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# Bis(*N*,*N*′-dimethylethylenediammonium) tris(oxalato-$\kappa^2O^1,O^2$)cobaltate(II) dihydrate: an ion-pair complex

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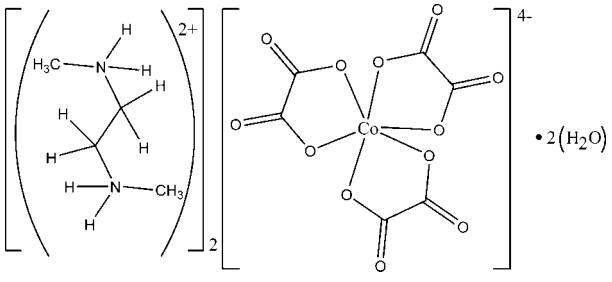
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.047; $wR$ factor = 0.133; data-to-parameter ratio = 17.7.

The $Co^{II}$ ion in the title complex, $(C_4H_{14}N_2)_2[Co(C_2O_4)_3]\cdot 2H_2O$, is coordinated by three oxalate ions, resulting in a distorted octahedral geometry. Two uncoordinated water molecules are present in asymmetric unit. Intermolecular N—H···O and O—H···O hydrogen bonds between the different entities stabilize the crystal structure.

## Related literature

For related structures: see Diallo *et al.* (2008); Gaye *et al.* (2011); Hao *et al.* (2010); Kelly *et al.* (2005); Zhang *et al.*, (2009).



## Experimental

### Crystal data

$(C_4H_{14}N_2)_2[Co(C_2O_4)_3]\cdot 2H_2O$
$M_r$ = 539.37
Monoclinic, $P2_1/c$
$a$ = 12.625 (3) Å
$b$ = 13.411 (4) Å
$c$ = 16.996 (2) Å
$\beta$ = 125.91 (2)°
$V$ = 2330.7 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.81 mm$^{-1}$
$T$ = 293 K
0.50 × 0.48 × 0.26 mm

### Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min}$ = 0.720, $T_{max}$ = 0.800
9121 measured reflections
5342 independent reflections
4178 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.133
$S$ = 1.05
5333 reflections
302 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.48 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N9—H9*N*1···O8 | 0.90 | 1.86 | 2.668 (3) | 148 |
| O14—H14*O*···O7 | 0.96 | 1.94 | 2.876 (4) | 163 |
| N7—H7*NB*···O1 | 0.90 | 1.90 | 2.769 (3) | 161 |
| O13—H13*W*···O10 | 0.96 | 1.91 | 2.755 (3) | 146 |
| N10—H10*M*···O11$^{i}$ | 0.90 | 1.94 | 2.814 (3) | 165 |
| N10—H10*N*···O9$^{ii}$ | 0.90 | 1.83 | 2.721 (3) | 173 |
| N9—H9*N*2···O13$^{iii}$ | 0.90 | 1.80 | 2.679 (3) | 163 |
| N8—H8*NA*···O6$^{iv}$ | 0.90 | 1.94 | 2.829 (3) | 170 |
| N8—H8*NB*···O7$^{v}$ | 0.90 | 2.07 | 2.916 (3) | 156 |
| N8—H8*NB*···O8$^{v}$ | 0.90 | 2.25 | 2.801 (3) | 119 |
| N7—H7*NA*···O12$^{vi}$ | 0.90 | 1.97 | 2.751 (3) | 144 |
| O13—H13*O*···O12$^{vii}$ | 0.95 | 1.75 | 2.698 (3) | 174 |

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

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *COLLECT*; data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *CRYSTALBUILDER* (Welter, 2006); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5577).

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# supporting information

*Acta Cryst.* (2011). E**67**, m1269 [doi:10.1107/S1600536811031357]

