

# Hexaaquacobalt(II) ( $\mu_2$ -triethylene-tetraminehexaacetato)diaquadacobalt(II) tetrahydrate

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

$R$  factor = 0.054

$wR$  factor = 0.127

Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex,  $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (TTHAH<sub>6</sub> = triethylenetetraminehexaacetic acid), consists of discrete  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations and  $[\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2]^{2-}$  binuclear anionic units. Each Co(II) ion in the binuclear units is coordinated by one water and half a TTHA<sup>6-</sup> anion as a pentadentate ligand, giving a distorted octahedral arrangement. The  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cation lies on a center of inversion in the crystal and exhibits strong hydrogen-bond interactions with four carboxylate groups from the TTHA<sup>6-</sup> ligand and the water molecules, leading to the formation of a three-dimensional network.

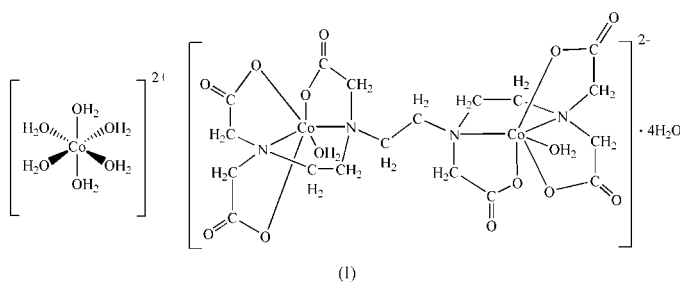
Received 8 August 2003

Accepted 3 September 2003

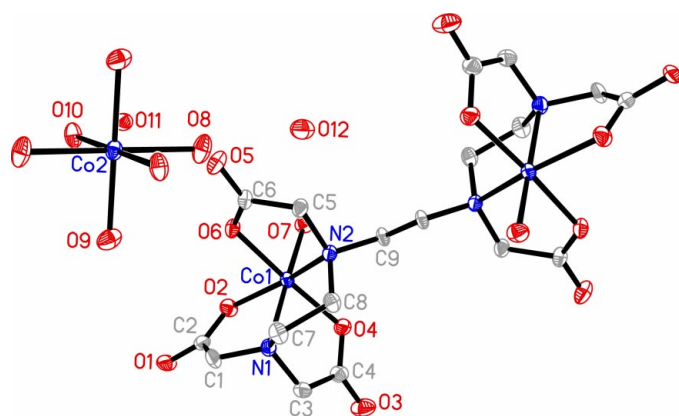
Online 11 September 2003

## Comment

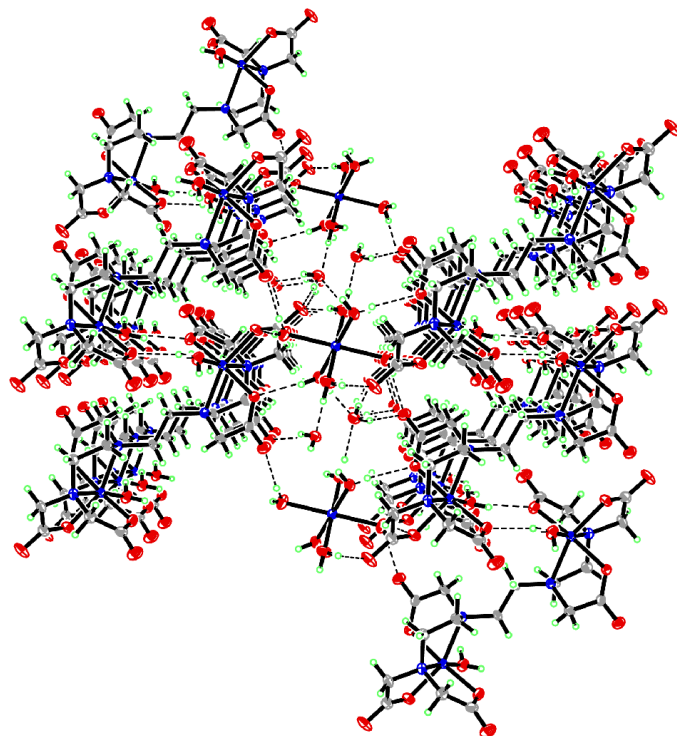
Polyoxometalate magnetic clusters, as candidates for single-molecule magnets (SMMs), have attracted considerable interest for their applications in magnetism and materials chemistry (Beattie *et al.*, 1998; Brechin *et al.*, 2002). TTHAH<sub>6</sub> (triethylenetetraminehexaacetic acid), as a multidentate ligand with ten potential coordinating sites, can play an important role in the self-assembly of magnetic molecules. In an effort to synthesize oligomeric Co–O cluster compounds by the hydrothermal reaction of  $\text{Co}(\text{OH})_2$ ,  $\text{CF}_3\text{COOH}$  and TTHAH<sub>6</sub> in water, a new polyoxometalate compound,  $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ , (I), was isolated. We report here its synthesis and crystal structure.



