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Pentaaquatri-μ_3-hydroxido-tris(iminodiacetato)-μ_3-oxido-*tetrahedro*-calcium(II)tricobalt(III) 2.54-hydrate

Tomoharu Ama,* Toshiaki Yonemura, Shogo Morita and Masanori Yamaguchi

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan
Correspondence e-mail: tomama@cc.kochi-u.ac.jp

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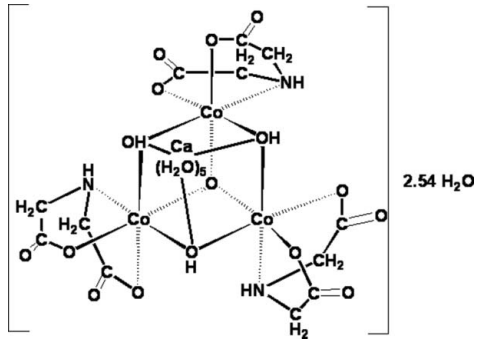
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.012 Å; disorder in solvent or counterion; R factor = 0.060; wR factor = 0.207; data-to-parameter ratio = 16.3.

In the title compound, $[CaCo_3(C_4H_5NO_4)_3(OH)_3O(H_2O)_5]\cdot 2.54H_2O$, the Co atom is octahedrally coordinated by one iminodiacetate (ida) dianion as a facial *O*,*N*,*O*′-tridentate ligand, two μ_3-OH groups and one μ_3-O ligand, forming an partial Co_3O_4 cubane cluster. This unit coordinates to a Ca^{II} cation in an *O*,*O*′,*O*″-tridentate fashion, generating a distorted $CaCo_3O_4$ cubane-type cluster. The Ca—μ_3-O distances [2.429 (5)–2.572 (6) Å] are much longer than the Co—μ_3—O bonds [1.895 (5)–1.941 (5) Å]. The Ca^{II} cation is also coordinated by five water molecules with Ca—O distances in the range 2.355 (6)–2.543 (6) Å. There are three additional uncoordinated water molecules in the asymmetric unit, the occupancy of which refined to 0.54 (3). In H_2O (or D_2O), the title complex hydrolyses to Ca^{2+}_{aq} cations and $[Co_3(ida)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^{2-}$ anions.

Related literature

For the synthesis and chemistry of partial Co_3O_4 cubane clusters, see: Ama *et al.* (1997, 2000, 2001, 2006). For the chemistry and structure of $CaMn_4O_4$ clusters in the OEC (oxygen evolution center) of plants, see: Barber & Murray (2008); Rappaport & Diner (2008); Sauer *et al.* (2008); Yocum (2008). For a related structure, see: Ama *et al.* (1995).



Experimental

Crystal data

$[CaCo_3(C_4H_5NO_4)_3(OH)_3O(H_2O)_5]\cdot 2.54H_2O$
M_r = 812.92
Triclinic, $P\overline{1}$
a = 10.474 (3) Å
b = 11.303 (7) Å
c = 12.588 (5) Å
α = 75.88 (4)°
β = 100.92 (3)°
γ = 104.58 (3)°
V = 1385.6 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.06 mm^{-1}
T = 296 K
0.40 × 0.40 × 0.05 mm

Data collection

Rigaku AFC-7S diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.673, T_{max} = 0.902
6713 measured reflections
6360 independent reflections
3290 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.076
3 standard reflections every 150 reflections
intensity decay: 4.8%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.207
S = 1.00
6360 reflections
389 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.17 e Å^{-3}
$\Delta\rho_{min}$ = −1.13 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O1	1.877 (5)	Ca1—O2	2.572 (6)
Co1—O2	1.903 (5)	Ca1—O3	2.527 (6)
Co1—O4	1.941 (5)	Ca1—O4	2.429 (5)
Co2—O1	1.888 (4)	Ca1—O17	2.355 (6)
Co2—O2	1.907 (5)	Ca1—O18	2.411 (6)
Co2—O3	1.895 (5)	Ca1—O19	2.543 (6)
Co3—O1	1.866 (5)	Ca1—O20	2.406 (6)
Co3—O3	1.915 (5)	Ca1—O21	2.471 (8)
Co3—O4	1.921 (5)		

Data collection: *WinAFC* (Rigaku/MSC, 2000); cell refinement: *WinAFC*; data reduction: *CrystalStructure* (Rigaku/MSC, 2007); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2753).

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supporting information

Acta Cryst. (2010). E**66**, m483–m484 [doi:10.1107/S1600536810010998]

Pentaaquatri-μ_3-hydroxido-tris(iminodiacetato)-μ_3-oxido-*tetrahedro*-calcium(II)tricobalt(III) 2.54-hydrate

Tomoharu Ama, Toshiaki Yonemura, Shogo Morita and Masanori Yamaguchi

S1. Comment

We have previously reported on the structures of some $[Co_3(L)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^{n+}$ (L: tridentate ligand) complexes which form incomplete cubane Co_3O_4 clusters (Ama *et al.*, 1997, 2000,2001, 2006). While many such cationic $[Co_3(L)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^{n+}$ complexes are known, we could find no mention of an anionic complex in our survey of the literature. The title compound was formed during an attempt to prepare the anionic complex $[Co_3(ida)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^{2-}$.

Investigations of the $CaMn_3O_4$ cluster are important to gain an understanding of the chemistry of O_2 evolution centers (OEC) in plants (Yocum, 2008; Sauer *et al.*, 2008; Barber & Murray, 2008; Rappaport & Diner, 2008). The Mn clusters in the OEC are of interest due to their unique structure, photoreaction mechanisms, and redox chemistry. Moreover, as the covalent radius of Co (1.33 Å) is similar to that of Mn (1.35 Å), we were interested in the preparation of the cobalt analogue, $CaCo_3O_4$, as a model of OEC.