# Bis(*N*,*N*′-dimethylethylenediammonium) tris(oxalato-$\kappa^2O^1,O^2$)cobaltate(II) dihydrate: an ion-pair complex

**Papa Aly Gaye, Adama Sy, Ibrahima Elhadj Thiam, Mohamed Gaye and Pascal Retailleau**

## S1. Comment

The title salt, $(C_4H_{14}N_2)_2[Co(C_2O_4)_3](H_2O)_2$, was obtained as an unexpected product by reaction of the employed ligand $(C_6H_{10}N_2O_2)_n$, in a methanolic medium. The hydrolytically unstable cyclic ligand apparently is oxidatively hydrolyzed in the presence of metal ions, leading to the oxalate dianion (Diallo *et al.*, 2008; Kelly *et al.*, 2005). This species, which is generated *in situ*, acts with cobat(II) ions resulting in the formation of the title compound. A similar reaction was found elsewhere (Zhang *et al.*, 2009). Recently, we published the structure of an organic-inorganic hybrid salt involving the dimethylethylenediammonium cation, $[C_4H_{14}N_2]^{2+}$ and complex anion, $[Cu(C_2O_4)_2]^{2-}$ (Gaye *et al.*, 2011). A homologous salt, with $[Co(C_2O_4)_3]^{4-}$ as the anionic moiety is reported here. The Fig. 1 shows the dimethylethylenediammonium cation, $[C_4H_{24}N_2]^{2+}$, and the complex anion, $[Co(C_2O_4)_3]^{4-}$. The asymmetric unit contains two organic cations, one anion and two water molecules. The geometrical parameters of the $[C_4H_{24}N_2]^{+}$, cation are similar to those found in salt with the $[Cu(C_2O_4)_2]^{2-}$ cationic complex (Gaye *et al.*, 2011). The $Co^{II}$ ion of the complex anion adopts a distorted octahedral coordination involving four equatorial O atoms (O1, O2, O4, O5) two quasi axial O atoms (O3, O6) of oxalate ligands (Fig. 1). The equatorial Co–O distances are 2.1009 (17) Å (Co–O1), 2.0751 (18) Å (Co–O2), 2.0693 (17) (13) Å (Co–O4) and 2.0659 (17) Å (Co–O5) respectively, and are significantly longer than the axial Co–O distance of 2.1163 (19) Å (Co–O3), 2.1070 (17) Å (Co–O6). The bond distances in the complex anion are comparable with those reported for the $[Co^{III}(Hbiim)_3]_2[Co^{II}_3(ox)_3].4H_2O$ compound (Hao *et al.*, 2010), where Hbiim is 2,2′-biimidazole and ox is oxalate. Two lattice water molecules are also present in the asymmetric unit. In the crystal structure, intramolecular N–H···$O_{ox}$ hydrogen bonds connect the ionic entities. $O_{water}$–H···$O_{ox}$ hydrogen bonds are also observed (Table 2).

## S2. Experimental

In a 50 ml round bottom flask introduce Dimethyl oxalate (2.36 g, 0.020 mol) dissolved in ethanol (10 ml). *N*,*N*′-dimethyl-1,2-diaminoethane (1.77 g, 0.020 mol) in ethanol (10 ml), was added to yield immediately a quantitative precipitate. The white precipitate formed, was separated by filtration, washed with methanol and ether and dried under vacuum (Yield 3.32 g, 58.5%); m.p.=240 °C. $^1$H NMR in $CDCl_3$, $\delta$ (p.p.m.): 3.1, s, 12H, –CH3; 3.5, s, 8H, –$CH_2$. $^{13}$C NMR in $CDCl_3$, $\delta$ (p.p.m.): 34.86, N—$CH_3$, 46.12, N—$CH_2$, 157.56, C=O. IR (cm$^{-1}$) 1598 (C=O), 1284 (C—N). Anal. Calc. for $C_{12}H_{20}N_4O_4$ (%): C, 50.62; H, 7.11; N, 19.68. Found: C, 50.60; H, 7.09; N, 19.71. Mass spectrum (m/*z*) 284, 162, 134, 106, 78. Into a methanolic solution (5 ml) of cobalt chloride hexahydratee (0.2974 g, 1.25 mmol) was added a methanolic solution (10 ml) of the ligand prepared above (0.3554 g, 1.25 mmol). The resulting mixture is heated at 60°C for thirty minutes. The pink solution was filtered and then allowed to evaporate slowly in an open atmosphere. After two days, pink crystals suitable for X-ray analysis were obtained. The crystals were separated, washed with cold methanol and dried (yield: 83%); Anal. Calc. for $C_{14}H_{32}CoN_4O_{14}$(%): C, 31.18; H, 5.98; N, 10.39. Found: C, 31.16; H, 6.01; N, 10.37. Selected IR data (cm$^{-1}$, KBr pellet): 3335, 1635, 1601, 1580, 1193, 765.

### S3. Refinement

Nine reflections affected by the backstop or clearly outlier data were omitted from the refinement. All H atoms were refined using a riding model. The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å) with *U*ĩso~(H)= 1.5Ueq(C), but were allowed to rotate freely about the adjacent C—C bonds. The other H atoms were refined using a riding model, with C—H = 0.97 Å (resp N—H = 0.90 Å) and $U_{iso}$(H) = 1.2Ueq(C or N).

