

## Poly[triaqua-hexa- $\mu$ -cyanido-terbium(III)-trisilver(I)]: a 4f–4d bimetallic coordination polymer

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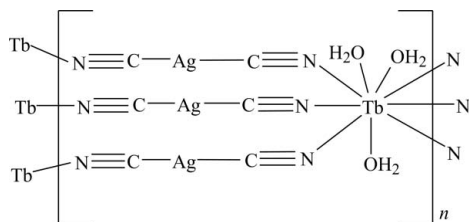
Received 30 May 2007; accepted 13 June 2007

Key indicators: single-crystal X-ray study;  $T = 290$  K; mean  $\sigma(\text{N}-\text{C}) = 0.006$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.047; data-to-parameter ratio = 10.8.

The title compound,  $[\text{Ag}_3\text{Tb}(\text{CN})_6(\text{H}_2\text{O})_3]_n$ , consists of hydrated  $\text{Tb}^{3+}$  cations that are linked with dicyanoargentate anions into a three-dimensional network. The resultant  $\text{TbN}_6\text{O}_3$  coordination polyhedra have a tricapped trigonal prismatic geometry. Six N atoms from the dicyanoargentate groups form the corners of the trigonal prisms, while the O atoms of three water molecules reside in the capping positions to complete the coordination environment around terbium. Argentophilic interactions give rise to a two-dimensional network of Ag atoms. All of the atoms in the structure are located on special crystallographic positions. Only one unique atom of each type is found in the structure. The site symmetry of each is: Tb ( $\bar{6}2m$ ), Ag ( $2/m$ ), C ( $m$ ), N ( $m$ ), O ( $m2m$ ) and H ( $m$ ).

### Related literature

The title compound is isostructural with the previously reported gold analog,  $\text{Tb}[\text{Au}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$  (Tanner *et al.*, 2005). These compounds adopt the  $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$  structure type (Assefa *et al.*, 1994, 1995), which has also been reported for several other tris(dicyanoargentate)lanthanide trihydrates or tris(dicyanoaurate)lanthanide trihydrates (Colis, Larochele *et al.*, 2005). Detailed spectroscopic properties have been reported for the title compound (Rawashdeh-Omary *et al.*, 2000; Tanner *et al.*, 2005). For related literature, see: Ahrland *et al.* (1985); Colis, Staples *et al.* (2005).



### Experimental

#### Crystal data

$[\text{Ag}_3\text{Tb}(\text{CN})_6(\text{H}_2\text{O})_3]$   
 $M_r = 692.70$   
 Hexagonal,  $P6_3/mcm$   
 $a = 6.6692$  (11) Å  
 $c = 18.371$  (2) Å  
 $V = 707.63$  (19) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 9.04$  mm<sup>-1</sup>  
 $T = 290$  (2) K  
 $0.29 \times 0.14 \times 0.10$  mm

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 Absorption correction: analytical (*XPREP*; Bruker, 2000)  
 $T_{\min} = 0.320$ ,  $T_{\max} = 0.438$   
 849 measured reflections

260 independent reflections  
 226 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 3%

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.047$   
 $S = 1.14$   
 260 reflections

24 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.68$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.51$  e Å<sup>-3</sup>

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2007).

The authors gladly acknowledge the Department of Energy and Oak Ridge National Laboratory for the loan of an Enraf–Nonius CAD-4 X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2030).

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**supplementary materials**

*Acta Cryst.* (2007). E63, i162 [ doi:10.1107/S1600536807029133 ]

## Poly[triaqua-hexa- $\mu$ -cyanido-terbium(III)trisilver(I)]: a 4f-4d bimetallic coordination polymer

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### Comment

Compounds containing lanthanide ions and dicyanometallate (*e.g.* dicyanoargentate, dicyanoaurate) anions have been extensively studied in recent years due to the interesting structural and optical properties of these systems (Tanner *et al.*, 2005; Colis & Staples *et al.*, 2005). It has been shown in both Tb[Ag(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O and Tb[Au(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O that donor-acceptor energy transfer processes occur. In these systems, exclusive excitation of the donor dicyanoaurate or dicyanoargentate moieties leads to sensitized luminescence from the acceptor Tb(III) (Rawashdeh-Omary *et al.*, 2000; Tanner *et al.*, 2005). The sensitized luminescence is reportedly much stronger in Tb[Ag(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O than in Tb[Au(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O due to a larger spectral overlap between the [Ag(CN)<sub>2</sub><sup>-</sup>] emission and the Tb(III) absorption (Rawashdeh-Omary *et al.*, 2000). However, while the structure of Tb[Au(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O has been previously reported (Tanner *et al.*, 2005), the structure of Tb[Ag(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O has not. For this reason, a structural study of the title compound was undertaken.

Fig. 1 shows the coordination geometry around the terbium atom and the atomic labeling scheme. The environment of the Tb ion consists of six N-bound CN<sup>-</sup> groups coordinated approximately end-on, resulting in a trigonal prismatic arrangement. Only the N atoms are shown in Fig. 1, but the overall cyanide coordination is clearly evident in the packing diagram shown in Fig. 2. Three water molecules cap the three rectangular faces of the prism. The result is a tricapped trigonal prismatic coordination geometry around the Tb<sup>3+</sup> with a *D*<sub>3h</sub> site symmetry. The three O atoms of the water molecules are coplanar with the Tb atom, by symmetry. Each silver atom is coordinated to the carbon atoms of two cyanide anions, resulting in nearly linear Ag(CN)<sub>2</sub><sup>-</sup> units as found in other dicyanoargentates. This arrangement is shown in the packing diagram of Fig. 2. In the structure, the [TbN<sub>6</sub>O<sub>3</sub>] polyhedra are arranged in layers found in the crystallographic *ab* plane. As shown in Fig. 2, these alternating layers of Ag atoms and Tb polyhedra are bridged with cyanide linkages resulting in an overall three-dimensional framework. The silver atoms form a Kagomé lattice, also found in the *ab* plane, that separates the layers of terbium polyhedra. Every Ag atom has four nearest Ag neighbors, with a uniform Ag...Ag separation of 3.3346 (5) Å. The overall structural features are unchanged in the title compound as compared with the isostructural Tb[Au(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O. The title compound contains a larger cell volume than Tb[Au(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O due largely to the greater Ag...Ag separation as compared to the shorter Au...Au separation of 3.31 (1) Å (Tanner *et al.*, 2005). This is consistent with the well established observation that aurophilic interactions are stronger than argentophilic interactions (Ahrland *et al.*, 1985).

### Experimental

Tb(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (99.9%) and KAg(CN)<sub>2</sub> (99.9%) were purchased from Alfa Aesar. An aqueous Tb<sup>3+</sup> solution (0.13 M) was prepared from the Tb(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O. The reaction involved placing a sealed quartz tube containing 0.10 ml of the aqueous Tb<sup>3+</sup> solution and 7.7 mg (39 μmol) of the KAg(CN)<sub>2</sub> into a preheated box oven. The tube was left in the oven at 393 K for 3 d. Colorless single crystals of Tb[Ag(CN)<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O in the form of hexagonal plates were isolated as the sole solid product contained in a colorless mother liquor. The observed yield was 51%.

## Refinement

The unique H-atom in the structure was located in a Fourier difference map and then fixed at a distance of 0.85 Å from the oxygen atom. The coordinates of the H atom were restrained to ensure a reasonable geometry for the water molecule and  $U_{\text{iso}}(\text{H})$  was fixed at  $1.2U_{\text{eq}}(\text{O})$ .

## Figures

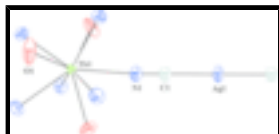


Fig. 1. An illustration of the coordination environment around the terbium and silver atoms. 50% thermal ellipsoids are shown.



Fig. 2. A view of the packing diagram of **I** viewed perpendicular to the *c* axis. Hydrogen atoms not shown.

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### Crystal data

$[\text{Ag}_3\text{Tb}(\text{CN})_6(\text{H}_2\text{O})_3]$

$M_r = 692.70$

Hexagonal,  $P6_3/mcm$

Hall symbol: -P 6c 2

$a = 6.6692(11) \text{ \AA}$

$b = 6.6692(11) \text{ \AA}$

$c = 18.371(2) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 707.63(19) \text{ \AA}^3$

$Z = 2$

$F_{000} = 628$

$D_x = 3.251 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8.3\text{--}21.1^\circ$

$\mu = 9.04 \text{ mm}^{-1}$

$T = 290(2) \text{ K}$

Prism, colorless

$0.29 \times 0.14 \times 0.10 \text{ mm}$

### Data collection

Enraf-Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 290(2) \text{ K}$

$\theta/2\theta$  scans

Absorption correction: analytical  
(XPREP; Bruker, 2000)

$R_{\text{int}} = 0.056$

$\theta_{\text{max}} = 25.3^\circ$

$\theta_{\text{min}} = 2.2^\circ$

$h = 0 \rightarrow 6$

$k = 0 \rightarrow 6$

$l = -22 \rightarrow 22$

$T_{\min} = 0.320$ ,  $T_{\max} = 0.438$   
 849 measured reflections  
 260 independent reflections  
 226 reflections with  $I > 2\sigma(I)$

3 standard reflections  
 every 120 min  
 intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.019$$

$$wR(F^2) = 0.047$$

$$S = 1.14$$

260 reflections

24 parameters

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

$$w = 1/[\sigma^2(F_o^2) + (0.0134P)^2 + 0.104P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL97,  
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0152 (8)

### 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Tb1	1.0000	0.0000	0.2500	0.0141 (3)
Ag1	0.5000	0.0000	0.0000	0.0364 (3)
N1	0.7414 (6)	0.0000	0.1502 (2)	0.0287 (9)
C1	0.6558 (8)	0.0000	0.0970 (2)	0.0277 (11)
O1	1.3630 (8)	0.0000	0.2500	0.0471 (16)
H1	1.4199	0.0000	0.2086	0.057*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Tb1	0.0161 (3)	0.0161 (3)	0.0101 (3)	0.00803 (15)	0.000	0.000
Ag1	0.0416 (4)	0.0406 (5)	0.0265 (3)	0.0203 (2)	-0.01559 (18)	0.000