The crystal structure of (I) is composed of discrete  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations and  $[\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2]^{2-}$  binuclear anionic units, as shown in Fig. 1. The  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations exhibit a distorted octahedral arrangement in which the Co(II) atom is coordinated by six water O atoms. The Co–O bond lengths range from 2.044 (4) to 2.120 (4) Å. The binuclear anion  $[\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2]^{2-}$  is centrosymmetric with the midpoint of the ethylene C–C bond on an inversion center, the same arrangement as in  $[\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}_2(\text{TTHA})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (Li *et al.*, 1999) and similar to that in  $[\text{Cr}_2(\text{TTHA})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (Fallon & Gatehouse, 1974). Each



**Figure 1**  
ORTEP drawing of the title compound, showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.



**Figure 2**  
Packing diagram, viewed along the *b* axis, showing the hydrogen-bond interactions as dashed lines.

Co(II) ion in  $[\text{Co}_2(\text{TTHA})(\text{H}_2\text{O})_2]^{2-}$  has a distorted octahedral geometry and is bonded to two N atoms and three carboxylate O atoms from half of the  $\text{TTHA}^{6-}$  ligand, as well as one water molecule. The Co1–N1 and Co1–N2 bond lengths are 2.148 (4) and 2.205 (4) Å, respectively, and the Co–O distances are in the range 2.054 (4)–2.102 (3) Å. There are hydrogen-bond interactions (average O...O distance 2.791 Å) between the O atoms of the four carboxylate groups from the  $\text{TTHA}^{6-}$  ligand and the water molecules, leading to a three-dimensional array, as shown in Fig. 2. The distances and

angles around Co are listed in Table 1 and the hydrogen-bond interactions are given in Table 2.

## Experimental

A mixture of  $\text{Co}(\text{OH})_2$  (0.186 g, 2 mmol),  $\text{TTHAH}_6$  (0.202 g, 0.5 mmol),  $\text{CF}_3\text{COOH}$  (0.077 ml, 0.1 mol) and  $\text{H}_2\text{O}$  (10 ml) was sealed in a 25 ml stainless-steel reactor with a Teflon liner. The reaction system was heated at 443 K for 72 h. After slow cooling to room temperature, purple crystals were collected by filtration.

### Crystal data

$[\text{Co}(\text{H}_2\text{O})_6]\text{Co}_2(\text{C}_{18}\text{H}_{28}\text{N}_4\text{O}_{14}) \cdot 4\text{H}_2\text{O}$   
 $M_r = 881.39$   
 Triclinic,  $P\bar{1}$   
 $a = 7.3671$  (2) Å  
 $b = 8.6295$  (4) Å  
 $c = 15.0272$  (7) Å  
 $\alpha = 73.543$  (2)°  
 $\beta = 83.409$  (3)°  
 $\gamma = 70.465$  (2)°  
 $V = 863.26$  (6) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.695$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1425 reflections  
 $\theta = 1.4\text{--}25.0^\circ$   
 $\mu = 1.52$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Rectangular parallelepiped, purple  
 0.52 × 0.20 × 0.10 mm

### Data collection

Bruker SMART CCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.609$ ,  $T_{\text{max}} = 0.859$   
 4522 measured reflections