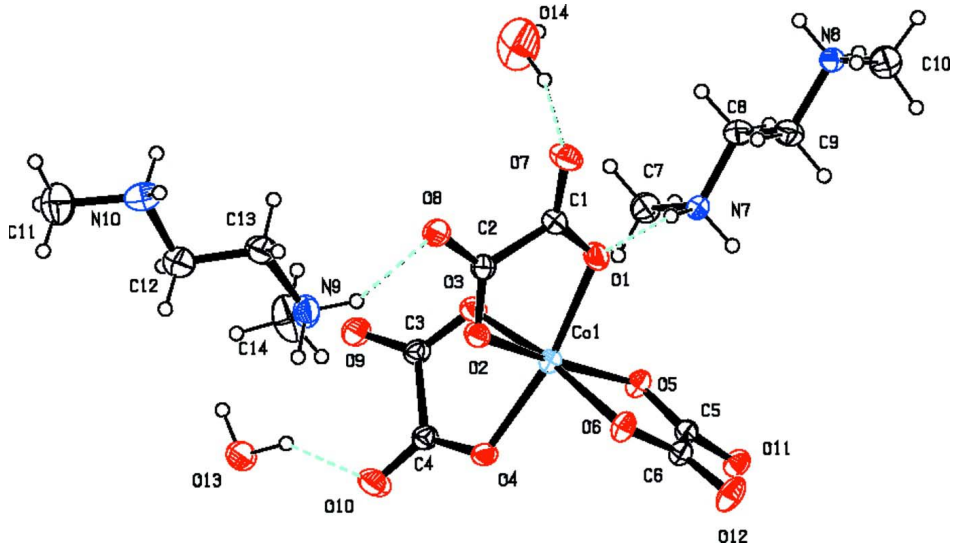


**Figure 1**

An *ORTEP* view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

**Bis(*N*,*N*′-dimethylethylenediammonium) tris(oxalato-$\kappa^2O^1,O^2$)cobaltate(II) dihydrate**

*Crystal data*

$(C_4H_{14}N_2)_2[Co(C_2O_4)_3]\cdot 2H_2O$
$M_r$ = 539.37
Monoclinic, $P2_1/c$
$a$ = 12.625 (3) Å
$b$ = 13.411 (4) Å
$c$ = 16.996 (2) Å
$\beta$ = 125.91 (2)°
$V$ = 2330.7 (11) Å$^3$
$Z$ = 4
$F(000)$ = 1132
$D_x$ = 1.537 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71070 Å
Cell parameters from 5427 reflections
$\theta$ = 0.4–27.5°
$\mu$ = 0.81 mm$^{-1}$
$T$ = 293 K
Cube, pink
0.50 × 0.48 × 0.26 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube, Nonius Kappa CCD
Graphite monochromator
Detector resolution: 9 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min}$ = 0.720, $T_{max}$ = 0.800
9121 measured reflections
5342 independent reflections
4178 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 3.4°
$h$ = −16→16
$k$ = −16→17
$l$ = −21→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.133$
$S = 1.05$
5333 reflections
302 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 2.554P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.48$ e Å$^{-3}$

*Special details*

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

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.19856 (3) | 0.25025 (2) | 0.04584 (2) | 0.02870 (12) |
| O1 | 0.1066 (2) | 0.28305 (14) | 0.11324 (14) | 0.0380 (4) |
| O2 | 0.1676 (2) | 0.40241 (14) | 0.02043 (14) | 0.0373 (4) |
| O3 | 0.38888 (19) | 0.27837 (17) | 0.17225 (13) | 0.0404 (5) |
| O4 | 0.30589 (18) | 0.24570 (14) | −0.01047 (13) | 0.0341 (4) |
| O5 | 0.19519 (17) | 0.09766 (13) | 0.06110 (12) | 0.0326 (4) |
| O6 | 0.02190 (17) | 0.21331 (13) | −0.08801 (13) | 0.0342 (4) |
| O7 | 0.0523 (2) | 0.41384 (16) | 0.16340 (16) | 0.0492 (5) |
| O8 | 0.1380 (2) | 0.53582 (14) | 0.08303 (15) | 0.0423 (5) |
| O9 | 0.5759 (2) | 0.33994 (19) | 0.20796 (14) | 0.0520 (6) |
| O10 | 0.4998 (2) | 0.2882 (2) | 0.02668 (16) | 0.0600 (7) |
| O11 | 0.09729 (19) | −0.03816 (13) | −0.02854 (13) | 0.0358 (4) |
| O12 | −0.0938 (2) | 0.07973 (15) | −0.17267 (13) | 0.0477 (5) |
| C1 | 0.0942 (3) | 0.3754 (2) | 0.12066 (18) | 0.0321 (5) |
| C2 | 0.1363 (3) | 0.44434 (19) | 0.06991 (18) | 0.0319 (5) |
| C3 | 0.4665 (3) | 0.3009 (2) | 0.15178 (18) | 0.0335 (6) |
| C4 | 0.4215 (3) | 0.2767 (2) | 0.04675 (18) | 0.0328 (5) |
| C5 | 0.1060 (2) | 0.05329 (18) | −0.01538 (16) | 0.0268 (5) |
| C6 | 0.0010 (2) | 0.12061 (18) | −0.09993 (17) | 0.0288 (5) |
| C11 | 0.4502 (4) | 0.9703 (3) | 0.1245 (3) | 0.0728 (11) |
| H11A | 0.5370 | 0.9437 | 0.1670 | 0.109* |
| H11B | 0.4438 | 1.0308 | 0.1516 | 0.109* |
| H11C | 0.4316 | 0.9839 | 0.0621 | 0.109* |
| N10 | 0.3537 (3) | 0.8959 (2) | 0.11339 (17) | 0.0477 (6) |
| H10N | 0.3732 | 0.8813 | 0.1722 | 0.057* |

