
| O13A | 0.860 (3) | 0.0808 (10) | -0.2136 (12) | 0.063 (4) | 0.40 (3) |
| O14A | 0.810 (3) | 0.2057 (12) | -0.1686 (12) | 0.074 (4) | 0.40 (3) |
| Cl1B | 0.7844 (14) | 0.1280 (7) | -0.1622 (6) | 0.0479 (16) | 0.60 (3) |
| O11B | 0.6498 (15) | 0.1036 (8) | -0.1448 (7) | 0.051 (2) | 0.60 (3) |
| O12B | 0.8977 (12) | 0.1255 (8) | -0.1006 (6) | 0.056 (2) | 0.60 (3) |
| O13B | 0.8144 (15) | 0.0963 (8) | -0.2287 (6) | 0.064 (3) | 0.60 (3) |
| O14B | 0.750 (2) | 0.2000 (8) | -0.1816 (7) | 0.076 (3) | 0.60 (3) |
| Cl2A | 0.6555 (9) | 0.0780 (5) | 0.3226 (4) | 0.0424 (12) | 0.78 (3) |
| O21A | 0.5765 (11) | 0.1464 (5) | 0.3243 (6) | 0.066 (2) | 0.78 (3) |
| O22A | 0.7030 (10) | 0.0638 (6) | 0.3946 (4) | 0.062 (2) | 0.78 (3) |
| O23A | 0.5501 (11) | 0.0220 (4) | 0.2981 (6) | 0.065 (2) | 0.78 (3) |

| | | | | | |
|------|-------------|-------------|-------------|-----------|-----------|
| O24A | 0.7821 (9) | 0.0858 (7) | 0.2801 (4) | 0.081 (3) | 0.78 (3) |
| Cl2B | 0.661 (4) | 0.073 (2) | 0.317 (2) | 0.060 (5) | 0.22 (3) |
| O21B | 0.610 (4) | 0.1450 (16) | 0.2989 (19) | 0.053 (6) | 0.22 (3) |
| O22B | 0.733 (4) | 0.0437 (17) | 0.381 (2) | 0.065 (5) | 0.22 (3) |
| O23B | 0.571 (4) | 0.027 (2) | 0.272 (2) | 0.066 (5) | 0.22 (3) |
| O24B | 0.783 (3) | 0.049 (2) | 0.2882 (15) | 0.071 (5) | 0.22 (3) |
| O1WA | 0.6542 (14) | 0.0192 (9) | 0.1411 (7) | 0.079 (4) | 0.493 (3) |
| O1WB | 0.721 (2) | 0.0144 (13) | 0.1481 (12) | 0.054 (5) | 0.268 (3) |
| O1WC | 0.842 (2) | -0.0011 (8) | 0.1552 (8) | 0.058 (4) | 0.239 (3) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|--------------|--------------|--------------|--------------|--------------|---------------|
| Ba1 | 0.02904 (15) | 0.02521 (14) | 0.04255 (17) | 0.00132 (10) | 0.00089 (10) | -0.00540 (11) |
| Co1 | 0.0275 (3) | 0.0241 (3) | 0.0336 (3) | 0.0011 (2) | 0.0035 (2) | -0.0029 (2) |
| O1 | 0.0309 (15) | 0.0251 (15) | 0.0476 (19) | 0.0022 (12) | -0.0083 (13) | -0.0040 (13) |
| N1 | 0.0362 (19) | 0.0289 (19) | 0.037 (2) | -0.0018 (15) | 0.0072 (15) | -0.0018 (16) |
| C1 | 0.052 (3) | 0.049 (3) | 0.065 (4) | 0.019 (2) | 0.015 (3) | -0.007 (3) |
| O2 | 0.0332 (16) | 0.0273 (16) | 0.058 (2) | -0.0005 (12) | -0.0026 (14) | 0.0005 (15) |
| N2 | 0.0336 (19) | 0.031 (2) | 0.040 (2) | 0.0002 (15) | 0.0013 (15) | -0.0011 (16) |
| C2 | 0.041 (3) | 0.041 (3) | 0.056 (3) | 0.013 (2) | 0.005 (2) | -0.007 (2) |
| O3 | 0.0348 (16) | 0.0409 (18) | 0.0354 (18) | 0.0054 (13) | -0.0043 (13) | 0.0019 (14) |
| N3 | 0.0327 (19) | 0.045 (2) | 0.040 (2) | 0.0041 (17) | 0.0069 (16) | -0.0030 (18) |
| C3 | 0.057 (3) | 0.029 (2) | 0.048 (3) | -0.001 (2) | 0.000 (2) | 0.008 (2) |
| O4 | 0.0332 (16) | 0.0265 (15) | 0.0403 (18) | 0.0056 (12) | -0.0102 (12) | -0.0067 (13) |
| N4 | 0.0350 (19) | 0.0272 (18) | 0.035 (2) | 0.0008 (15) | 0.0057 (15) | -0.0068 (15) |
| C4 | 0.047 (3) | 0.041 (3) | 0.043 (3) | -0.011 (2) | 0.008 (2) | 0.007 (2) |
| O5 | 0.0372 (17) | 0.0359 (18) | 0.047 (2) | 0.0083 (13) | -0.0064 (14) | -0.0124 (15) |
| C5 | 0.039 (3) | 0.033 (2) | 0.054 (3) | -0.008 (2) | 0.002 (2) | -0.003 (2) |
| O6 | 0.051 (2) | 0.0442 (19) | 0.040 (2) | 0.0051 (15) | -0.0151 (15) | -0.0055 (16) |
| C6 | 0.037 (2) | 0.036 (2) | 0.050 (3) | -0.005 (2) | -0.001 (2) | -0.005 (2) |
| C7 | 0.045 (3) | 0.041 (3) | 0.043 (3) | 0.003 (2) | 0.007 (2) | -0.015 (2) |
| C8 | 0.048 (3) | 0.041 (3) | 0.046 (3) | 0.006 (2) | 0.016 (2) | -0.008 (2) |
| C9 | 0.047 (3) | 0.072 (4) | 0.059 (4) | -0.016 (3) | 0.016 (3) | -0.007 (3) |
| C10 | 0.043 (3) | 0.051 (3) | 0.059 (3) | 0.002 (2) | 0.020 (2) | -0.008 (3) |
| C11 | 0.045 (3) | 0.034 (2) | 0.039 (3) | 0.000 (2) | 0.001 (2) | 0.002 (2) |
| C12 | 0.034 (2) | 0.033 (2) | 0.028 (2) | -0.0013 (18) | -0.0015 (17) | 0.0001 (18) |
| C13 | 0.027 (2) | 0.030 (2) | 0.038 (2) | 0.0033 (17) | -0.0002 (17) | -0.0061 (18) |
| C14 | 0.030 (2) | 0.033 (2) | 0.035 (2) | 0.0061 (17) | 0.0020 (17) | -0.0075 (19) |
| C15 | 0.025 (2) | 0.037 (2) | 0.029 (2) | -0.0004 (17) | -0.0038 (16) | -0.0079 (18) |
| C16 | 0.032 (2) | 0.047 (3) | 0.031 (2) | 0.003 (2) | -0.0022 (17) | -0.003 (2) |
| C17 | 0.048 (3) | 0.038 (3) | 0.035 (3) | 0.001 (2) | 0.001 (2) | -0.003 (2) |
| C18 | 0.034 (2) | 0.032 (2) | 0.039 (3) | 0.0022 (18) | -0.0061 (18) | 0.0016 (19) |
| C19 | 0.031 (2) | 0.026 (2) | 0.034 (2) | -0.0013 (16) | -0.0025 (17) | -0.0028 (18) |
| C20 | 0.035 (2) | 0.029 (2) | 0.043 (3) | 0.0009 (18) | -0.0058 (19) | -0.002 (2) |
| C21 | 0.040 (3) | 0.037 (3) | 0.064 (4) | 0.010 (2) | -0.013 (2) | -0.011 (2) |
| C22 | 0.044 (3) | 0.049 (3) | 0.063 (4) | 0.012 (2) | -0.024 (2) | -0.007 (3) |
| Cl1A | 0.049 (4) | 0.040 (4) | 0.054 (4) | -0.001 (3) | 0.010 (3) | 0.013 (3) |

| | | | | | | |
|------|-------------|-----------|-------------|--------------|--------------|-------------|
| O11A | 0.047 (5) | 0.039 (5) | 0.055 (5) | -0.001 (4) | 0.003 (4) | 0.015 (4) |
| O12A | 0.050 (5) | 0.049 (5) | 0.058 (5) | 0.007 (4) | 0.003 (4) | 0.005 (4) |
| O13A | 0.065 (7) | 0.063 (6) | 0.062 (7) | 0.013 (5) | 0.022 (5) | 0.006 (5) |
| O14A | 0.073 (8) | 0.053 (7) | 0.093 (8) | 0.006 (7) | -0.019 (7) | 0.024 (6) |
| Cl1B | 0.049 (3) | 0.057 (3) | 0.037 (2) | 0.0143 (18) | 0.0014 (18) | 0.0026 (18) |
| O11B | 0.042 (3) | 0.064 (5) | 0.049 (4) | 0.011 (4) | 0.008 (3) | 0.006 (4) |
| O12B | 0.049 (3) | 0.066 (4) | 0.051 (4) | 0.009 (4) | -0.006 (3) | 0.001 (4) |
| O13B | 0.058 (5) | 0.100 (6) | 0.035 (4) | 0.024 (5) | 0.006 (4) | -0.002 (4) |
| O14B | 0.081 (7) | 0.063 (5) | 0.080 (6) | 0.004 (6) | -0.018 (5) | 0.025 (4) |
| Cl2A | 0.0529 (19) | 0.035 (2) | 0.0386 (17) | -0.0050 (18) | -0.0023 (13) | 0.0003 (14) |
| O21A | 0.076 (5) | 0.045 (3) | 0.074 (5) | 0.008 (3) | -0.011 (4) | -0.010 (4) |
| O22A | 0.074 (4) | 0.065 (5) | 0.046 (4) | 0.015 (3) | -0.001 (3) | 0.007 (3) |
| O23A | 0.082 (4) | 0.034 (3) | 0.074 (5) | -0.020 (3) | -0.022 (4) | 0.006 (4) |
| O24A | 0.097 (4) | 0.070 (6) | 0.083 (4) | -0.021 (4) | 0.046 (3) | -0.011 (4) |
| Cl2B | 0.075 (8) | 0.034 (6) | 0.069 (9) | 0.014 (5) | 0.002 (6) | -0.003 (5) |
| O21B | 0.071 (10) | 0.020 (8) | 0.066 (12) | -0.001 (7) | -0.002 (9) | 0.004 (8) |
| O22B | 0.086 (10) | 0.039 (9) | 0.068 (10) | 0.012 (7) | -0.003 (8) | -0.002 (7) |
| O23B | 0.086 (9) | 0.043 (9) | 0.069 (11) | 0.000 (7) | 0.008 (8) | -0.007 (8) |
| O24B | 0.091 (9) | 0.046 (8) | 0.076 (10) | 0.009 (7) | 0.012 (7) | -0.006 (7) |
| O1WA | 0.100 (8) | 0.095 (7) | 0.042 (5) | 0.000 (7) | 0.005 (6) | -0.007 (5) |
| O1WB | 0.067 (9) | 0.056 (8) | 0.038 (8) | -0.005 (8) | 0.004 (8) | 0.001 (6) |
| O1WC | 0.077 (8) | 0.045 (7) | 0.052 (8) | -0.012 (6) | 0.010 (6) | -0.012 (6) |

Geometric parameters (Å, °)

| | | | |
|----------------------|------------|----------|-----------|
| Ba1—O1 | 2.688 (3) | C5—H5B | 0.9900 |
| Ba1—O4 | 2.690 (3) | O6—C22 | 1.339 (6) |
| Ba1—O1WB | 2.75 (2) | O6—C18 | 1.370 (5) |
| Ba1—O1WA | 2.774 (14) | C6—H6A | 0.9900 |
| Ba1—O5 | 2.814 (3) | C6—H6B | 0.9900 |
| Ba1—O11A | 2.853 (19) | C7—C8 | 1.503 (6) |
| Ba1—O2 ⁱ | 2.860 (3) | C7—H7A | 0.9900 |
| Ba1—O2 | 2.861 (3) | C7—H7B | 0.9900 |
| Ba1—O12B | 2.863 (10) | C8—H8A | 0.9900 |
| Ba1—O5 ⁱⁱ | 2.901 (3) | C8—H8B | 0.9900 |
| Ba1—O12A | 2.955 (15) | C9—H9A | 0.9800 |
| Ba1—O1WC | 2.972 (17) | C9—H9B | 0.9800 |
| Co1—O1 | 2.044 (3) | C9—H9C | 0.9800 |
| Co1—O4 | 2.075 (3) | C10—H10A | 0.9800 |
| Co1—N1 | 2.199 (3) | C10—H10B | 0.9800 |
| Co1—N3 | 2.220 (3) | C10—H10C | 0.9800 |
| Co1—N4 | 2.344 (4) | C11—C12 | 1.484 (6) |
| Co1—N2 | 2.414 (4) | C11—H11A | 0.9900 |
| O1—C13 | 1.330 (5) | C11—H11B | 0.9900 |
| N1—C5 | 1.472 (6) | C12—C13 | 1.351 (6) |
| N1—C10 | 1.484 (5) | C13—C14 | 1.448 (6) |
| N1—C4 | 1.485 (6) | C14—C15 | 1.432 (5) |
| C1—C2 | 1.484 (7) | C15—C16 | 1.326 (6) |

| | | | |
|--------------------------|------------|--------------------------|-------------|
| C1—N3 | 1.492 (6) | C15—H15 | 0.9500 |
| C1—H1A | 0.9900 | C16—H16 | 0.9500 |
| C1—H1B | 0.9900 | C17—C18 | 1.471 (6) |
| O2—C14 | 1.252 (5) | C17—H17A | 0.9900 |
| O2—Ba1 ⁱ | 2.860 (3) | C17—H17B | 0.9900 |
| N2—C3 | 1.466 (6) | C18—C19 | 1.353 (6) |
| N2—C2 | 1.479 (5) | C19—C20 | 1.469 (6) |
| N2—C11 | 1.486 (6) | C20—C21 | 1.429 (6) |
| C2—H2A | 0.9900 | C21—C22 | 1.320 (7) |
| C2—H2B | 0.9900 | C21—H21 | 0.9500 |
| O3—C16 | 1.334 (5) | C22—H22 | 0.9500 |
| O3—C12 | 1.366 (5) | Cl1A—O12A | 1.35 (2) |
| N3—C9 | 1.470 (6) | Cl1A—O13A | 1.40 (2) |
| N3—C8 | 1.481 (6) | Cl1A—O14A | 1.47 (3) |
| C3—C4 | 1.511 (6) | Cl1A—O11A | 1.59 (2) |
| C3—H3A | 0.9900 | Cl1B—O11B | 1.342 (18) |
| C3—H3B | 0.9900 | Cl1B—O14B | 1.383 (17) |
| O4—C19 | 1.325 (5) | Cl1B—O13B | 1.433 (15) |
| N4—C17 | 1.471 (5) | Cl1B—O12B | 1.484 (15) |
| N4—C7 | 1.477 (5) | Cl2A—O22A | 1.423 (11) |
| N4—C6 | 1.490 (5) | Cl2A—O21A | 1.425 (12) |
| C4—H4A | 0.9900 | Cl2A—O23A | 1.434 (10) |
| C4—H4B | 0.9900 | Cl2A—O24A | 1.444 (11) |
| O5—C20 | 1.254 (5) | Cl2B—O24B | 1.33 (5) |
| O5—Ba1 ⁱⁱ | 2.901 (3) | Cl2B—O23B | 1.40 (4) |
| C5—C6 | 1.497 (6) | Cl2B—O21B | 1.42 (4) |
| C5—H5A | 0.9900 | Cl2B—O22B | 1.43 (5) |
| | | | |
| O1—Ba1—O4 | 56.75 (8) | N1—C4—H4A | 109.6 |
| O1—Ba1—O1WB | 101.1 (5) | C3—C4—H4A | 109.6 |
| O4—Ba1—O1WB | 74.2 (5) | N1—C4—H4B | 109.6 |
| O1—Ba1—O1WA | 94.5 (3) | C3—C4—H4B | 109.6 |
| O4—Ba1—O1WA | 78.8 (3) | H4A—C4—H4B | 108.1 |
| O1—Ba1—O5 | 111.22 (8) | C20—O5—Ba1 | 112.8 (3) |
| O4—Ba1—O5 | 60.20 (8) | C20—O5—Ba1 ⁱⁱ | 127.8 (3) |
| O1WB—Ba1—O5 | 85.5 (4) | Ba1—O5—Ba1 ⁱⁱ | 115.92 (10) |
| O1WA—Ba1—O5 | 97.9 (3) | N1—C5—C6 | 112.4 (4) |
| O1—Ba1—O11A | 73.1 (4) | N1—C5—H5A | 109.1 |
| O4—Ba1—O11A | 117.6 (4) | C6—C5—H5A | 109.1 |
| O1WA—Ba1—O11A | 144.0 (5) | N1—C5—H5B | 109.1 |
| O5—Ba1—O11A | 118.1 (4) | C6—C5—H5B | 109.1 |
| O1—Ba1—O2 ⁱ | 121.15 (8) | H5A—C5—H5B | 107.9 |
| O4—Ba1—O2 ⁱ | 146.50 (9) | C22—O6—C18 | 118.5 (4) |
| O1WB—Ba1—O2 ⁱ | 73.8 (5) | N4—C6—C5 | 110.4 (4) |
| O1WA—Ba1—O2 ⁱ | 67.9 (3) | N4—C6—H6A | 109.6 |
| O5—Ba1—O2 ⁱ | 126.20 (8) | C5—C6—H6A | 109.6 |
| O11A—Ba1—O2 ⁱ | 89.4 (4) | N4—C6—H6B | 109.6 |
| O1—Ba1—O2 | 59.51 (8) | C5—C6—H6B | 109.6 |

| | | | |
|---------------------------------------|-------------|---------------|-----------|
| O4—Ba1—O2 | 107.01 (8) | H6A—C6—H6B | 108.1 |
| O1WB—Ba1—O2 | 87.0 (5) | N4—C7—C8 | 109.4 (4) |
| O1WA—Ba1—O2 | 74.4 (3) | N4—C7—H7A | 109.8 |
| O5—Ba1—O2 | 166.61 (9) | C8—C7—H7A | 109.8 |
| O11A—Ba1—O2 | 70.2 (4) | N4—C7—H7B | 109.8 |
| O2 ⁱ —Ba1—O2 | 61.66 (10) | C8—C7—H7B | 109.8 |
| O1—Ba1—O12B | 76.5 (3) | H7A—C7—H7B | 108.2 |
| O4—Ba1—O12B | 84.3 (3) | N3—C8—C7 | 110.9 (4) |
| O1WB—Ba1—O12B | 155.1 (5) | N3—C8—H8A | 109.5 |
| O5—Ba1—O12B | 72.8 (2) | C7—C8—H8A | 109.5 |
| O2 ⁱ —Ba1—O12B | 129.0 (3) | N3—C8—H8B | 109.5 |
| O2—Ba1—O12B | 111.7 (2) | C7—C8—H8B | 109.5 |
| O1—Ba1—O5 ⁱⁱ | 149.97 (9) | H8A—C8—H8B | 108.1 |
| O4—Ba1—O5 ⁱⁱ | 123.92 (8) | N3—C9—H9A | 109.5 |
| O1WB—Ba1—O5 ⁱⁱ | 107.8 (5) | N3—C9—H9B | 109.5 |
| O1WA—Ba1—O5 ⁱⁱ | 115.4 (3) | H9A—C9—H9B | 109.5 |
| O5—Ba1—O5 ⁱⁱ | 64.08 (10) | N3—C9—H9C | 109.5 |
| O11A—Ba1—O5 ⁱⁱ | 83.3 (4) | H9A—C9—H9C | 109.5 |
| O2 ⁱ —Ba1—O5 ⁱⁱ | 75.82 (9) | H9B—C9—H9C | 109.5 |
| O2—Ba1—O5 ⁱⁱ | 128.99 (9) | N1—C10—H10A | 109.5 |
| O12B—Ba1—O5 ⁱⁱ | 73.8 (3) | N1—C10—H10B | 109.5 |