In the title complex, each Co atom is coordinated by one ida (iminodiacetato) molecule which acts as a *facial* tridentate (*O,N,O′*) ligand, two μ_2-OH groups and one μ_3-O ligand, forming a Co_3O_4 cluster. This cluster further coordinates to Ca^{II} in a tridentate manner generating a distorted $CaCo_3O_4$ cubane-type cluster. The μ_2-O—Co distances are 1.895 (5) - 1.941 (5)Å and the Co—μ_2-O—Co′ angles are 94.5 (2) – 95.8 (2)°. In the T1 isomer (Ama *et al.*, 1995) of $[Co_3(edma)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^+$ (edma: ethylenediaminemonoacetato), the corresponding distances and angles are 1.899 (3) -1.923 (2)Å and 95.0 (1) - 96.2 (1)°. Hence the structure of the Co_3O_4 cluster in the title compound resembles that of $[Co_3(edma)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]^+$ cation. As the Ca^{2+} cation is coordinated by the three μ_3-OH ligands of the Co_3O_4 cluster, the $CaCo_3O_4$ cluster can be considered to be a distorted cubane cluster. The Ca—μ_3-O distances (2.429 (5) – 2.572 (6) Å) are much longer than Co—μ_3-O (1.895 (5) - 1.921 (5) Å). The μ_3-O—Ca—μ_3-O′ angles (59.84 (16) - 63.09 (16)) are smaller than those involving cobalt, μ_3-O—Co—μ_3-O′ (84.0 (2) - 85.6 (2)°) and Co—μ_3-O—Co′ (94.5 (2) - 95.8 (2)) in the Co_3O_4 cluster. There are three additional uncoordinated water molecules in the asymmetric unit, the occupancy of one of these solvates that has the largest U_{eq} value refines to 0.54 (3).

S2. Experimental

To a suspension of 7.0 g of $KHCO_3$ in 10 cm^3 of water, a solution 2.38 g of cobalt(II) chloride hexahydrate and 4 cm^3 of 30% H_2O_2 in 10 cm^3 of water was added dropwise with stirring at below 0° C. After the solution was stirred for 15 min, 10 cm^3 of H_2O containing 1.3 g of H_2ida was added and then stirred overnight. The solution was acidified to pH 1.0 with 30% $HClO_4$, stirred for 30 min, pH adjusted to 8.3 with 2 mol dm^{-3} KOH aqueous solution and then stirred for 2.5 h at 45°C. Filtering off the insoluble white-brown precipitate, the filtrate was loaded onto a QAE-Sephadex column (Cl^- form). The adsorbed band was developed with 0.2 mol dm^{-3} KCl Solution. The eluate from the fifth brown band was collected and concentrated to a small volume and then methanol was added to deposit KCl. After removing the KCl by filtration, potassium salt ($K_2[Co_3(ida)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]$ 3.25 H_2O) was obtained by standing the filtrate in a refrigerator.

Yield: 76 mg. (Anal. Found: C, 18.45; H, 3.21; N, 5.34%. Calcd for $C_{12}H_{24.5}N_3O_{19.25}K_2Co_3$ ($K_2[Co_3(ida)_3(\mu_2\text{-}OH)(\mu_3\text{-}O)]$ 3.25 H_2O): C, 18.62; H, 3.19; N, 5.43%. This potassium salt was dissolved in a small amount of water, which was loaded to a QAE-Sephadex column (Cl^- form; ø 6.5 cm × 3.5 cm) and then eluted with 500 cm^3 of water to remove the K^+ ion in the solution. The adsorbed brown band was eluted out with 0.5 mol dm^{-3} of $CaCl_2$. The eluted solution was concentrated to a few cm^3 and then ethanol and diethylether were added. As the solution was separated into a brown and an uncolored layers, the colorless layer was removed by decantation. After these procedures were repeated several times, a large amount of ethanol was added and the solution allowed to stand overnight at room temperature. The resulting brown precipitate was collected and washed with ethanol. This crude solid was recrystallized from water by adding ethanol. Anal. Found: C, 17.84; H, 4.04; N, 5.11%. Calcd for $C_{12}H_{33.08}N_3O_{23.54}CaCo_3$ ($[Ca(H_2O)_5Co_3(ida)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]$ 2.54 H_2O): C, 17.73; H, 4.09; N, 5.17%. ^1H NMR: (δ=4.22 and 3.24ppm; J_{gem}=17.6 Hz) and (δ=4.03 and 3.24ppm; J_{gem}=17.2 Hz).

S3. Refinement

All H atoms of the fragment containing $CaCo_3O_4$ cluster were positioned geometrically (C—H = 0.95 Å, N—H = 0.91 Å and O—H = 0.84 Å) and refined as riding, with U_{iso}(H)= 1.2 U_{eq} of the parent atom. The H atoms of the solvate water molecules were found in the difference Fourier synthesis, constrained to O—H = 0.84Å and then refined as riding.