| | | | | |
|---|---|---|---|---|
| H10M | 0.2729 | 0.9225 | 0.0771 | 0.057* |
| C12 | 0.3555 (4) | 0.8048 (3) | 0.0674 (3) | 0.0550 (8) |
| H12A | 0.4417 | 0.7746 | 0.1064 | 0.066* |
| H12B | 0.3337 | 0.8194 | 0.0035 | 0.066* |
| C13 | 0.2585 (3) | 0.7372 (3) | 0.0593 (2) | 0.0548 (9) |
| H13A | 0.1719 | 0.7653 | 0.0144 | 0.066* |
| H13B | 0.2744 | 0.7310 | 0.1222 | 0.066* |
| N9 | 0.2635 (3) | 0.6321 (2) | 0.02300 (19) | 0.0516 (7) |
| H9N1 | 0.2019 | 0.5941 | 0.0192 | 0.062* |
| H9N2 | 0.2412 | 0.6386 | −0.0377 | 0.062* |
| C14 | 0.3862 (4) | 0.5786 (4) | 0.0800 (3) | 0.0795 (13) |
| H14A | 0.4520 | 0.6153 | 0.0807 | 0.119* |
| H14B | 0.3757 | 0.5141 | 0.0518 | 0.119* |
| H14C | 0.4122 | 0.5709 | 0.1452 | 0.119* |
| O13 | 0.7540 (2) | 0.3562 (2) | 0.14165 (16) | 0.0632 (7) |
| H13O | 0.8069 | 0.3745 | 0.2082 | 0.095* |
| H13W | 0.6669 | 0.3440 | 0.1227 | 0.095* |
| O14 | 0.2551 (4) | 0.4143 (3) | 0.3690 (2) | 0.1119 (14) |
| H14O | 0.1813 | 0.4028 | 0.3031 | 0.168* |
| H14W | 0.2973 | 0.3604 | 0.4146 | 0.168* |
| N8 | −0.1051 (2) | 0.12399 (17) | 0.28323 (16) | 0.0366 (5) |
| H8NA | −0.0724 | 0.1751 | 0.3256 | 0.044* |
| H8NB | −0.0788 | 0.0667 | 0.3173 | 0.044* |
| N7 | 0.1385 (2) | 0.11853 (17) | 0.22373 (15) | 0.0323 (5) |
| H7NA | 0.1035 | 0.0668 | 0.1821 | 0.039* |
| H7NB | 0.1129 | 0.1752 | 0.1888 | 0.039* |
| C7 | 0.2830 (3) | 0.1114 (3) | 0.2847 (2) | 0.0470 (7) |
| H7A | 0.3200 | 0.1654 | 0.3304 | 0.070* |
| H7B | 0.3126 | 0.1149 | 0.2441 | 0.070* |
| H7C | 0.3098 | 0.0491 | 0.3191 | 0.070* |
| C8 | 0.0909 (3) | 0.1176 (2) | 0.2861 (2) | 0.0435 (7) |
| H8C | 0.1306 | 0.1720 | 0.3325 | 0.052* |
| H8D | 0.1152 | 0.0554 | 0.3218 | 0.052* |
| C9 | −0.0551 (3) | 0.1289 (2) | 0.2227 (2) | 0.0431 (7) |
| H9A | −0.0790 | 0.1923 | 0.1889 | 0.052* |
| H9B | −0.0944 | 0.0761 | 0.1745 | 0.052* |
| C10 | −0.2507 (3) | 0.1290 (3) | 0.2196 (2) | 0.0522 (8) |
| H10A | −0.2781 | 0.1938 | 0.1902 | 0.078* |
| H10B | −0.2828 | 0.1173 | 0.2579 | 0.078* |
| H10C | −0.2849 | 0.0792 | 0.1698 | 0.078* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.02854 (19) | 0.02694 (19) | 0.02907 (19) | −0.00288 (13) | 0.01603 (15) | −0.00256 (13) |
| O1 | 0.0469 (11) | 0.0303 (9) | 0.0484 (11) | −0.0013 (9) | 0.0343 (10) | 0.0026 (8) |
| O2 | 0.0533 (11) | 0.0260 (9) | 0.0479 (11) | −0.0014 (8) | 0.0383 (10) | −0.0007 (8) |
| O3 | 0.0336 (10) | 0.0596 (13) | 0.0273 (9) | −0.0106 (9) | 0.0175 (8) | −0.0065 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O4 | 0.0287 (9) | 0.0466 (11) | 0.0263 (9) | −0.0050 (8) | 0.0157 (7) | −0.0088 (7) |
| O5 | 0.0323 (9) | 0.0259 (9) | 0.0267 (8) | 0.0001 (7) | 0.0101 (7) | 0.0016 (7) |
| O6 | 0.0315 (9) | 0.0238 (9) | 0.0313 (9) | 0.0001 (7) | 0.0095 (8) | 0.0033 (7) |
| O7 | 0.0695 (15) | 0.0436 (12) | 0.0593 (13) | 0.0075 (11) | 0.0517 (12) | 0.0045 (10) |
| O8 | 0.0601 (13) | 0.0273 (10) | 0.0505 (12) | −0.0033 (9) | 0.0385 (11) | −0.0035 (8) |
| O9 | 0.0340 (11) | 0.0808 (17) | 0.0327 (10) | −0.0197 (11) | 0.0148 (9) | −0.0160 (10) |
| O10 | 0.0396 (12) | 0.107 (2) | 0.0396 (12) | −0.0170 (13) | 0.0268 (10) | −0.0131 (12) |
| O11 | 0.0424 (10) | 0.0249 (9) | 0.0337 (9) | 0.0000 (8) | 0.0188 (8) | 0.0001 (7) |
| O12 | 0.0432 (11) | 0.0347 (11) | 0.0292 (10) | −0.0058 (9) | 0.0010 (9) | −0.0006 (8) |
| C1 | 0.0327 (13) | 0.0331 (13) | 0.0326 (13) | 0.0011 (11) | 0.0203 (11) | 0.0018 (10) |
| C2 | 0.0355 (14) | 0.0286 (13) | 0.0332 (13) | −0.0005 (10) | 0.0210 (11) | 0.0006 (10) |
| C3 | 0.0303 (13) | 0.0386 (15) | 0.0258 (12) | −0.0009 (11) | 0.0133 (10) | −0.0023 (10) |
| C4 | 0.0292 (13) | 0.0390 (14) | 0.0273 (12) | −0.0012 (11) | 0.0150 (11) | −0.0022 (10) |
| C5 | 0.0282 (12) | 0.0255 (12) | 0.0252 (11) | 0.0004 (9) | 0.0147 (10) | 0.0018 (9) |
| C6 | 0.0293 (12) | 0.0262 (12) | 0.0254 (11) | −0.0004 (10) | 0.0128 (10) | 0.0013 (9) |
| C11 | 0.058 (2) | 0.071 (3) | 0.086 (3) | −0.004 (2) | 0.041 (2) | 0.003 (2) |
| N10 | 0.0509 (15) | 0.0483 (15) | 0.0315 (12) | 0.0179 (12) | 0.0171 (11) | 0.0057 (10) |
| C12 | 0.056 (2) | 0.061 (2) | 0.0536 (19) | −0.0043 (17) | 0.0353 (17) | −0.0044 (16) |
| C13 | 0.0442 (18) | 0.081 (3) | 0.0441 (17) | −0.0077 (16) | 0.0286 (15) | −0.0094 (16) |
| N9 | 0.0537 (16) | 0.0543 (16) | 0.0420 (14) | −0.0178 (13) | 0.0253 (13) | 0.0014 (12) |
| C14 | 0.059 (2) | 0.085 (3) | 0.088 (3) | 0.000 (2) | 0.040 (2) | 0.028 (2) |
| O13 | 0.0463 (13) | 0.104 (2) | 0.0393 (12) | −0.0317 (13) | 0.0251 (10) | −0.0199 (12) |
| O14 | 0.138 (3) | 0.080 (2) | 0.077 (2) | −0.014 (2) | 0.040 (2) | 0.0358 (18) |
| N8 | 0.0499 (14) | 0.0315 (11) | 0.0385 (12) | −0.0079 (10) | 0.0315 (11) | −0.0056 (9) |
| N7 | 0.0361 (11) | 0.0314 (11) | 0.0307 (10) | −0.0083 (9) | 0.0204 (9) | −0.0060 (9) |
| C7 | 0.0385 (15) | 0.059 (2) | 0.0353 (14) | −0.0051 (14) | 0.0171 (12) | 0.0006 (13) |
| C8 | 0.0480 (16) | 0.0519 (18) | 0.0325 (14) | −0.0062 (14) | 0.0248 (13) | −0.0056 (12) |
| C9 | 0.0486 (17) | 0.0490 (17) | 0.0361 (14) | 0.0001 (14) | 0.0273 (13) | 0.0006 (12) |
| C10 | 0.0488 (18) | 0.055 (2) | 0.0487 (18) | 0.0006 (15) | 0.0261 (15) | 0.0021 (15) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—O5 | 2.0663 (19) | C13—H13A | 0.9700 |
| Co1—O4 | 2.0680 (19) | C13—H13B | 0.9700 |
| Co1—O2 | 2.075 (2) | N9—C14 | 1.446 (5) |
| Co1—O1 | 2.1004 (19) | N9—H9N1 | 0.9000 |
| Co1—O6 | 2.1079 (19) | N9—H9N2 | 0.9000 |
| Co1—O3 | 2.116 (2) | C14—H14A | 0.9600 |
| O1—C1 | 1.264 (3) | C14—H14B | 0.9600 |
| O2—C2 | 1.253 (3) | C14—H14C | 0.9600 |
| O3—C3 | 1.254 (3) | O13—H13O | 0.9484 |
| O4—C4 | 1.259 (3) | O13—H13W | 0.9606 |
| O5—C5 | 1.263 (3) | O14—H14O | 0.9599 |
| O6—C6 | 1.262 (3) | O14—H14W | 0.9599 |
| O7—C1 | 1.235 (3) | N8—C9 | 1.490 (3) |
| O8—C2 | 1.245 (3) | N8—C10 | 1.490 (4) |
| O9—C3 | 1.243 (3) | N8—H8NA | 0.9000 |
| O10—C4 | 1.229 (3) | N8—H8NB | 0.9000 |

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|---|---|---|---|
| O11—C5 | 1.240 (3) | N7—C7 | 1.480 (4) |
| O12—C6 | 1.235 (3) | N7—C8 | 1.494 (3) |
| C1—C2 | 1.555 (3) | N7—H7NA | 0.9000 |
| C3—C4 | 1.557 (3) | N7—H7NB | 0.9000 |
| C5—C6 | 1.550 (3) | C7—H7A | 0.9600 |
| C11—N10 | 1.498 (5) | C7—H7B | 0.9600 |
| C11—H11A | 0.9600 | C7—H7C | 0.9600 |
| C11—H11B | 0.9600 | C8—C9 | 1.501 (4) |
| C11—H11C | 0.9600 | C8—H8C | 0.9700 |
| N10—C12 | 1.458 (4) | C8—H8D | 0.9700 |
| N10—H10N | 0.9000 | C9—H9A | 0.9700 |
| N10—H10M | 0.9000 | C9—H9B | 0.9700 |
| C12—C13 | 1.463 (5) | C10—H10A | 0.9600 |
| C12—H12A | 0.9700 | C10—H10B | 0.9600 |
| C12—H12B | 0.9700 | C10—H10C | 0.9600 |
| C13—N9 | 1.555 (5) | | |

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|---|---|---|---|
| O5—Co1—O4 | 95.52 (8) | C12—C13—N9 | 111.9 (3) |
| O5—Co1—O2 | 170.01 (8) | C12—C13—H13A | 109.2 |
| O4—Co1—O2 | 91.57 (7) | N9—C13—H13A | 109.2 |
| O5—Co1—O1 | 94.60 (7) | C12—C13—H13B | 109.2 |
| O4—Co1—O1 | 168.55 (7) | N9—C13—H13B | 109.2 |
| O2—Co1—O1 | 79.08 (7) | H13A—C13—H13B | 107.9 |
| O5—Co1—O6 | 79.40 (7) | C14—N9—C13 | 117.4 (3) |
| O4—Co1—O6 | 93.41 (8) | C14—N9—H9N1 | 107.9 |
| O2—Co1—O6 | 93.19 (8) | C13—N9—H9N1 | 107.9 |
| O1—Co1—O6 | 93.70 (8) | C14—N9—H9N2 | 107.9 |
| O5—Co1—O3 | 98.27 (8) | C13—N9—H9N2 | 107.9 |
| O4—Co1—O3 | 79.23 (7) | H9N1—N9—H9N2 | 107.2 |
| O2—Co1—O3 | 89.95 (9) | N9—C14—H14A | 109.5 |
| O1—Co1—O3 | 94.04 (8) | N9—C14—H14B | 109.5 |
| O6—Co1—O3 | 172.08 (8) | H14A—C14—H14B | 109.5 |
| C1—O1—Co1 | 113.60 (16) | N9—C14—H14C | 109.5 |
| C2—O2—Co1 | 113.38 (16) | H14A—C14—H14C | 109.5 |
| C3—O3—Co1 | 111.60 (16) | H14B—C14—H14C | 109.5 |
| C4—O4—Co1 | 114.24 (16) | H13O—O13—H13W | 108.1 |
| C5—O5—Co1 | 114.15 (15) | H14O—O14—H14W | 121.4 |
| C6—O6—Co1 | 113.20 (15) | C9—N8—C10 | 109.8 (2) |
| O7—C1—O1 | 126.1 (2) | C9—N8—H8NA | 109.7 |
| O7—C1—C2 | 118.8 (2) | C10—N8—H8NA | 109.7 |
| O1—C1—C2 | 115.1 (2) | C9—N8—H8NB | 109.7 |
| O8—C2—O2 | 125.7 (2) | C10—N8—H8NB | 109.7 |
| O8—C2—C1 | 117.5 (2) | H8NA—N8—H8NB | 108.2 |
| O2—C2—C1 | 116.8 (2) | C7—N7—C8 | 110.2 (2) |
| O9—C3—O3 | 125.8 (2) | C7—N7—H7NA | 109.6 |
| O9—C3—C4 | 117.5 (2) | C8—N7—H7NA | 109.6 |
| O3—C3—C4 | 116.7 (2) | C7—N7—H7NB | 109.6 |
| O10—C4—O4 | 125.7 (2) | C8—N7—H7NB | 109.6 |

