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# Poly[[tetraaqua($\mu_4$-imidazole-4,5-dicarboxylato)($\mu_3$-imidazole-4,5-dicarboxylato)-$\mu_3$-sulfato-$\mu_2$-sulfato-cobalt(II)digadolinium(III)] monohydrate]

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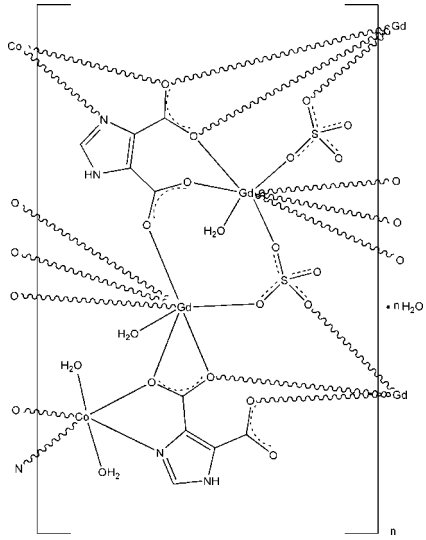
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.022; $wR$ factor = 0.054; data-to-parameter ratio = 10.6.

The asymmetric unit of the title compound, {[$CoGd_2(C_5H_2N_2O_4)_2(SO_4)_2(H_2O)_4]\cdot H_2O$}$_n$, contains one $Co^{II}$ ion, two $Gd^{III}$ ions, two imidazole-4,5-dicarboxylate ligands, two $SO_4^{2-}$ anions, four coordinated water molecules and one uncoordinated water molecule. The $Co^{II}$ ion is six-coordinated by two O atoms from two coordinated water molecules, as well as two O atoms and two N atoms from two imidazole-4,5-dicarboxylate ligands, giving a slightly distorted octahedral geometry. Both $Gd^{III}$ ions are eight-coordinated in a distorted bicapped trigonal–prismatic geometry. One $Gd^{III}$ ion is coordinated by four O atoms from two imidazole-4,5-dicarboxylate ligands, three O atoms from three $SO_4^{2-}$ anions and a water O atom; the other $Gd^{III}$ ion is bonded to five O atoms from three imidazole-4,5-dicarboxylate ligands, two O atoms from two $SO_4^{2-}$ anions as well as a water O atom. These metal coordination units are connected by bridging imidazole-4,5-dicarboxylate and sulfate ligands, generating a heterometallic layer parallel to the *ac* plane. The layers are stacked along the *b* axis *via* N—H···O, O—H···O, and C—H···O hydrogen-bonding interactions, generating a three-dimensional framework.

## Related literature

For applications of lanthanide–transition metal heterometallic complexes with bridging multifunctional organic ligands, see: Cheng *et al.* (2006); Kuang *et al.* (2007); Sun *et al.* (2006); Zhu *et al.* (2010).




## Experimental

### Crystal data

$[CoGd_2(C_5H_2N_2O_4)_2(SO_4)_2(H_2O)_4]\cdot H_2O$
$M_r$ = 963.82
Triclinic, $P\overline{1}$
$a$ = 9.0916 (5) Å
$b$ = 10.7714 (6) Å
$c$ = 12.9736 (7) Å
$\alpha$ = 93.119 (1)°
$\beta$ = 96.416 (1)°
$\gamma$ = 108.840 (1)°
$V$ = 1189.35 (11) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 6.48 mm$^{-1}$
$T$ = 296 K
0.20 × 0.18 × 0.15 mm

### Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.284, $T_{max}$ = 0.378
6174 measured reflections
4208 independent reflections
3790 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.054
$S$ = 1.02
4208 reflections
397 parameters
17 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.79 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.81 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{i}$ | 0.87 (4) | 1.96 (4) | 2.820 (5) | 172 (5) |
| O1$W$—H1$W$···O5$W^{ii}$ | 0.81 (4) | 1.95 (3) | 2.745 (5) | 169 (6) |
| N3—H2···O14$^{iii}$ | 0.87 (3) | 1.93 (3) | 2.787 (4) | 169 (4) |
| O2$W$—H3$W$···O1$^{i}$ | 0.80 (3) | 2.09 (4) | 2.878 (5) | 171 (5) |
| O2$W$—H4$W$···O14$^{i}$ | 0.81 (4) | 2.04 (4) | 2.842 (5) | 172 (5) |
| O2$W$—H4$W$···O15$^{i}$ | 0.81 (4) | 2.52 (4) | 3.035 (5) | 123 (4) |
| O3$W$—H5$W$···O12$^{iv}$ | 0.82 (3) | 1.95 (4) | 2.734 (4) | 162 (5) |
| O3$W$—H6$W$···O14$^{v}$ | 0.83 (3) | 2.41 (4) | 2.919 (4) | 120 (3) |
| O4$W$—H7$W$···O3$^{vi}$ | 0.82 (3) | 2.49 (3) | 3.306 (6) | 174 (6) |
| O4$W$—H8$W$···O5$W^{iii}$ | 0.82 (5) | 1.89 (5) | 2.700 (6) | 175 (6) |
| O5$W$—H9$W$···O12$^{v}$ | 0.85 (4) | 1.99 (4) | 2.797 (6) | 161 (5) |
| O5$W$—H10$W$···O1$^{i}$ | 0.85 (5) | 1.93 (5) | 2.728 (5) | 157 (6) |
| C3—H3···O3$^{vii}$ | 0.93 | 2.44 | 3.193 (5) | 138 |

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The author acknowledges South China Normal University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HP2018).