## supplementary materials

N1	0.0273 (16)	0.038 (3)	0.0243 (18)	0.0190 (13)	-0.0030 (15)	0.000
C1	0.0262 (18)	0.033 (3)	0.026 (2)	0.0166 (15)	-0.0024 (18)	0.000
O1	0.041 (2)	0.097 (5)	0.022 (2)	0.049 (3)	0.000	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Tb1—O1	2.421 (5)	Ag1—Ag1 <sup>i</sup>	3.3346 (5)
Tb1—N1	2.517 (4)	N1—C1	1.132 (6)
Ag1—C1	2.063 (5)	O1—H1	0.8500
O1 <sup>ii</sup> —Tb1—O1 <sup>iii</sup>	120.000 (1)	N1 <sup>ii</sup> —Tb1—N1 <sup>v</sup>	139.92 (7)
O1 <sup>ii</sup> —Tb1—O1	120.000 (1)	O1 <sup>ii</sup> —Tb1—N1 <sup>vi</sup>	69.96 (3)
O1 <sup>iii</sup> —Tb1—O1	120.0	O1 <sup>iii</sup> —Tb1—N1 <sup>vi</sup>	133.26 (9)
O1 <sup>ii</sup> —Tb1—N1 <sup>iv</sup>	133.26 (9)	O1—Tb1—N1 <sup>vi</sup>	69.96 (3)
O1 <sup>iii</sup> —Tb1—N1 <sup>iv</sup>	69.96 (3)	N1 <sup>iv</sup> —Tb1—N1 <sup>vi</sup>	72.81 (14)
O1—Tb1—N1 <sup>iv</sup>	69.96 (3)	N1—Tb1—N1 <sup>vi</sup>	139.92 (7)
O1 <sup>ii</sup> —Tb1—N1	69.96 (3)	N1 <sup>iii</sup> —Tb1—N1 <sup>vi</sup>	93.48 (18)
O1 <sup>iii</sup> —Tb1—N1	69.96 (3)	N1 <sup>ii</sup> —Tb1—N1 <sup>vi</sup>	139.92 (7)
O1—Tb1—N1	133.26 (9)	N1 <sup>v</sup> —Tb1—N1 <sup>vi</sup>	72.81 (14)
N1 <sup>iv</sup> —Tb1—N1	139.92 (7)	C1—Ag1—C1 <sup>vii</sup>	180.00 (12)
O1 <sup>ii</sup> —Tb1—N1 <sup>iii</sup>	69.96 (3)	C1—Ag1—Ag1 <sup>i</sup>	104.59 (7)
O1 <sup>iii</sup> —Tb1—N1 <sup>iii</sup>	133.26 (9)	C1 <sup>vii</sup> —Ag1—Ag1 <sup>i</sup>	75.41 (7)
O1—Tb1—N1 <sup>iii</sup>	69.96 (3)	C1—Ag1—Ag1 <sup>viii</sup>	75.41 (7)
N1 <sup>iv</sup> —Tb1—N1 <sup>iii</sup>	139.92 (7)	C1 <sup>vii</sup> —Ag1—Ag1 <sup>viii</sup>	104.59 (7)
N1—Tb1—N1 <sup>iii</sup>	72.81 (14)	Ag1 <sup>i</sup> —Ag1—Ag1 <sup>viii</sup>	180.0
O1 <sup>ii</sup> —Tb1—N1 <sup>ii</sup>	133.26 (9)	C1—Ag1—Ag1 <sup>ix</sup>	75.41 (7)
O1 <sup>iii</sup> —Tb1—N1 <sup>ii</sup>	69.96 (3)	C1 <sup>vii</sup> —Ag1—Ag1 <sup>ix</sup>	104.59 (7)
O1—Tb1—N1 <sup>ii</sup>	69.96 (3)	Ag1 <sup>i</sup> —Ag1—Ag1 <sup>ix</sup>	60.0
N1 <sup>iv</sup> —Tb1—N1 <sup>ii</sup>	93.48 (18)	Ag1 <sup>viii</sup> —Ag1—Ag1 <sup>ix</sup>	120.0
N1—Tb1—N1 <sup>ii</sup>	72.81 (14)	C1—Ag1—Ag1 <sup>x</sup>	104.59 (7)
N1 <sup>iii</sup> —Tb1—N1 <sup>ii</sup>	72.81 (14)	C1 <sup>vii</sup> —Ag1—Ag1 <sup>x</sup>	75.41 (7)
O1 <sup>ii</sup> —Tb1—N1 <sup>v</sup>	69.96 (3)	Ag1 <sup>i</sup> —Ag1—Ag1 <sup>x</sup>	120.0
O1 <sup>iii</sup> —Tb1—N1 <sup>v</sup>	69.96 (3)	Ag1 <sup>viii</sup> —Ag1—Ag1 <sup>x</sup>	60.0
O1—Tb1—N1 <sup>v</sup>	133.26 (9)	Ag1 <sup>ix</sup> —Ag1—Ag1 <sup>x</sup>	180.0
N1 <sup>iv</sup> —Tb1—N1 <sup>v</sup>	72.81 (14)	C1—N1—Tb1	167.0 (4)
N1—Tb1—N1 <sup>v</sup>	93.48 (18)	N1—C1—Ag1	180.0 (4)
N1 <sup>iii</sup> —Tb1—N1 <sup>v</sup>	139.92 (7)	Tb1—O1—H1	116.5

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

Fig. 1

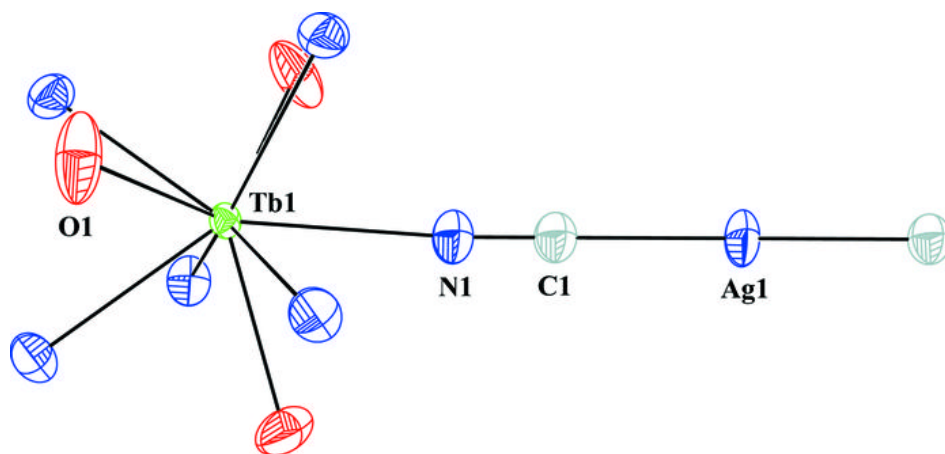


Fig. 2