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| O10—C4—C3 | 118.7 (2) | H7NA—N7—H7NB | 108.1 |
| O4—C4—C3 | 115.6 (2) | N7—C7—H7A | 109.5 |
| O11—C5—O5 | 125.7 (2) | N7—C7—H7B | 109.5 |
| O11—C5—C6 | 118.1 (2) | H7A—C7—H7B | 109.5 |
| O5—C5—C6 | 116.2 (2) | N7—C7—H7C | 109.5 |
| O12—C6—O6 | 125.9 (2) | H7A—C7—H7C | 109.5 |
| O12—C6—C5 | 118.0 (2) | H7B—C7—H7C | 109.5 |
| O6—C6—C5 | 116.1 (2) | N7—C8—C9 | 109.1 (2) |
| N10—C11—H11A | 109.5 | N7—C8—H8C | 109.9 |
| N10—C11—H11B | 109.5 | C9—C8—H8C | 109.9 |
| H11A—C11—H11B | 109.5 | N7—C8—H8D | 109.9 |
| N10—C11—H11C | 109.5 | C9—C8—H8D | 109.9 |
| H11A—C11—H11C | 109.5 | H8C—C8—H8D | 108.3 |
| H11B—C11—H11C | 109.5 | N8—C9—C8 | 109.8 (2) |
| C12—N10—C11 | 111.0 (3) | N8—C9—H9A | 109.7 |
| C12—N10—H10N | 109.4 | C8—C9—H9A | 109.7 |
| C11—N10—H10N | 109.4 | N8—C9—H9B | 109.7 |
| C12—N10—H10M | 109.4 | C8—C9—H9B | 109.7 |
| C11—N10—H10M | 109.4 | H9A—C9—H9B | 108.2 |
| H10N—N10—H10M | 108.0 | N8—C10—H10A | 109.5 |
| N10—C12—C13 | 107.1 (3) | N8—C10—H10B | 109.5 |
| N10—C12—H12A | 110.3 | H10A—C10—H10B | 109.5 |
| C13—C12—H12A | 110.3 | N8—C10—H10C | 109.5 |
| N10—C12—H12B | 110.3 | H10A—C10—H10C | 109.5 |
| C13—C12—H12B | 110.3 | H10B—C10—H10C | 109.5 |
| H12A—C12—H12B | 108.6 | | |