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# supplementary materials

*Acta Cryst.* (2011). E**67**, m1741-m1742 [ **doi:10.1107/S160053681104726X** ]

# Poly[[tetraaqua($\mu_4$-imidazole-4,5-dicarboxylato)($\mu_3$-imidazole-4,5-dicarboxylato)-$\mu_3$-sulfato-$\mu_2$-sulfato-cobalt(II)digadolinium(III)] monohydrate]

**L.-C. Zhu**

## Comment

In the past few years, lanthanide-transition metal heterometallic complexs with bridging multifunctionnal organic ligands are of increasing interest, not only because of their impressive topological structures, but also due to their versatile applications in ion exchange, magnetism, bimetallic catalysis and luminescent probe(Cheng *et al.*, 2006; Kuang *et al.*, 2007; Sun *et al.*, 2006; Zhu *et al.*, 2010). As an extension of this research, the structure of the title compound, a new heterometallic coordination polymer, (I), has been determined which is presented in this artcle.

The asymmetric unite of the title compound (Fig. 1), contains one $Co^{II}$ ion, two $Gd^{III}$ ions, two imidazole-4, 5-dicarboxylate ligands, two $SO_4^{2-}$ anions, four coordinated water molecules and one uncoordinated water molecule. The $Co^{II}$ ion is six-coordinated with two O atoms from two coordinated water molecules, two O atoms and two N atoms from two imidazole-4, 5-dicarboxylate ligands, giving a slightly distorted octahedral geometry. Both $Gd^{III}$ ions are eight-coordinated in a bicapped trigonal prismatic coordination geometry. One $Gd^{III}$ ion is coordinated by four O atoms from two imidazole-4,5-dicarboxylate ligands, three O atoms from three $SO_4^{2-}$ anions and one water molecule; the other $Gd^{III}$ ion is bonded to five O atoms from three imidazole-4, 5-dicarboxylate ligands, two O atoms from two $SO_4^{2-}$ anions as well as one coordinated water molecule. These metal coordination units are connected by bridging imidazole-4, 5-dicarboxylate and sulfate ligands, generating a two-dimensional heterometallic layer. The two-dimensional layers are stacked along *b* axis *via* N—H···O, O—H···O, and C—H···O hydrogen-bonding interactions to generate the three-dimensional framework(Table 1 and Fig. 2).

## Experimental

A mixture of $CoSO_4.7H_2O$(0.141 g, 0.5 mmol), $Gd_2O_3$(0.09 g, 0.25 mmol), imidazole-4,5-dicarboxylic acid (0.156 g, 1 mmol), and $H_2O$(7 ml) was sealed in a 20 ml Teflon-lined reaction vessel at 443 K for 5 days then slowly cooled to room temperature. The product was collected by filtration, washed with water and air-dried. Red block crystals suitable for X-ray analysis were obtained.

## Refinement

H atoms bonded to C atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å and $U_{iso}$(H) = 1.2 $U_{eq}$(C). H atoms bonded to N atoms and H atoms of water molecules were found from difference Fourier maps and refined isotropically with a restraint of N—H = 0.87 Å, O—H = 0.82 or 0.86 Å and $U_{iso}$(H) = 1.5 $U_{eq}$(N, O).

**Figures**

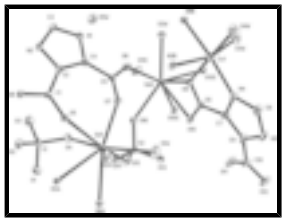

Fig. 1. The molecular structure showing the atomic-numbering scheme and displacement ellipsoids drawn at the 30% probability level. Symmetry codes: (A) 2 - *x*, 1 - *y*, 1 - *z*; (B) 1 - *x*, 1 - *y*, 1 - *z*; (C) 1 - *x*, 1 - *y*, -*z*.

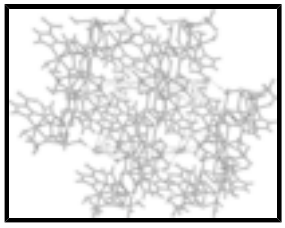

Fig. 2. A view of the three-dimensional structure of the title compound, the hydrogen bonding interactions showed as broken lines.

**Poly[[tetraaqua(μ$_4$-imidazole-4,5-dicarboxylato)(μ$_3$-imidazole-4,5- dicarboxylato)-μ$_3$-sulfato-μ$_2$-sulfato-cobalt(II)digadolinium(III)] monohydrate]**