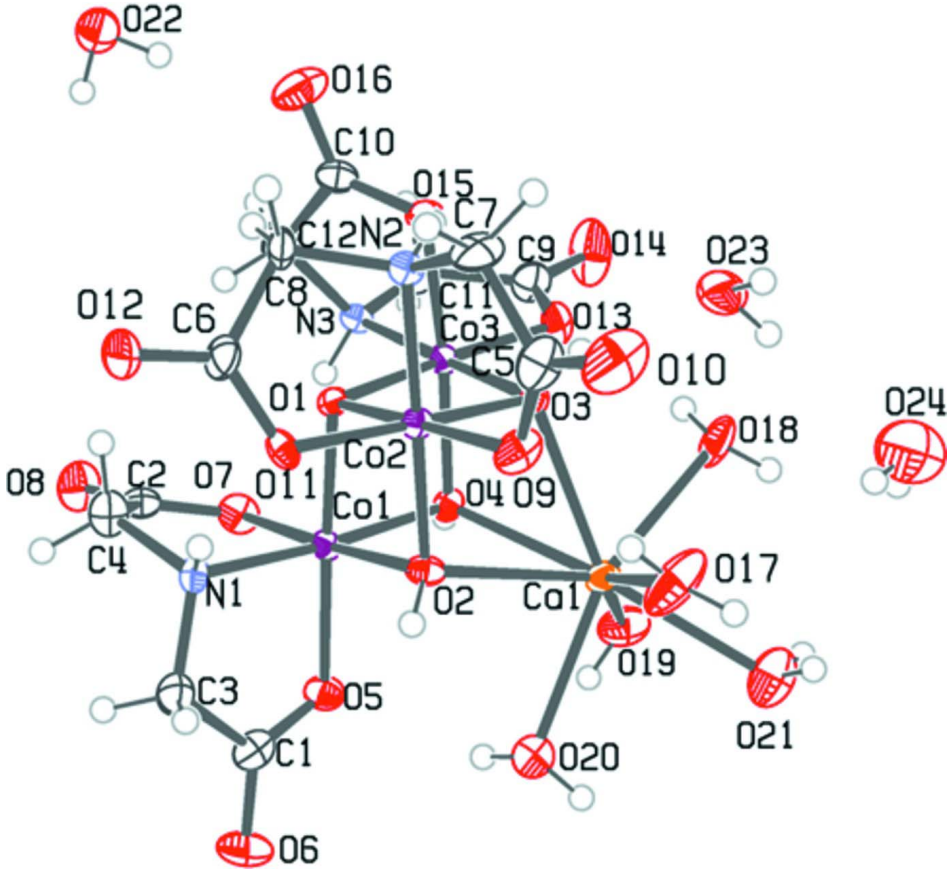

Figure 1

The asymmetric unit of the title compound showing the atom-labeling scheme and with 50% probability displacement ellipsoids.

Pentaaquatri-μ_3-hydroxido-tris(iminodiacetato)-μ_3-oxido- *tetrahedro*-calcium(II)tricobalt(III) 2.54-hydrate

Crystal data

$[CaCo_3(C_4H_5NO_4)_3(OH)_3O(H_2O)_5]\cdot 2.54H_2O$
$M_r = 812.92$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 10.474$ (3) Å
$b = 11.303$ (7) Å
$c = 12.588$ (5) Å
$\alpha = 75.88$ (4)°
$\beta = 100.92$ (3)°
$\gamma = 104.58$ (3)°
$V = 1385.6$ (10) Å^3
$Z = 2$
$F(000) = 830.80$
$D_x = 1.948$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 12 reflections
$\theta = 15.1$–15.8°
$\mu = 2.06$ mm^{-1}
$T = 296$ K
Plate, brown
0.40 × 0.40 × 0.05 mm

Data collection

Rigaku AFC-7S diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.673$, $T_{max} = 0.902$
6713 measured reflections
6360 independent reflections
3290 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.076$
$\theta_{max} = 27.5$°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 150 reflections
intensity decay: 4.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.207$
$S = 1.00$
6360 reflections
389 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.0001$
$\Delta\rho_{max} = 1.17$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-3}

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (wR) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co(1)	0.71696 (10)	0.72533 (9)	0.93041 (8)	0.0137 (2)	
Co(2)	0.73172 (10)	0.93813 (9)	0.75658 (8)	0.0141 (2)	
Co(3)	0.51954 (10)	0.72856 (9)	0.74180 (8)	0.0140 (2)	
Ca(1)	0.81420 (15)	0.67221 (15)	0.69882 (13)	0.0190 (3)	
O(1)	0.6046 (4)	0.8286 (4)	0.8436 (4)	0.0141 (10)	
O(2)	0.8387 (5)	0.8207 (4)	0.8306 (4)	0.0176 (11)	
O(3)	0.6625 (5)	0.8240 (4)	0.6610 (4)	0.0154 (10)	
O(4)	0.6435 (5)	0.6261 (4)	0.8183 (4)	0.0160 (10)	
O(5)	0.8438 (5)	0.6279 (5)	1.0143 (4)	0.0224 (12)	
O(6)	1.0147 (6)	0.6325 (6)	1.1499 (5)	0.0377 (16)	
O(7)	0.5867 (5)	0.6299 (5)	1.0215 (4)	0.0227 (12)	

O(8)	0.4950 (6)	0.6300 (6)	1.1655 (5)	0.0327 (14)	
O(9)	0.8615 (5)	1.0388 (5)	0.6638 (4)	0.0256 (12)	
O(10)	0.8934 (7)	1.2014 (6)	0.5255 (6)	0.052 (2)	
O(11)	0.7888 (5)	1.0409 (4)	0.8634 (4)	0.0176 (11)	
O(12)	0.7064 (8)	1.1589 (7)	0.9394 (5)	0.051 (2)	
O(13)	0.4431 (5)	0.6281 (5)	0.6339 (4)	0.0228 (12)	
O(14)	0.2633 (7)	0.4911 (7)	0.5851 (6)	0.051 (2)	
O(15)	0.4032 (5)	0.8393 (5)	0.6783 (4)	0.0203 (11)	
O(16)	0.2518 (6)	0.9176 (6)	0.7259 (5)	0.0399 (16)	
O(17)	0.9506 (7)	0.8551 (6)	0.6103 (6)	0.050 (2)	
O(18)	0.6561 (6)	0.6337 (6)	0.5383 (5)	0.0358 (16)	
O(19)	0.7455 (5)	0.4350 (6)	0.7370 (5)	0.0348 (15)	
O(20)	0.9788 (6)	0.6105 (6)	0.8499 (5)	0.0313 (14)	
O(21)	0.9474 (6)	0.5947 (6)	0.5991 (5)	0.0395 (16)	
O(22)	0.0992 (5)	0.9178 (6)	0.8899 (5)	0.0315 (14)	
O(23)	0.6372 (6)	0.8910 (6)	0.4401 (5)	0.0411 (17)	
O(24)	0.8213 (16)	0.7798 (16)	0.3566 (14)	0.068 (4)	0.54 (3)
N(1)	0.7746 (6)	0.8266 (5)	1.0404 (5)	0.0168 (12)	
N(2)	0.6218 (5)	1.0576 (5)	0.6830 (5)	0.0149 (12)	
N(3)	0.3720 (6)	0.6372 (5)	0.8218 (5)	0.0167 (12)	
C(1)	0.9207 (8)	0.6772 (7)	1.0912 (6)	0.0236 (17)	
C(2)	0.5724 (7)	0.6812 (7)	1.0984 (6)	0.0195 (15)	
C(3)	0.8963 (8)	0.7956 (8)	1.1112 (7)	0.0279 (18)	
C(4)	0.6595 (8)	0.8098 (7)	1.0997 (7)	0.0251 (17)	
C(5)	0.8276 (9)	1.1327 (8)	0.5968 (7)	0.0300 (19)	
C(6)	0.7038 (9)	1.1044 (7)	0.8667 (6)	0.0253 (17)	
C(7)	0.6939 (9)	1.1555 (8)	0.6011 (7)	0.031 (2)	
C(8)	0.5893 (8)	1.1025 (7)	0.7744 (6)	0.0213 (16)	
C(9)	0.3283 (8)	0.5566 (8)	0.6488 (7)	0.0266 (18)	
C(10)	0.3213 (7)	0.8398 (7)	0.7426 (6)	0.0217 (16)	
C(11)	0.2752 (8)	0.5578 (7)	0.7508 (7)	0.0246 (17)	
C(12)	0.3138 (8)	0.7343 (7)	0.8439 (6)	0.0237 (17)	
H(1)	0.7947	0.9079	1.0048	0.020*	
H(2)	0.5452	1.0172	0.6476	0.018*	
H(3)	0.4015	0.5889	0.8864	0.020*	
H(4)	0.8859	0.7841	1.1867	0.033*	
H(5)	0.9702	0.8623	1.0944	0.033*	
H(6)	0.6091	0.8711	1.0637	0.030*	
H(7)	0.6904	0.8183	1.1738	0.030*	
H(8)	0.7057	1.2340	0.6207	0.037*	
H(9)	0.6423	1.1567	0.5303	0.037*	
H(10)	0.5117	1.0479	0.8014	0.026*	
H(11)	0.5732	1.1844	0.7478	0.026*	
H(12)	0.1962	0.5897	0.7294	0.030*	
H(13)	0.2551	0.4749	0.7923	0.030*	
H(14)	0.3632	0.7642	0.9071	0.028*	
H(15)	0.2237	0.7009	0.8558	0.028*	
H(16)	0.9166	0.8498	0.8586	0.021*	

H(17)	0.6408	0.8554	0.5940	0.018*	
H(18)	0.6107	0.5500	0.8413	0.019*	
H(19)	0.9347	0.9179	0.6258	0.060*	
H(20)	1.0115	0.8682	0.5710	0.060*	
H(21)	0.6803	0.5862	0.5078	0.043*	
H(22)	0.5806	0.5997	0.5577	0.043*	
H(23)	0.7839	0.4056	0.7991	0.042*	
H(24)	0.6626	0.4130	0.7365	0.042*	
H(25)	0.9410	0.5690	0.9048	0.038*	
H(26)	1.0209	0.5666	0.8310	0.038*	
H(27)	0.8977	0.5387	0.5677	0.047*	
H(28)	0.9823	0.6540	0.5514	0.047*	
H(29)	0.1383	0.8707	0.9402	0.038*	
H(30)	0.1340	0.8916	0.8478	0.038*	
H(31)	0.6683	0.8379	0.4229	0.049*	
H(32)	0.6765	0.9500	0.3952	0.049*	
H(33)	0.8162	0.7109	0.3878	0.079*	0.54
H(34)	0.8708	0.8215	0.3978	0.079*	0.54