| O1—Ba1—O12A | 85.8 (4) | H10A—C10—H10B | 109.5 |
| O4—Ba1—O12A | 93.0 (4) | N1—C10—H10C | 109.5 |
| O1WA—Ba1—O12A | 169.9 (4) | H10A—C10—H10C | 109.5 |
| O5—Ba1—O12A | 72.6 (3) | H10B—C10—H10C | 109.5 |
| O11A—Ba1—O12A | 45.6 (5) | C12—C11—N2 | 111.3 (4) |
| O2 ⁱ —Ba1—O12A | 120.5 (4) | C12—C11—H11A | 109.4 |
| O2—Ba1—O12A | 114.1 (3) | N2—C11—H11A | 109.4 |
| O5 ⁱⁱ —Ba1—O12A | 64.3 (4) | C12—C11—H11B | 109.4 |
| O1—Ba1—O1WC | 114.0 (3) | N2—C11—H11B | 109.4 |
| O4—Ba1—O1WC | 71.0 (3) | H11A—C11—H11B | 108.0 |
| O5—Ba1—O1WC | 64.8 (3) | C13—C12—O3 | 123.3 (4) |
| O2 ⁱ —Ba1—O1WC | 82.8 (3) | C13—C12—C11 | 124.2 (4) |
| O2—Ba1—O1WC | 108.7 (3) | O3—C12—C11 | 112.5 (4) |
| O5 ⁱⁱ —Ba1—O1WC | 91.4 (3) | O1—C13—C12 | 121.8 (4) |
| O1—Co1—O4 | 76.70 (11) | O1—C13—C14 | 119.4 (4) |
| O1—Co1—N1 | 122.08 (13) | C12—C13—C14 | 118.7 (4) |
| O4—Co1—N1 | 100.96 (12) | O2—C14—C15 | 123.7 (4) |
| O1—Co1—N3 | 100.86 (13) | O2—C14—C13 | 121.5 (4) |
| O4—Co1—N3 | 124.07 (13) | C15—C14—C13 | 114.8 (4) |
| N1—Co1—N3 | 124.08 (13) | C16—C15—C14 | 121.8 (4) |
| O1—Co1—N4 | 153.71 (12) | C16—C15—H15 | 119.1 |
| O4—Co1—N4 | 82.53 (11) | C14—C15—H15 | 119.1 |
| N1—Co1—N4 | 77.40 (13) | C15—C16—O3 | 122.6 (4) |
| N3—Co1—N4 | 77.62 (12) | C15—C16—H16 | 118.7 |
| O1—Co1—N2 | 81.95 (12) | O3—C16—H16 | 118.7 |
| O4—Co1—N2 | 152.96 (12) | C18—C17—N4 | 113.1 (4) |
| N1—Co1—N2 | 76.58 (12) | C18—C17—H17A | 109.0 |

| | | | |
|--------------------------|-------------|----------------|------------|
| N3—Co1—N2 | 75.99 (13) | N4—C17—H17A | 109.0 |
| N4—Co1—N2 | 122.15 (12) | C18—C17—H17B | 109.0 |
| C13—O1—Co1 | 131.9 (2) | N4—C17—H17B | 109.0 |
| C13—O1—Ba1 | 114.1 (2) | H17A—C17—H17B | 107.8 |
| Co1—O1—Ba1 | 113.82 (11) | C19—C18—O6 | 123.0 (4) |
| C5—N1—C10 | 110.3 (4) | C19—C18—C17 | 124.1 (4) |
| C5—N1—C4 | 108.4 (3) | O6—C18—C17 | 112.9 (4) |
| C10—N1—C4 | 108.1 (4) | O4—C19—C18 | 122.3 (4) |
| C5—N1—Co1 | 110.6 (3) | O4—C19—C20 | 118.9 (4) |
| C10—N1—Co1 | 107.3 (3) | C18—C19—C20 | 118.7 (4) |
| C4—N1—Co1 | 112.1 (3) | O5—C20—C21 | 124.2 (4) |
| C2—C1—N3 | 112.0 (4) | O5—C20—C19 | 121.3 (4) |
| C2—C1—H1A | 109.2 | C21—C20—C19 | 114.5 (4) |
| N3—C1—H1A | 109.2 | C22—C21—C20 | 122.0 (4) |
| C2—C1—H1B | 109.2 | C22—C21—H21 | 119.0 |