*Crystal data*

| | |
|---|---|
| $[CoGd_2(C_5H_2N_2O_4)_2(SO_4)_2(H_2O)_4]\cdot H_2O$ | $Z = 2$ |
| $M_r = 963.82$ | $F(000) = 914$ |
| Triclinic, $P\overline{1}$ | $D_x = 2.691$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 9.0916$ (5) Å | Cell parameters from 4033 reflections |
| $b = 10.7714$ (6) Å | $\theta = 2.4$–$27.9°$ |
| $c = 12.9736$ (7) Å | $\mu = 6.48$ mm$^{-1}$ |
| $\alpha = 93.119$ (1)° | $T = 296$ K |
| $\beta = 96.416$ (1)° | Block, red |
| $\gamma = 108.840$ (1)° | 0.20 × 0.18 × 0.15 mm |
| $V = 1189.35$ (11) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII area-detector diffractometer | 4208 independent reflections |
| Radiation source: fine-focus sealed tube | 3790 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.016$ |
| φ and ω scan | $\theta_{max} = 25.2°$, $\theta_{min} = 1.6°$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $h = -10\rightarrow8$ |
| $T_{min} = 0.284$, $T_{max} = 0.378$ | $k = -9\rightarrow12$ |
| 6174 measured reflections | $l = -14\rightarrow15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.022$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.054$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.02$ | $w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.3497P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 4208 reflections | $(\Delta/\sigma)_{max} = 0.002$ |
| 397 parameters | $\Delta\rho_{max} = 0.79$ e Å$^{-3}$ |
| 17 restraints | $\Delta\rho_{min} = -0.81$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Gd1 | 0.90952 (2) | 0.549083 (19) | 0.364770 (14) | 0.01526 (7) |
| Gd2 | 0.37043 (2) | 0.410578 (19) | 0.108204 (14) | 0.01441 (7) |
| Co1 | 0.35411 (7) | 0.78823 (6) | 0.27426 (4) | 0.01829 (13) |
| S1 | 0.92233 (13) | 0.22231 (10) | 0.40357 (8) | 0.0196 (2) |
| S2 | 0.77447 (12) | 0.42234 (10) | 0.09511 (7) | 0.0157 (2) |
| C1 | 0.7564 (5) | 0.3980 (4) | 0.5774 (3) | 0.0152 (9) |
| C2 | 0.5906 (5) | 0.3349 (4) | 0.5377 (3) | 0.0175 (9) |
| C3 | 0.3614 (5) | 0.1987 (4) | 0.5498 (3) | 0.0224 (10) |
| H3 | 0.2790 | 0.1358 | 0.5738 | 0.027* |
| C4 | 0.4925 (5) | 0.3440 (4) | 0.4526 (3) | 0.0176 (9) |
| C5 | 0.5166 (5) | 0.4170 (4) | 0.3574 (3) | 0.0179 (9) |
| C6 | 0.5196 (5) | 0.6976 (4) | 0.1215 (3) | 0.0183 (9) |
| C7 | 0.5717 (5) | 0.8417 (4) | 0.1198 (3) | 0.0198 (9) |
| C8 | 0.5810 (6) | 1.0356 (4) | 0.1824 (3) | 0.0262 (11) |
| H8 | 0.5656 | 1.1038 | 0.2221 | 0.031* |
| C9 | 0.6687 (5) | 0.9312 (4) | 0.0646 (3) | 0.0212 (10) |
| C10 | 0.7527 (5) | 0.9224 (4) | −0.0265 (3) | 0.0253 (10) |

| | | | | |
|---|---|---|---|---|
| N1 | 0.3480 (4) | 0.2571 (4) | 0.4626 (3) | 0.0219 (8) |
| N2 | 0.5066 (4) | 0.2422 (3) | 0.5971 (3) | 0.0188 (8) |
| N3 | 0.6720 (5) | 1.0523 (3) | 0.1057 (3) | 0.0251 (9) |
| N4 | 0.5169 (4) | 0.9092 (3) | 0.1936 (3) | 0.0209 (8) |
| O1 | 1.0507 (4) | 0.2115 (3) | 0.3471 (2) | 0.0307 (8) |
| O2 | 0.9891 (4) | 0.2677 (3) | 0.5141 (2) | 0.0260 (7) |
| O3 | 0.7976 (4) | 0.0979 (3) | 0.3993 (3) | 0.0429 (10) |
| O4 | 0.8622 (4) | 0.3220 (3) | 0.3559 (2) | 0.0236 (7) |
| O5 | 0.8508 (3) | 0.4831 (3) | 0.5314 (2) | 0.0191 (6) |
| O6 | 0.8087 (3) | 0.3626 (3) | 0.6615 (2) | 0.0195 (6) |
| O7 | 0.6446 (3) | 0.5035 (3) | 0.3536 (2) | 0.0227 (7) |
| O8 | 0.4026 (4) | 0.3819 (3) | 0.2864 (2) | 0.0291 (8) |
| O9 | 0.4237 (4) | 0.6481 (3) | 0.1835 (2) | 0.0216 (7) |
| O10 | 0.5663 (3) | 0.6222 (3) | 0.0648 (2) | 0.0201 (7) |
| O11 | 0.7322 (4) | 0.8084 (3) | −0.0689 (3) | 0.0373 (9) |
| O12 | 0.8336 (4) | 1.0256 (3) | −0.0559 (3) | 0.0371 (9) |
| O13 | 0.7800 (4) | 0.5049 (3) | 0.0081 (2) | 0.0261 (7) |
| O14 | 0.8239 (4) | 0.3108 (3) | 0.0655 (2) | 0.0302 (8) |
| O15 | 0.8852 (4) | 0.5027 (3) | 0.1839 (2) | 0.0315 (8) |
| O16 | 0.6158 (4) | 0.3748 (3) | 0.1261 (2) | 0.0296 (8) |
| H1 | 0.260 (4) | 0.251 (5) | 0.426 (3) | 0.044* |
| H2 | 0.725 (5) | 1.128 (3) | 0.087 (4) | 0.044* |
| O1W | 0.8720 (5) | 0.7325 (3) | 0.2745 (3) | 0.0411 (9) |
| H1W | 0.931 (6) | 0.807 (3) | 0.275 (4) | 0.062* |
| H2W | 0.843 (7) | 0.703 (5) | 0.216 (2) | 0.062* |
| O2W | 0.1300 (4) | 0.3676 (4) | 0.1756 (3) | 0.0301 (8) |
| H3W | 0.115 (5) | 0.331 (5) | 0.227 (2) | 0.045* |
| H4W | 0.046 (4) | 0.359 (5) | 0.143 (3) | 0.045* |
| O3W | 0.1637 (4) | 0.7554 (3) | 0.1538 (2) | 0.0305 (8) |
| H5W | 0.166 (7) | 0.811 (3) | 0.113 (3) | 0.046* |
| H6W | 0.131 (6) | 0.686 (3) | 0.114 (3) | 0.046* |
| O4W | 0.2924 (5) | 0.9293 (4) | 0.3611 (3) | 0.0402 (9) |
| H7W | 0.267 (6) | 0.916 (6) | 0.419 (2) | 0.060* |
| H8W | 0.221 (5) | 0.949 (6) | 0.330 (4) | 0.060* |
| O5W | 0.0564 (5) | −0.0166 (4) | 0.2481 (3) | 0.0440 (10) |
| H9W | 0.079 (7) | −0.006 (5) | 0.187 (2) | 0.066* |
| H10W | 0.028 (7) | 0.046 (4) | 0.271 (4) | 0.066* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Gd1 | 0.01463 (12) | 0.01957 (12) | 0.01160 (11) | 0.00505 (9) | 0.00226 (8) | 0.00460 (8) |
| Gd2 | 0.01453 (12) | 0.01764 (12) | 0.01186 (11) | 0.00550 (9) | 0.00300 (8) | 0.00492 (8) |
| Co1 | 0.0212 (3) | 0.0206 (3) | 0.0141 (3) | 0.0069 (2) | 0.0050 (2) | 0.0054 (2) |
| S1 | 0.0214 (6) | 0.0180 (5) | 0.0181 (5) | 0.0053 (4) | 0.0011 (4) | 0.0022 (4) |
| S2 | 0.0164 (5) | 0.0211 (5) | 0.0111 (5) | 0.0077 (4) | 0.0024 (4) | 0.0041 (4) |
| C1 | 0.020 (2) | 0.017 (2) | 0.0083 (19) | 0.0053 (18) | 0.0044 (17) | 0.0013 (16) |
| C2 | 0.022 (2) | 0.021 (2) | 0.0102 (19) | 0.0082 (18) | 0.0032 (17) | 0.0004 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C3 | 0.021 (2) | 0.024 (2) | 0.020 (2) | 0.0035 (19) | 0.0038 (19) | 0.0055 (18) |
| C4 | 0.018 (2) | 0.021 (2) | 0.013 (2) | 0.0056 (18) | 0.0011 (17) | 0.0031 (17) |
| C5 | 0.017 (2) | 0.029 (2) | 0.010 (2) | 0.0095 (19) | 0.0058 (17) | 0.0057 (17) |
| C6 | 0.018 (2) | 0.020 (2) | 0.015 (2) | 0.0039 (18) | −0.0011 (18) | 0.0041 (18) |
| C7 | 0.023 (2) | 0.018 (2) | 0.018 (2) | 0.0057 (18) | 0.0050 (18) | 0.0017 (17) |
| C8 | 0.038 (3) | 0.017 (2) | 0.025 (2) | 0.009 (2) | 0.012 (2) | 0.0031 (19) |
| C9 | 0.026 (3) | 0.014 (2) | 0.021 (2) | 0.0034 (18) | 0.0045 (19) | 0.0031 (18) |
| C10 | 0.027 (3) | 0.024 (3) | 0.023 (2) | 0.003 (2) | 0.010 (2) | 0.005 (2) |
| N1 | 0.016 (2) | 0.031 (2) | 0.0177 (19) | 0.0067 (17) | 0.0005 (15) | 0.0044 (16) |
| N2 | 0.020 (2) | 0.0204 (19) | 0.0142 (17) | 0.0039 (15) | 0.0035 (15) | 0.0047 (14) |
| N3 | 0.035 (2) | 0.0154 (19) | 0.025 (2) | 0.0043 (17) | 0.0127 (18) | 0.0081 (16) |
| N4 | 0.024 (2) | 0.0188 (19) | 0.0185 (18) | 0.0050 (16) | 0.0045 (16) | 0.0011 (15) |
| O1 | 0.033 (2) | 0.046 (2) | 0.0184 (16) | 0.0199 (16) | 0.0057 (14) | 0.0000 (15) |
| O2 | 0.037 (2) | 0.0269 (17) | 0.0154 (15) | 0.0120 (15) | 0.0022 (14) | 0.0038 (13) |
| O3 | 0.031 (2) | 0.0262 (19) | 0.057 (2) | −0.0065 (15) | −0.0102 (18) | 0.0148 (17) |
| O4 | 0.0266 (18) | 0.0222 (16) | 0.0229 (16) | 0.0107 (14) | −0.0012 (14) | 0.0020 (13) |
| O5 | 0.0160 (16) | 0.0252 (16) | 0.0149 (14) | 0.0041 (13) | 0.0030 (12) | 0.0064 (12) |
| O6 | 0.0167 (16) | 0.0296 (17) | 0.0125 (14) | 0.0070 (13) | 0.0029 (12) | 0.0074 (12) |
| O7 | 0.0161 (16) | 0.0295 (17) | 0.0225 (16) | 0.0057 (13) | 0.0029 (13) | 0.0122 (13) |
| O8 | 0.0191 (17) | 0.048 (2) | 0.0167 (16) | 0.0052 (15) | 0.0010 (13) | 0.0133 (15) |
| O9 | 0.0276 (18) | 0.0182 (15) | 0.0193 (15) | 0.0049 (13) | 0.0105 (13) | 0.0067 (12) |
| O10 | 0.0246 (17) | 0.0149 (15) | 0.0209 (15) | 0.0048 (13) | 0.0084 (13) | 0.0036 (12) |
| O11 | 0.053 (2) | 0.0187 (18) | 0.037 (2) | 0.0021 (16) | 0.0258 (18) | 0.0011 (15) |
| O12 | 0.050 (2) | 0.0236 (18) | 0.039 (2) | 0.0061 (16) | 0.0248 (18) | 0.0103 (15) |
| O13 | 0.0230 (18) | 0.042 (2) | 0.0184 (16) | 0.0142 (15) | 0.0053 (13) | 0.0170 (14) |
| O14 | 0.039 (2) | 0.0200 (17) | 0.0346 (18) | 0.0095 (15) | 0.0187 (16) | 0.0038 (14) |
| O15 | 0.035 (2) | 0.0346 (19) | 0.0158 (16) | 0.0001 (15) | 0.0002 (14) | −0.0013 (14) |
| O16 | 0.0236 (18) | 0.045 (2) | 0.0275 (17) | 0.0164 (15) | 0.0122 (14) | 0.0208 (15) |
| O1W | 0.053 (3) | 0.029 (2) | 0.035 (2) | 0.0081 (18) | −0.0066 (19) | 0.0089 (16) |
| O2W | 0.0199 (18) | 0.049 (2) | 0.0271 (18) | 0.0154 (16) | 0.0092 (14) | 0.0182 (16) |
| O3W | 0.035 (2) | 0.0295 (18) | 0.0251 (17) | 0.0100 (16) | −0.0016 (15) | 0.0045 (14) |
| O4W | 0.055 (3) | 0.041 (2) | 0.032 (2) | 0.0265 (19) | 0.0098 (18) | 0.0015 (18) |
| O5W | 0.063 (3) | 0.040 (2) | 0.043 (2) | 0.028 (2) | 0.026 (2) | 0.0114 (18) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Gd1—O7 | 2.283 (3) | C3—N2 | 1.314 (5) |
| Gd1—O2$^{i}$ | 2.319 (3) | C3—N1 | 1.336 (5) |
| Gd1—O4 | 2.337 (3) | C3—H3 | 0.9300 |
| Gd1—O15 | 2.343 (3) | C4—N1 | 1.370 (5) |
| Gd1—O5 | 2.375 (3) | C4—C5 | 1.498 (5) |
| Gd1—O1W | 2.447 (3) | C5—O7 | 1.242 (5) |
| Gd1—O6$^{i}$ | 2.498 (3) | C5—O8 | 1.249 (5) |
| Gd1—O5$^{i}$ | 2.562 (3) | C6—O9 | 1.263 (5) |
| Gd1—C1$^{i}$ | 2.905 (4) | C6—O10 | 1.268 (5) |
| Gd1—Gd1$^{i}$ | 4.0465 (4) | C6—C7 | 1.471 (6) |
| Gd2—O11$^{ii}$ | 2.244 (3) | C7—C9 | 1.373 (6) |
| Gd2—O13$^{ii}$ | 2.338 (3) | C7—N4 | 1.399 (5) |

| | | | |
|---|---|---|---|
| Gd2—O8 | 2.348 (3) | C8—N4 | 1.320 (5) |
| Gd2—O2W | 2.361 (3) | C8—N3 | 1.347 (6) |
| Gd2—O16 | 2.373 (3) | C8—H8 | 0.9300 |
| Gd2—O10$^{ii}$ | 2.414 (3) | C9—N3 | 1.372 (5) |
| Gd2—O10 | 2.535 (3) | C9—C10 | 1.493 (6) |
| Gd2—O9 | 2.561 (3) | C10—O12 | 1.226 (5) |
| Gd2—C6 | 2.934 (4) | C10—O11 | 1.265 (5) |
| Gd2—Gd2$^{ii}$ | 4.0349 (4) | N1—H1 | 0.87 (4) |
| Co1—N4 | 2.058 (4) | N2—Co1$^{iii}$ | 2.086 (3) |
| Co1—N2$^{iii}$ | 2.086 (3) | N3—H2 | 0.87 (3) |
| Co1—O6$^{iii}$ | 2.096 (3) | O2—Gd1$^{i}$ | 2.319 (3) |
| Co1—O4W | 2.097 (4) | O5—Gd1$^{i}$ | 2.562 (3) |
| Co1—O3W | 2.122 (3) | O6—Co1$^{iii}$ | 2.096 (3) |
| Co1—O9 | 2.157 (3) | O6—Gd1$^{i}$ | 2.498 (3) |
| S1—O3 | 1.443 (3) | O10—Gd2$^{ii}$ | 2.414 (3) |
| S1—O1 | 1.478 (3) | O11—Gd2$^{ii}$ | 2.244 (3) |
| S1—O2 | 1.483 (3) | O13—Gd2$^{ii}$ | 2.338 (3) |
| S1—O4 | 1.486 (3) | O1W—H1W | 0.81 (4) |
| S2—O14 | 1.459 (3) | O1W—H2W | 0.789 (19) |
| S2—O15 | 1.469 (3) | O2W—H3W | 0.80 (3) |
| S2—O13 | 1.470 (3) | O2W—H4W | 0.81 (4) |
| S2—O16 | 1.476 (3) | O3W—H5W | 0.82 (3) |
| C1—O5 | 1.264 (5) | O3W—H6W | 0.83 (3) |
| C1—O6 | 1.269 (5) | O4W—H7W | 0.82 (3) |
| C1—C2 | 1.458 (6) | O4W—H8W | 0.82 (5) |
| C1—Gd1$^{i}$ | 2.905 (4) | O5W—H9W | 0.85 (4) |
| C2—C4 | 1.369 (6) | O5W—H10W | 0.85 (5) |
| C2—N2 | 1.377 (5) | | |
| O7—Gd1—O2$^{i}$ | 103.56 (11) | O4W—Co1—O3W | 93.45 (14) |
| O7—Gd1—O4 | 87.61 (10) | N4—Co1—O9 | 78.00 (12) |
| O2$^{i}$—Gd1—O4 | 139.04 (10) | N2$^{iii}$—Co1—O9 | 87.71 (13) |
| O7—Gd1—O15 | 90.06 (11) | O6$^{iii}$—Co1—O9 | 91.82 (11) |
| O2$^{i}$—Gd1—O15 | 137.61 (11) | O4W—Co1—O9 | 178.18 (14) |
| O4—Gd1—O15 | 80.42 (11) | O3W—Co1—O9 | 87.04 (13) |
| O7—Gd1—O5 | 76.05 (10) | O3—S1—O1 | 112.2 (2) |
| O2$^{i}$—Gd1—O5 | 71.43 (10) | O3—S1—O2 | 108.8 (2) |
| O4—Gd1—O5 | 73.46 (10) | O1—S1—O2 | 107.78 (19) |
| O15—Gd1—O5 | 150.71 (11) | O3—S1—O4 | 110.53 (19) |
| O7—Gd1—O1W | 77.94 (12) | O1—S1—O4 | 107.51 (18) |
| O2$^{i}$—Gd1—O1W | 74.57 (11) | O2—S1—O4 | 110.02 (17) |
| O4—Gd1—O1W | 146.18 (11) | O14—S2—O15 | 108.6 (2) |
| O15—Gd1—O1W | 69.33 (12) | O14—S2—O13 | 109.56 (18) |
| O5—Gd1—O1W | 130.26 (12) | O15—S2—O13 | 107.94 (19) |
| O7—Gd1—O6$^{i}$ | 164.37 (9) | O14—S2—O16 | 110.07 (19) |
| O2$^{i}$—Gd1—O6$^{i}$ | 76.75 (10) | O15—S2—O16 | 109.10 (19) |