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co(1)	0.0127 (4)	0.0144 (5)	0.0121 (4)	0.0010 (3)	0.0026 (3)	−0.0006 (3)
Co(2)	0.0116 (4)	0.0139 (5)	0.0152 (4)	0.0011 (3)	0.0034 (3)	−0.0007 (3)
Co(3)	0.0110 (4)	0.0161 (5)	0.0135 (4)	0.0006 (3)	0.0026 (3)	−0.0024 (3)
Ca(1)	0.0147 (7)	0.0214 (8)	0.0208 (7)	0.0042 (6)	0.0039 (6)	−0.0027 (6)
O(1)	0.012 (2)	0.014 (2)	0.018 (2)	0.003 (2)	−0.0010 (19)	−0.008 (2)
O(2)	0.013 (2)	0.016 (2)	0.020 (2)	0.002 (2)	−0.000 (2)	−0.001 (2)
O(3)	0.018 (2)	0.015 (2)	0.013 (2)	0.003 (2)	0.004 (2)	−0.001 (2)
O(4)	0.018 (2)	0.012 (2)	0.018 (2)	0.004 (2)	0.005 (2)	−0.003 (2)
O(5)	0.025 (2)	0.018 (2)	0.023 (2)	0.008 (2)	0.001 (2)	−0.000 (2)
O(6)	0.032 (3)	0.039 (3)	0.038 (3)	0.019 (3)	−0.007 (2)	0.001 (3)
O(7)	0.020 (2)	0.018 (2)	0.024 (2)	−0.004 (2)	0.007 (2)	0.001 (2)
O(8)	0.029 (3)	0.034 (3)	0.032 (3)	−0.003 (2)	0.017 (2)	−0.002 (2)
O(9)	0.020 (2)	0.021 (2)	0.034 (3)	0.001 (2)	0.015 (2)	0.002 (2)
O(10)	0.058 (4)	0.040 (4)	0.057 (4)	0.018 (3)	0.039 (4)	0.025 (3)
O(11)	0.020 (2)	0.017 (2)	0.015 (2)	−0.000 (2)	−0.002 (2)	−0.009 (2)
O(12)	0.067 (5)	0.073 (5)	0.033 (3)	0.046 (4)	−0.014 (3)	−0.033 (3)
O(13)	0.015 (2)	0.031 (3)	0.019 (2)	−0.007 (2)	0.009 (2)	−0.006 (2)
O(14)	0.035 (3)	0.069 (5)	0.052 (4)	−0.022 (3)	0.012 (3)	−0.045 (4)
O(15)	0.016 (2)	0.023 (2)	0.021 (2)	0.007 (2)	0.002 (2)	−0.001 (2)
O(16)	0.034 (3)	0.038 (3)	0.050 (4)	0.019 (3)	0.020 (3)	0.008 (3)
O(17)	0.041 (4)	0.034 (3)	0.083 (5)	0.003 (3)	0.043 (4)	−0.005 (3)
O(18)	0.028 (3)	0.048 (4)	0.045 (3)	0.006 (3)	0.010 (2)	−0.033 (3)
O(19)	0.020 (3)	0.033 (3)	0.047 (3)	0.002 (2)	0.006 (2)	−0.002 (3)
O(20)	0.030 (3)	0.036 (3)	0.030 (3)	0.009 (2)	0.004 (2)	−0.009 (2)
O(21)	0.040 (3)	0.029 (3)	0.051 (4)	−0.003 (2)	0.025 (3)	−0.007 (3)
O(22)	0.020 (2)	0.039 (3)	0.037 (3)	0.002 (2)	0.002 (2)	−0.016 (2)

O(23)	0.039 (3)	0.053 (4)	0.029 (3)	0.020 (3)	0.009 (3)	0.010 (3)
O(24)	0.063 (10)	0.071 (11)	0.066 (10)	0.016 (9)	0.003 (8)	−0.009 (9)
N(1)	0.021 (3)	0.015 (3)	0.015 (3)	0.003 (2)	0.006 (2)	−0.004 (2)
N(2)	0.013 (2)	0.013 (2)	0.017 (3)	−0.001 (2)	0.003 (2)	−0.001 (2)
N(3)	0.015 (3)	0.017 (3)	0.016 (3)	0.004 (2)	−0.000 (2)	−0.001 (2)
C(1)	0.023 (4)	0.018 (4)	0.029 (4)	0.004 (3)	0.010 (3)	0.001 (3)
C(2)	0.015 (3)	0.019 (3)	0.023 (3)	0.003 (2)	0.001 (3)	−0.002 (3)
C(3)	0.026 (4)	0.034 (4)	0.028 (4)	0.008 (3)	0.002 (3)	−0.014 (3)
C(4)	0.024 (4)	0.022 (4)	0.027 (4)	−0.004 (3)	0.009 (3)	−0.006 (3)
C(5)	0.028 (4)	0.025 (4)	0.037 (5)	−0.002 (3)	0.014 (3)	−0.008 (3)
C(6)	0.038 (4)	0.021 (4)	0.023 (4)	0.014 (3)	0.005 (3)	−0.008 (3)
C(7)	0.036 (4)	0.023 (4)	0.034 (4)	0.018 (3)	0.012 (4)	0.013 (3)
C(8)	0.029 (4)	0.025 (4)	0.015 (3)	0.010 (3)	0.005 (3)	−0.007 (3)
C(9)	0.019 (3)	0.029 (4)	0.031 (4)	−0.000 (3)	0.005 (3)	−0.009 (3)
C(10)	0.016 (3)	0.021 (4)	0.025 (4)	0.003 (3)	−0.001 (3)	−0.003 (3)
C(11)	0.019 (3)	0.023 (4)	0.035 (4)	−0.005 (3)	0.009 (3)	−0.016 (3)
C(12)	0.022 (4)	0.022 (4)	0.027 (4)	0.004 (3)	0.011 (3)	0.000 (3)

Geometric parameters (Å, º)

Co(1)—O(1)	1.877 (5)	N(3)—C(11)	1.491 (10)
Co(1)—O(2)	1.903 (5)	N(3)—C(12)	1.484 (12)
Co(1)—O(4)	1.941 (5)	C(1)—C(3)	1.511 (14)
Co(1)—O(5)	1.932 (5)	C(2)—C(4)	1.511 (10)
Co(1)—O(7)	1.894 (5)	C(5)—C(7)	1.499 (14)
Co(1)—N(1)	1.923 (6)	C(6)—C(8)	1.503 (11)
Co(2)—O(1)	1.888 (4)	C(9)—C(11)	1.498 (14)
Co(2)—O(2)	1.907 (5)	C(10)—C(12)	1.518 (10)
Co(2)—O(3)	1.895 (5)	O(2)—H(16)	0.842
Co(2)—O(9)	1.918 (5)	O(3)—H(17)	0.843
Co(2)—O(11)	1.904 (5)	O(4)—H(18)	0.842
Co(2)—N(2)	1.943 (6)	O(17)—H(19)	0.841
Co(3)—Ca(1)	3.466 (2)	O(17)—H(20)	0.844
Co(3)—O(1)	1.866 (5)	O(18)—H(21)	0.840
Co(3)—O(3)	1.915 (5)	O(18)—H(22)	0.840
Co(3)—O(4)	1.921 (5)	O(19)—H(23)	0.840
Co(3)—O(13)	1.913 (6)	O(19)—H(24)	0.839
Co(3)—O(15)	1.897 (5)	O(20)—H(25)	0.840
Co(3)—N(3)	1.936 (6)	O(20)—H(26)	0.840
Ca(1)—O(2)	2.572 (6)	O(21)—H(27)	0.840
Ca(1)—O(3)	2.527 (6)	O(21)—H(28)	0.840
Ca(1)—O(4)	2.429 (5)	O(22)—H(29)	0.837
Ca(1)—O(17)	2.355 (6)	O(22)—H(30)	0.839
Ca(1)—O(18)	2.411 (6)	O(23)—H(31)	0.837
Ca(1)—O(19)	2.543 (6)	O(23)—H(32)	0.836
Ca(1)—O(20)	2.406 (6)	O(24)—H(33)	0.775
Ca(1)—O(21)	2.471 (8)	O(24)—H(34)	0.809
O(5)—C(1)	1.280 (9)	N(1)—H(1)	0.910

O(6)—C(1)	1.249 (10)	N(2)—H(2)	0.910
O(7)—C(2)	1.292 (11)	N(3)—H(3)	0.910
O(8)—C(2)	1.220 (10)	C(3)—H(4)	0.951
O(9)—C(5)	1.267 (10)	C(3)—H(5)	0.951
O(10)—C(5)	1.227 (11)	C(4)—H(6)	0.951
O(11)—C(6)	1.288 (12)	C(4)—H(7)	0.947
O(12)—C(6)	1.215 (13)	C(7)—H(8)	0.951
O(13)—C(9)	1.287 (9)	C(7)—H(9)	0.950
O(14)—C(9)	1.219 (12)	C(8)—H(10)	0.952
O(15)—C(10)	1.288 (11)	C(8)—H(11)	0.950
O(16)—C(10)	1.234 (12)	C(11)—H(12)	0.951
N(1)—C(3)	1.477 (10)	C(11)—H(13)	0.948
N(1)—C(4)	1.485 (12)	C(12)—H(14)	0.951
N(2)—C(7)	1.475 (10)	C(12)—H(15)	0.951
N(2)—C(8)	1.489 (12)		

O(1)—Co(1)—O(2)	83.4 (2)	Co(2)—O(11)—C(6)	113.5 (4)
O(1)—Co(1)—O(4)	82.8 (2)	Co(3)—O(13)—C(9)	115.3 (6)
O(1)—Co(1)—O(5)	175.6 (2)	Co(3)—O(15)—C(10)	113.6 (4)
O(1)—Co(1)—O(7)	93.8 (2)	Co(1)—N(1)—C(3)	110.3 (6)
O(1)—Co(1)—N(1)	93.2 (2)	Co(1)—N(1)—C(4)	107.1 (4)
O(2)—Co(1)—O(4)	85.6 (2)	C(3)—N(1)—C(4)	115.2 (6)
O(2)—Co(1)—O(5)	92.3 (2)	Co(2)—N(2)—C(7)	109.6 (5)
O(2)—Co(1)—O(7)	176.1 (2)	Co(2)—N(2)—C(8)	104.6 (4)
O(2)—Co(1)—N(1)	97.0 (2)	C(7)—N(2)—C(8)	115.1 (6)
O(4)—Co(1)—O(5)	97.9 (2)	Co(3)—N(3)—C(11)	108.5 (5)
O(4)—Co(1)—O(7)	91.4 (2)	Co(3)—N(3)—C(12)	105.2 (4)
O(4)—Co(1)—N(1)	175.0 (2)	C(11)—N(3)—C(12)	111.8 (6)
O(5)—Co(1)—O(7)	90.5 (2)	O(5)—C(1)—O(6)	123.4 (8)
O(5)—Co(1)—N(1)	86.3 (2)	O(5)—C(1)—C(3)	117.9 (7)
O(7)—Co(1)—N(1)	85.8 (2)	O(6)—C(1)—C(3)	118.7 (7)
O(1)—Co(2)—O(2)	82.9 (2)	O(7)—C(2)—O(8)	122.9 (7)
O(1)—Co(2)—O(3)	82.7 (2)	O(7)—C(2)—C(4)	114.9 (6)
O(1)—Co(2)—O(9)	175.7 (2)	O(8)—C(2)—C(4)	122.2 (8)
O(1)—Co(2)—O(11)	91.0 (2)	N(1)—C(3)—C(1)	110.2 (7)
O(1)—Co(2)—N(2)	96.5 (2)	N(1)—C(4)—C(2)	109.2 (7)
O(2)—Co(2)—O(3)	84.0 (2)	O(9)—C(5)—O(10)	124.4 (9)
O(2)—Co(2)—O(9)	94.7 (2)	O(9)—C(5)—C(7)	117.0 (7)
O(2)—Co(2)—O(11)	94.9 (2)	O(10)—C(5)—C(7)	118.4 (8)
O(2)—Co(2)—N(2)	179.2 (2)	O(11)—C(6)—O(12)	125.5 (8)
O(3)—Co(2)—O(9)	93.4 (2)	O(11)—C(6)—C(8)	115.3 (8)
O(3)—Co(2)—O(11)	173.8 (2)	O(12)—C(6)—C(8)	119.1 (9)
O(3)—Co(2)—N(2)	96.4 (2)	N(2)—C(7)—C(5)	111.7 (7)
O(9)—Co(2)—O(11)	92.8 (2)	N(2)—C(8)—C(6)	109.6 (7)
O(9)—Co(2)—N(2)	86.0 (2)	O(13)—C(9)—O(14)	123.7 (9)
O(11)—Co(2)—N(2)	84.6 (2)	O(13)—C(9)—C(11)	116.2 (7)
Ca(1)—Co(3)—O(1)	93.60 (17)	O(14)—C(9)—C(11)	120.2 (7)
Ca(1)—Co(3)—O(3)	45.55 (17)	O(15)—C(10)—O(16)	124.6 (7)

Ca(1)—Co(3)—O(4)	42.59 (16)	O(15)—C(10)—C(12)	114.8 (7)
Ca(1)—Co(3)—O(13)	82.93 (19)	O(16)—C(10)—C(12)	120.6 (8)
Ca(1)—Co(3)—O(15)	139.35 (16)	N(3)—C(11)—C(9)	112.4 (6)
Ca(1)—Co(3)—N(3)	136.5 (2)	N(3)—C(12)—C(10)	107.0 (7)
O(1)—Co(3)—O(3)	82.8 (2)	Co(1)—O(2)—H(16)	117.0
O(1)—Co(3)—O(4)	83.6 (2)	Co(2)—O(2)—H(16)	116.9
O(1)—Co(3)—O(13)	176.3 (2)	Ca(1)—O(2)—H(16)	117.0
O(1)—Co(3)—O(15)	90.4 (2)	Co(2)—O(3)—H(17)	116.3
O(1)—Co(3)—N(3)	96.7 (2)	Co(3)—O(3)—H(17)	116.2
O(3)—Co(3)—O(4)	85.1 (2)	Ca(1)—O(3)—H(17)	116.2
O(3)—Co(3)—O(13)	93.8 (2)	Co(1)—O(4)—H(18)	116.3
O(3)—Co(3)—O(15)	95.2 (2)	Co(3)—O(4)—H(18)	116.3
O(3)—Co(3)—N(3)	177.9 (2)	Ca(1)—O(4)—H(18)	116.4
O(4)—Co(3)—O(13)	94.6 (2)	Ca(1)—O(17)—H(19)	109.5
O(4)—Co(3)—O(15)	174.0 (2)	Ca(1)—O(17)—H(20)	133.3
O(4)—Co(3)—N(3)	96.9 (2)	H(19)—O(17)—H(20)	117.1
O(13)—Co(3)—O(15)	91.3 (2)	Ca(1)—O(18)—H(21)	109.5
O(13)—Co(3)—N(3)	86.8 (2)	Ca(1)—O(18)—H(22)	109.5
O(15)—Co(3)—N(3)	82.8 (2)	H(21)—O(18)—H(22)	109.4
Co(3)—Ca(1)—O(2)	64.34 (12)	Ca(1)—O(19)—H(23)	109.4
Co(3)—Ca(1)—O(3)	32.76 (10)	Ca(1)—O(19)—H(24)	109.4
Co(3)—Ca(1)—O(4)	32.37 (12)	H(23)—O(19)—H(24)	109.6
Co(3)—Ca(1)—O(17)	111.7 (2)	Ca(1)—O(20)—H(25)	109.5
Co(3)—Ca(1)—O(18)	74.12 (19)	Ca(1)—O(20)—H(26)	109.5
Co(3)—Ca(1)—O(19)	97.28 (16)	H(25)—O(20)—H(26)	109.5
Co(3)—Ca(1)—O(20)	121.95 (18)	Ca(1)—O(21)—H(27)	109.4
Co(3)—Ca(1)—O(21)	153.06 (16)	Ca(1)—O(21)—H(28)	109.4
O(2)—Ca(1)—O(3)	59.84 (16)	H(27)—O(21)—H(28)	109.5
O(2)—Ca(1)—O(4)	62.91 (17)	H(29)—O(22)—H(30)	84.2
O(2)—Ca(1)—O(17)	78.2 (2)	H(31)—O(23)—H(32)	93.0
O(2)—Ca(1)—O(18)	132.2 (2)	H(33)—O(24)—H(34)	105.7
O(2)—Ca(1)—O(19)	128.8 (2)	Co(1)—N(1)—H(1)	108.0
O(2)—Ca(1)—O(20)	75.0 (2)	C(3)—N(1)—H(1)	108.1
O(2)—Ca(1)—O(21)	141.50 (19)	C(4)—N(1)—H(1)	107.9
O(3)—Ca(1)—O(4)	63.09 (16)	Co(2)—N(2)—H(2)	109.1
O(3)—Ca(1)—O(17)	79.3 (2)	C(7)—N(2)—H(2)	109.1
O(3)—Ca(1)—O(18)	72.5 (2)	C(8)—N(2)—H(2)	109.2
O(3)—Ca(1)—O(19)	126.86 (18)	Co(3)—N(3)—H(3)	110.4
O(3)—Ca(1)—O(20)	134.5 (2)	C(11)—N(3)—H(3)	110.3
O(3)—Ca(1)—O(21)	139.57 (19)	C(12)—N(3)—H(3)	110.5
O(4)—Ca(1)—O(17)	135.4 (2)	N(1)—C(3)—H(4)	109.3
O(4)—Ca(1)—O(18)	93.7 (2)	N(1)—C(3)—H(5)	109.3
O(4)—Ca(1)—O(19)	76.6 (2)	C(1)—C(3)—H(4)	109.3
O(4)—Ca(1)—O(20)	92.9 (2)	C(1)—C(3)—H(5)	109.3
O(4)—Ca(1)—O(21)	148.6 (2)	H(4)—C(3)—H(5)	109.4
O(17)—Ca(1)—O(18)	97.1 (2)	N(1)—C(4)—H(6)	109.5
O(17)—Ca(1)—O(19)	148.0 (2)	N(1)—C(4)—H(7)	109.7
O(17)—Ca(1)—O(20)	97.6 (2)	C(2)—C(4)—H(6)	109.3