| | | | |
|---|---|---|---|
| O5—Co1—O1—C1 | 177.89 (18) | Co1—O1—C1—O7 | −174.5 (2) |
| O4—Co1—O1—C1 | 25.8 (5) | Co1—O1—C1—C2 | 5.8 (3) |
| O2—Co1—O1—C1 | −9.93 (18) | Co1—O2—C2—O8 | 164.7 (2) |
| O6—Co1—O1—C1 | −102.47 (19) | Co1—O2—C2—C1 | −14.1 (3) |
| O3—Co1—O1—C1 | 79.24 (19) | O7—C1—C2—O8 | 7.1 (4) |
| O5—Co1—O2—C2 | 64.5 (5) | O1—C1—C2—O8 | −173.2 (2) |
| O4—Co1—O2—C2 | −160.22 (19) | O7—C1—C2—O2 | −174.1 (3) |
| O1—Co1—O2—C2 | 13.13 (18) | O1—C1—C2—O2 | 5.7 (4) |
| O6—Co1—O2—C2 | 106.28 (19) | Co1—O3—C3—O9 | 164.8 (3) |
| O3—Co1—O2—C2 | −80.99 (19) | Co1—O3—C3—C4 | −15.7 (3) |
| O5—Co1—O3—C3 | 108.9 (2) | Co1—O4—C4—O10 | −174.0 (3) |
| O4—Co1—O3—C3 | 14.76 (19) | Co1—O4—C4—C3 | 6.7 (3) |
| O2—Co1—O3—C3 | −76.8 (2) | O9—C3—C4—O10 | 6.8 (4) |
| O1—Co1—O3—C3 | −155.9 (2) | O3—C3—C4—O10 | −172.7 (3) |
| O6—Co1—O3—C3 | 36.6 (7) | O9—C3—C4—O4 | −173.8 (3) |
| O5—Co1—O4—C4 | −108.70 (19) | O3—C3—C4—O4 | 6.6 (4) |
| O2—Co1—O4—C4 | 78.35 (19) | Co1—O5—C5—O11 | 167.8 (2) |
| O1—Co1—O4—C4 | 43.4 (5) | Co1—O5—C5—C6 | −10.8 (3) |
| O6—Co1—O4—C4 | 171.64 (19) | Co1—O6—C6—O12 | −178.4 (2) |
| O3—Co1—O4—C4 | −11.30 (19) | Co1—O6—C6—C5 | 0.7 (3) |
| O4—Co1—O5—C5 | −83.76 (17) | O11—C5—C6—O12 | 7.4 (4) |

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| O2—Co1—O5—C5 | 51.3 (5) | O5—C5—C6—O12 | −173.9 (2) |
| O1—Co1—O5—C5 | 101.59 (18) | O11—C5—C6—O6 | −171.7 (2) |
| O6—Co1—O5—C5 | 8.69 (17) | O5—C5—C6—O6 | 7.0 (3) |
| O3—Co1—O5—C5 | −163.64 (17) | C11—N10—C12—C13 | −179.8 (3) |
| O5—Co1—O6—C6 | −4.67 (17) | N10—C12—C13—N9 | −172.8 (3) |
| O4—Co1—O6—C6 | 90.32 (18) | C12—C13—N9—C14 | 58.1 (4) |
| O2—Co1—O6—C6 | −177.91 (18) | C7—N7—C8—C9 | 177.9 (3) |
| O1—Co1—O6—C6 | −98.67 (18) | C10—N8—C9—C8 | −176.6 (3) |
| O3—Co1—O6—C6 | 68.9 (6) | N7—C8—C9—N8 | 177.7 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N9—H9*N*1···O8 | 0.90 | 1.86 | 2.668 (3) | 148 |
| O14—H14*O*···O7 | 0.96 | 1.94 | 2.876 (4) | 163 |
| N7—H7*NB*···O1 | 0.90 | 1.90 | 2.769 (3) | 161 |
| O13—H13*W*···O10 | 0.96 | 1.91 | 2.755 (3) | 146 |
| N10—H10*M*···O11$^{i}$ | 0.90 | 1.94 | 2.814 (3) | 165 |
| N10—H10*N*···O9$^{ii}$ | 0.90 | 1.83 | 2.721 (3) | 173 |
| N9—H9*N*2···O13$^{iii}$ | 0.90 | 1.80 | 2.679 (3) | 163 |
| N8—H8*NA*···O6$^{iv}$ | 0.90 | 1.94 | 2.829 (3) | 170 |
| N8—H8*NB*···O7$^{v}$ | 0.90 | 2.07 | 2.916 (3) | 156 |
| N8—H8*NB*···O8$^{v}$ | 0.90 | 2.25 | 2.801 (3) | 119 |
| N7—H7*NA*···O12$^{vi}$ | 0.90 | 1.97 | 2.751 (3) | 144 |
| O13—H13*O*···O12$^{vii}$ | 0.95 | 1.75 | 2.698 (3) | 174 |

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