| | | | |
|---|---|---|---|
| O4—Gd1—O6$^{i}$ | 102.43 (10) | O13—S2—O16 | 111.47 (17) |
| O15—Gd1—O6$^{i}$ | 80.01 (10) | O5—C1—O6 | 118.6 (4) |
| O5—Gd1—O6$^{i}$ | 118.09 (9) | O5—C1—C2 | 123.7 (3) |
| O1W—Gd1—O6$^{i}$ | 87.23 (12) | O6—C1—C2 | 117.7 (3) |
| O7—Gd1—O5$^{i}$ | 144.56 (9) | O5—C1—Gd1$^{i}$ | 61.8 (2) |
| O2$^{i}$—Gd1—O5$^{i}$ | 75.17 (10) | O6—C1—Gd1$^{i}$ | 58.9 (2) |
| O4—Gd1—O5$^{i}$ | 73.51 (10) | C2—C1—Gd1$^{i}$ | 163.6 (3) |
| O15—Gd1—O5$^{i}$ | 115.09 (11) | C4—C2—N2 | 109.0 (4) |
| O5—Gd1—O5$^{i}$ | 69.99 (11) | C4—C2—C1 | 135.5 (4) |
| O1W—Gd1—O5$^{i}$ | 132.85 (11) | N2—C2—C1 | 115.5 (3) |
| O6$^{i}$—Gd1—O5$^{i}$ | 50.97 (9) | N2—C3—N1 | 110.9 (4) |
| O7—Gd1—C1$^{i}$ | 168.66 (10) | N2—C3—H3 | 124.5 |
| O2$^{i}$—Gd1—C1$^{i}$ | 70.40 (11) | N1—C3—H3 | 124.5 |
| O4—Gd1—C1$^{i}$ | 91.09 (11) | C2—C4—N1 | 105.5 (3) |
| O15—Gd1—C1$^{i}$ | 100.83 (11) | C2—C4—C5 | 133.9 (4) |
| O5—Gd1—C1$^{i}$ | 92.78 (10) | N1—C4—C5 | 120.4 (4) |
| O1W—Gd1—C1$^{i}$ | 108.73 (12) | O7—C5—O8 | 125.4 (4) |
| O6$^{i}$—Gd1—C1$^{i}$ | 25.79 (9) | O7—C5—C4 | 119.5 (4) |
| O5$^{i}$—Gd1—C1$^{i}$ | 25.77 (10) | O8—C5—C4 | 115.1 (4) |
| O7—Gd1—Gd1$^{i}$ | 111.99 (7) | O9—C6—O10 | 119.1 (4) |
| O2$^{i}$—Gd1—Gd1$^{i}$ | 69.58 (7) | O9—C6—C7 | 117.3 (4) |
| O4—Gd1—Gd1$^{i}$ | 69.70 (7) | O10—C6—C7 | 123.6 (4) |
| O15—Gd1—Gd1$^{i}$ | 141.31 (9) | O9—C6—Gd2 | 60.5 (2) |
| O5—Gd1—Gd1$^{i}$ | 36.51 (7) | O10—C6—Gd2 | 59.4 (2) |
| O1W—Gd1—Gd1$^{i}$ | 144.09 (9) | C7—C6—Gd2 | 171.4 (3) |
| O6$^{i}$—Gd1—Gd1$^{i}$ | 82.97 (6) | C9—C7—N4 | 109.2 (4) |
| O5$^{i}$—Gd1—Gd1$^{i}$ | 33.48 (6) | C9—C7—C6 | 135.5 (4) |
| C1$^{i}$—Gd1—Gd1$^{i}$ | 57.20 (7) | N4—C7—C6 | 115.3 (4) |
| O11$^{ii}$—Gd2—O13$^{ii}$ | 104.05 (12) | N4—C8—N3 | 110.6 (4) |
| O11$^{ii}$—Gd2—O8 | 90.51 (12) | N4—C8—H8 | 124.7 |
| O13$^{ii}$—Gd2—O8 | 138.78 (11) | N3—C8—H8 | 124.7 |
| O11$^{ii}$—Gd2—O2W | 79.70 (13) | N3—C9—C7 | 105.2 (4) |
| O13$^{ii}$—Gd2—O2W | 75.63 (11) | N3—C9—C10 | 119.4 (4) |
| O8—Gd2—O2W | 69.29 (11) | C7—C9—C10 | 135.2 (4) |
| O11$^{ii}$—Gd2—O16 | 85.00 (13) | O12—C10—O11 | 125.0 (4) |
| O13$^{ii}$—Gd2—O16 | 139.36 (10) | O12—C10—C9 | 117.9 (4) |
| O8—Gd2—O16 | 79.29 (11) | O11—C10—C9 | 117.1 (4) |
| O2W—Gd2—O16 | 144.68 (10) | C3—N1—C4 | 108.3 (3) |
| O11$^{ii}$—Gd2—O10$^{ii}$ | 76.41 (10) | C3—N1—H1 | 125 (4) |
| O13$^{ii}$—Gd2—O10$^{ii}$ | 71.52 (10) | C4—N1—H1 | 126 (4) |
| O8—Gd2—O10$^{ii}$ | 149.64 (11) | C3—N2—C2 | 106.3 (3) |

| | | | |
|---|---|---|---|
| O2W—Gd2—O10$^{ii}$ | 132.68 (11) | C3—N2—Co1$^{iii}$ | 140.8 (3) |
| O16—Gd2—O10$^{ii}$ | 72.45 (10) | C2—N2—Co1$^{iii}$ | 112.8 (3) |
| O11$^{ii}$—Gd2—O10 | 145.26 (11) | C8—N3—C9 | 109.0 (4) |
| O13$^{ii}$—Gd2—O10 | 76.33 (10) | C8—N3—H2 | 125 (4) |
| O8—Gd2—O10 | 112.31 (10) | C9—N3—H2 | 126 (4) |
| O2W—Gd2—O10 | 131.93 (11) | C8—N4—C7 | 106.0 (4) |
| O16—Gd2—O10 | 74.61 (10) | C8—N4—Co1 | 139.7 (3) |
| O10$^{ii}$—Gd2—O10 | 70.80 (11) | C7—N4—Co1 | 114.0 (3) |
| O11$^{ii}$—Gd2—O9 | 163.85 (11) | S1—O2—Gd1$^{i}$ | 144.35 (18) |
| O13$^{ii}$—Gd2—O9 | 74.78 (10) | S1—O4—Gd1 | 141.43 (18) |
| O8—Gd2—O9 | 80.86 (10) | C1—O5—Gd1 | 143.6 (3) |
| O2W—Gd2—O9 | 84.47 (11) | C1—O5—Gd1$^{i}$ | 92.4 (2) |
| O16—Gd2—O9 | 106.54 (11) | Gd1—O5—Gd1$^{i}$ | 110.01 (11) |
| O10$^{ii}$—Gd2—O9 | 117.44 (9) | C1—O6—Co1$^{iii}$ | 115.4 (3) |
| O10—Gd2—O9 | 50.71 (9) | C1—O6—Gd1$^{i}$ | 95.3 (2) |
| O11$^{ii}$—Gd2—C6 | 169.70 (11) | Co1$^{iii}$—O6—Gd1$^{i}$ | 143.17 (13) |
| O13$^{ii}$—Gd2—C6 | 71.59 (11) | C5—O7—Gd1 | 145.3 (3) |
| O8—Gd2—C6 | 98.84 (11) | C5—O8—Gd2 | 134.4 (3) |
| O2W—Gd2—C6 | 107.59 (12) | C6—O9—Co1 | 115.0 (3) |
| O16—Gd2—C6 | 92.46 (12) | C6—O9—Gd2 | 94.1 (2) |
| O10$^{ii}$—Gd2—C6 | 93.30 (11) | Co1—O9—Gd2 | 149.36 (13) |
| O10—Gd2—C6 | 25.50 (10) | C6—O10—Gd2$^{ii}$ | 142.3 (3) |
| O9—Gd2—C6 | 25.43 (10) | C6—O10—Gd2 | 95.1 (2) |
| O11$^{ii}$—Gd2—Gd2$^{ii}$ | 112.07 (8) | Gd2$^{ii}$—O10—Gd2 | 109.20 (11) |
| O13$^{ii}$—Gd2—Gd2$^{ii}$ | 70.24 (7) | C10—O11—Gd2$^{ii}$ | 159.9 (3) |
| O8—Gd2—Gd2$^{ii}$ | 139.01 (7) | S2—O13—Gd2$^{ii}$ | 144.17 (19) |
| O2W—Gd2—Gd2$^{ii}$ | 145.64 (8) | S2—O15—Gd1 | 141.6 (2) |
| O16—Gd2—Gd2$^{ii}$ | 69.68 (7) | S2—O16—Gd2 | 142.69 (18) |
| O10$^{ii}$—Gd2—Gd2$^{ii}$ | 36.40 (6) | Gd1—O1W—H1W | 130 (4) |
| O10—Gd2—Gd2$^{ii}$ | 34.41 (6) | Gd1—O1W—H2W | 104 (4) |
| O9—Gd2—Gd2$^{ii}$ | 82.98 (6) | H1W—O1W—H2W | 108 (3) |
| C6—Gd2—Gd2$^{ii}$ | 57.82 (8) | Gd2—O2W—H3W | 122 (4) |
| N4—Co1—N2$^{iii}$ | 102.68 (14) | Gd2—O2W—H4W | 127 (3) |
| N4—Co1—O6$^{iii}$ | 169.67 (13) | H3W—O2W—H4W | 108 (3) |
| N2$^{iii}$—Co1—O6$^{iii}$ | 78.43 (12) | Co1—O3W—H5W | 120 (4) |
| N4—Co1—O4W | 100.20 (15) | Co1—O3W—H6W | 121 (4) |
| N2$^{iii}$—Co1—O4W | 92.40 (14) | H5W—O3W—H6W | 102 (3) |
| O6$^{iii}$—Co1—O4W | 89.98 (14) | Co1—O4W—H7W | 121 (4) |
| N4—Co1—O3W | 94.51 (14) | Co1—O4W—H8W | 113 (4) |
| N2$^{iii}$—Co1—O3W | 160.56 (13) | H7W—O4W—H8W | 104 (3) |
| O6$^{iii}$—Co1—O3W | 83.04 (12) | H9W—O5W—H10W | 110 (3) |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1$^{iv}$ | 0.87 (4) | 1.96 (4) | 2.820 (5) | 172 (5) |
| O1W—H1W···O5W$^{v}$ | 0.81 (4) | 1.95 (3) | 2.745 (5) | 169 (6) |
| N3—H2···O14$^{vi}$ | 0.87 (3) | 1.93 (3) | 2.787 (4) | 169 (4) |
| O2W—H3W···O1$^{iv}$ | 0.80 (3) | 2.09 (4) | 2.878 (5) | 171 (5) |
| O2W—H4W···O14$^{iv}$ | 0.81 (4) | 2.04 (4) | 2.842 (5) | 172 (5) |
| O2W—H4W···O15$^{iv}$ | 0.81 (4) | 2.52 (4) | 3.035 (5) | 123 (4) |
| O3W—H5W···O12$^{vii}$ | 0.82 (3) | 1.95 (4) | 2.734 (4) | 162 (5) |
| O3W—H6W···O14$^{ii}$ | 0.83 (3) | 2.41 (4) | 2.919 (4) | 120 (3) |
| O4W—H7W···O3$^{iii}$ | 0.82 (3) | 2.49 (3) | 3.306 (6) | 174 (6) |
| O4W—H8W···O5W$^{vi}$ | 0.82 (5) | 1.89 (5) | 2.700 (6) | 175 (6) |
| O5W—H9W···O12$^{ii}$ | 0.85 (4) | 1.99 (4) | 2.797 (6) | 161 (5) |
| O5W—H10W···O1$^{iv}$ | 0.85 (5) | 1.93 (5) | 2.728 (5) | 157 (6) |
| C3—H3···O3$^{viii}$ | 0.93 | 2.44 | 3.193 (5) | 138. |