O(17)—Ca(1)—O(21)	76.0 (2)	C(2)—C(4)—H(7)	109.5
O(18)—Ca(1)—O(19)	77.4 (2)	H(6)—C(4)—H(7)	109.6
O(18)—Ca(1)—O(20)	151.5 (2)	N(2)—C(7)—H(8)	108.7
O(18)—Ca(1)—O(21)	79.4 (2)	N(2)—C(7)—H(9)	108.8
O(19)—Ca(1)—O(20)	77.2 (2)	C(5)—C(7)—H(8)	109.0
O(19)—Ca(1)—O(21)	72.0 (2)	C(5)—C(7)—H(9)	109.1
O(20)—Ca(1)—O(21)	80.6 (2)	H(8)—C(7)—H(9)	109.4
Co(1)—O(1)—Co(2)	97.1 (2)	N(2)—C(8)—H(10)	109.5
Co(1)—O(1)—Co(3)	98.6 (2)	N(2)—C(8)—H(11)	109.6
Co(2)—O(1)—Co(3)	97.7 (2)	C(6)—C(8)—H(10)	109.4
Co(1)—O(2)—Co(2)	95.6 (2)	C(6)—C(8)—H(11)	109.5
Co(1)—O(2)—Ca(1)	101.5 (2)	H(10)—C(8)—H(11)	109.3
Co(2)—O(2)—Ca(1)	105.8 (2)	N(3)—C(11)—H(12)	108.6
Co(2)—O(3)—Co(3)	95.8 (2)	N(3)—C(11)—H(13)	108.8
Co(2)—O(3)—Ca(1)	107.9 (2)	C(9)—C(11)—H(12)	108.7
Co(3)—O(3)—Ca(1)	101.7 (2)	C(9)—C(11)—H(13)	108.8
Co(1)—O(4)—Co(3)	94.5 (2)	H(12)—C(11)—H(13)	109.6
Co(1)—O(4)—Ca(1)	105.5 (2)	N(3)—C(12)—H(14)	110.2
Co(3)—O(4)—Ca(1)	105.0 (2)	N(3)—C(12)—H(15)	110.3
Co(1)—O(5)—C(1)	113.7 (5)	C(10)—C(12)—H(14)	110.0
Co(1)—O(7)—C(2)	115.1 (4)	C(10)—C(12)—H(15)	110.0
Co(2)—O(9)—C(5)	115.6 (6)	H(14)—C(12)—H(15)	109.4

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(2)—H(16)···O(22)^{i}	0.84	1.88	2.707 (7)	168
O(3)—H(17)···O(23)	0.84	1.88	2.677 (7)	159
O(4)—H(18)···O(8)^{ii}	0.84	2.07	2.870 (7)	158
O(17)—H(19)···O(9)	0.84	1.92	2.744 (11)	168
O(17)—H(20)···O(10)^{iii}	0.84	2.10	2.850 (13)	148
O(18)—H(21)···O(14)^{iv}	0.84	1.87	2.699 (12)	168
O(18)—H(22)···O(13)	0.84	2.00	2.708 (9)	141
O(19)—H(23)···O(6)^{v}	0.84	2.21	2.829 (9)	131
O(19)—H(24)···O(8)^{ii}	0.84	2.14	2.863 (9)	145
O(20)—H(25)···O(5)	0.84	2.17	2.787 (9)	130
O(20)—H(26)···O(6)^{v}	0.84	2.15	2.765 (10)	130
O(21)—H(27)···O(14)^{iv}	0.84	2.34	3.043 (9)	142
O(21)—H(28)···O(10)^{iii}	0.84	1.99	2.801 (9)	164
O(22)—H(29)···O(12)^{vi}	0.84	2.04	2.800 (9)	152
O(22)—H(30)···O(16)	0.84	2.07	2.840 (10)	153
O(23)—H(31)···O(18)	0.84	2.40	2.909 (10)	120
O(23)—H(31)···O(24)	0.84	2.24	3.01 (2)	153
O(23)—H(32)···O(16)^{vii}	0.84	1.97	2.802 (8)	172
O(24)—H(33)···O(14)^{iv}	0.78	2.19	2.912 (18)	156
O(24)—H(34)···O(10)^{iii}	0.81	2.53	3.054 (18)	124
N(1)—H(1)···O(11)	0.91	2.03	2.857 (7)	150
N(1)—H(1)···O(22)^{vi}	0.91	2.55	3.121 (9)	122

N(2)—H(2)···O(15)	0.91	2.18	2.917 (7)	138
N(2)—H(2)···O(23)^{vii}	0.91	2.36	2.977 (9)	125
N(3)—H(3)···O(7)	0.91	2.36	3.038 (7)	132
N(3)—H(3)···O(7)^{ii}	0.91	2.49	3.259 (8)	143

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+2, -y+2, -z+1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+2, -y+1, -z+2$; (vi) $-x+1, -y+2, -z+2$; (vii) $-x+1, -y+2, -z+1$.