| N3—C1—H1B | 109.2 | C20—C21—H21 | 119.0 |
| H1A—C1—H1B | 107.9 | C21—C22—O6 | 123.1 (4) |
| C14—O2—Ba1 ⁱ | 124.5 (3) | C21—C22—H22 | 118.4 |
| C14—O2—Ba1 | 111.2 (2) | O6—C22—H22 | 118.4 |
| Ba1 ⁱ —O2—Ba1 | 118.33 (10) | O12A—C11A—O13A | 89.8 (18) |
| C3—N2—C2 | 111.1 (4) | O12A—C11A—O14A | 109.8 (13) |
| C3—N2—C11 | 108.9 (4) | O13A—C11A—O14A | 118.6 (14) |
| C2—N2—C11 | 109.8 (3) | O12A—C11A—O11A | 99.6 (12) |
| C3—N2—Co1 | 105.2 (3) | O13A—C11A—O11A | 109.7 (13) |
| C2—N2—Co1 | 108.4 (3) | O14A—C11A—O11A | 122.2 (15) |
| C11—N2—Co1 | 113.5 (3) | O12A—C11A—Ba1 | 52.5 (8) |
| N2—C2—C1 | 111.4 (4) | O13A—C11A—Ba1 | 121.1 (11) |
| N2—C2—H2A | 109.3 | O14A—C11A—Ba1 | 116.5 (12) |
| C1—C2—H2A | 109.3 | O11A—C11A—Ba1 | 51.0 (8) |
| N2—C2—H2B | 109.3 | C11A—O11A—Ba1 | 103.3 (10) |
| C1—C2—H2B | 109.3 | C11A—O12A—Ba1 | 106.3 (10) |
| H2A—C2—H2B | 108.0 | O11B—C11B—O14B | 101.1 (12) |
| C16—O3—C12 | 118.6 (3) | O11B—C11B—O13B | 108.6 (9) |
| C9—N3—C8 | 108.0 (4) | O14B—C11B—O13B | 101.2 (12) |
| C9—N3—C1 | 111.1 (4) | O11B—C11B—O12B | 111.0 (10) |
| C8—N3—C1 | 106.7 (4) | O14B—C11B—O12B | 111.2 (9) |
| C9—N3—Co1 | 109.7 (3) | O13B—C11B—O12B | 121.5 (12) |
| C8—N3—Co1 | 110.5 (2) | O11B—C11B—Ba1 | 61.1 (7) |
| C1—N3—Co1 | 110.8 (3) | O14B—C11B—Ba1 | 124.5 (8) |
| N2—C3—C4 | 109.5 (4) | O13B—C11B—Ba1 | 134.0 (9) |
| N2—C3—H3A | 109.8 | O12B—C11B—Ba1 | 50.2 (5) |
| C4—C3—H3A | 109.8 | C11B—O11B—Ba1 | 97.0 (7) |
| N2—C3—H3B | 109.8 | C11B—O12B—Ba1 | 106.3 (6) |
| C4—C3—H3B | 109.8 | O22A—C12A—O21A | 104.2 (9) |
| H3A—C3—H3B | 108.2 | O22A—C12A—O23A | 108.7 (6) |
| C19—O4—Co1 | 132.0 (2) | O21A—C12A—O23A | 108.1 (7) |
| C19—O4—Ba1 | 115.2 (2) | O22A—C12A—O24A | 111.8 (8) |
| Co1—O4—Ba1 | 112.64 (11) | O21A—C12A—O24A | 109.6 (6) |

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| C17—N4—C7 | 107.8 (3) | O23A—C12A—O24A | 113.9 (9) |
| C17—N4—C6 | 110.0 (3) | O24B—C12B—O23B | 90 (3) |
| C7—N4—C6 | 109.9 (3) | O24B—C12B—O21B | 116 (3) |
| C17—N4—Co1 | 114.3 (3) | O23B—C12B—O21B | 104 (3) |
| C7—N4—Co1 | 105.7 (3) | O24B—C12B—O22B | 85 (3) |
| C6—N4—Co1 | 108.8 (3) | O23B—C12B—O22B | 120 (3) |
| N1—C4—C3 | 110.4 (4) | O21B—C12B—O22B | 131 (3) |

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y, -z$.