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

**Fig. 1**

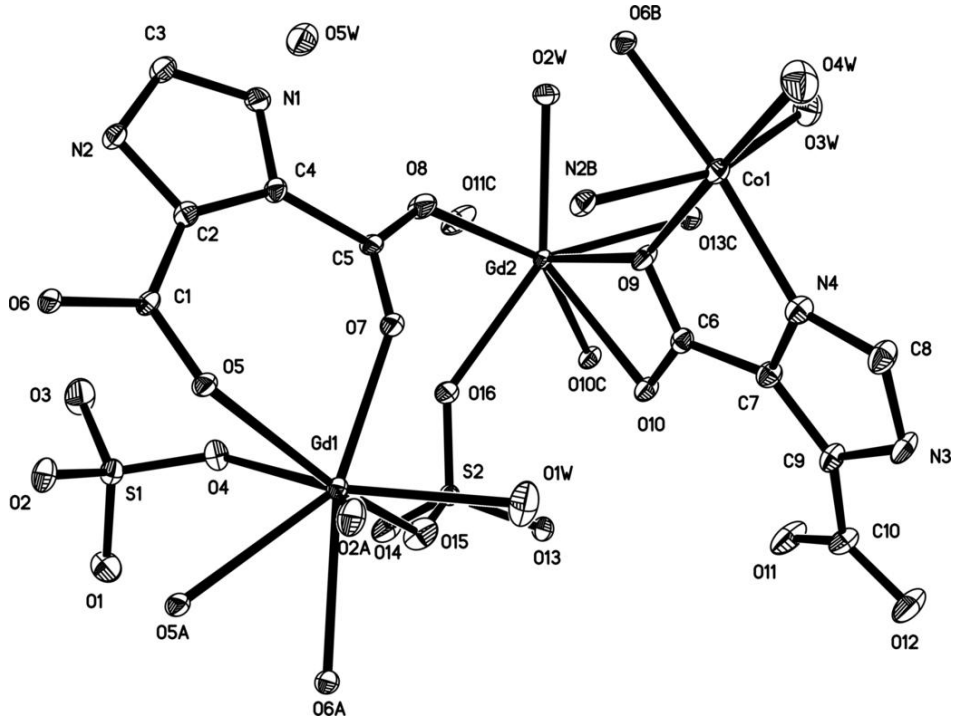
C3
O5W
O6B
O2W
O4W
N1
N2
C4
O8
O11C
N2B
Co1
O3W
C2
C5
Gd2
O13C
O9
N4
O6
C1
O7
C6
C8
O5
O3
O16
O10C
O10
C7
Gd1
S2
O1W
C9
N3
O2
S1
O4
O2A
O14
O15
O13
C10
O1
O11
O5A
O12
O6A

**Fig. 2**