3009 independent reflections  
 2629 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 25.1^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -8 \rightarrow 10$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.127$   
 $S = 1.06$   
 3009 reflections  
 259 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 5.0398P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.53$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co2–O9	2.044 (4)	Co1–O4	2.062 (4)
Co2–O10	2.097 (4)	Co1–O6	2.102 (3)
Co2–O8	2.120 (4)	Co1–N1	2.148 (4)
Co1–O2	2.054 (4)	Co1–N2	2.205 (4)
Co1–O7	2.062 (4)	C9–C9 <sup>i</sup>	1.526 (9)
O9–Co2–O10	90.84 (18)	O2–Co1–N2	156.56 (16)
O9–Co2–O8	91.8 (2)	O7–Co1–N2	101.78 (17)
O10–Co2–O8	98.25 (16)	O4–Co1–N2	96.53 (15)
O2–Co1–O7	95.27 (17)	O6–Co1–N2	78.88 (14)
O2–Co1–O4	98.33 (16)	N1–Co1–N2	84.07 (16)
O7–Co1–O4	93.62 (16)	C4–O4–Co1	115.8 (3)
O2–Co1–O6	86.14 (14)	C1–N1–Co1	105.4 (3)
O7–Co1–O6	87.02 (16)	C3–N1–Co1	107.7 (3)
O4–Co1–O6	175.40 (15)	C7–N1–Co1	105.2 (3)
O2–Co1–N1	80.23 (16)	C2–O2–Co1	116.0 (3)
O7–Co1–N1	173.02 (18)	C5–N2–Co1	109.1 (3)
O4–Co1–N1	81.83 (16)	C9–N2–Co1	109.0 (3)
O6–Co1–N1	97.93 (16)	C8–N2–Co1	103.6 (3)

Symmetry code: (i)  $2 - x, 3 - y, 2 - z$ .

**Table 2**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O9—H9C...O1 <sup>ii</sup>	0.84 (6)	1.89 (7)	2.717 (6)	172 (6)
O8—H8C...O2 <sup>ii</sup>	0.90 (2)	2.06 (2)	2.953 (6)	172 (5)
O12—H12A...O3 <sup>iii</sup>	0.85 (6)	2.05 (6)	2.895 (8)	174 (6)
O11—H11A...O1 <sup>iii</sup>	0.77 (6)	1.92 (7)	2.682 (6)	169 (7)
O10—H10B...O6 <sup>iv</sup>	0.77 (6)	2.02 (6)	2.783 (5)	170 (6)
O9—H9D...O11 <sup>iv</sup>	0.85 (6)	1.87 (7)	2.714 (6)	175 (6)

Symmetry codes: (ii)  $1+x, y, z$ ; (iii)  $1+x, y-1, z$ ; (iv)  $2-x, 3-y, 1-z$ .

H atoms bonded to C atoms were positioned geometrically (C—H 0.97 Å). The *U* values of the H atoms were set to  $1.2(U_{\text{eq}})$  of the parent atom. Water H atoms were located in a difference map and their positions refined. Three O—H distances were restrained [O12—H12B 0.85 (2), O8—H8C 0.92 (2), O10—H10A 0.82 (2)]. O—H bond lengths are in the range 0.76 to 0.90 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *XPREP* in *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *XS* in

*SHELXTL*; program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XL* in *SHELXTL*.

The authors acknowledge financial support of the Natural Science Foundation of China (No.20201010), the Natural Science Foundation of Fujian Province of China (No.E0220003/E0310030), the Ministry of Education, and the Ministry of Personnel of China.

## References

- Beattie, J. K., Hambley, T. W., Klepetko, J. A., Masters, A. F. & Turner, P. (1998). *Chem. Commun.* pp. 45–46.
- Brechin, E. K., Cardor, O., Caneschi, A., Cadiou, C., Harris, S. G., Parsons, S., Vonci, M. & Winpenny, R. E. P. (2002). *Chem. Commun.* pp. 1860–1861.
- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Fallon, G. D. & Gatehouse, B. M. (1974). *Acta Cryst.* **B30**, 1987–1992.
- Li, D. F., Liao, Z. R., Xiong, Y. (1999). *Acta Cryst.* **C55**, IUCr9900058.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA.