

## A coordination polymer of thallium(III) nitrate with 4,4'-bipyridine *N,N'*-dioxide

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### Key indicators

Single-crystal X-ray study  
 $T = 203\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$   
 Disorder in main residue  
 $R$  factor = 0.036  
 $wR$  factor = 0.107  
 Data-to-parameter ratio = 16.1

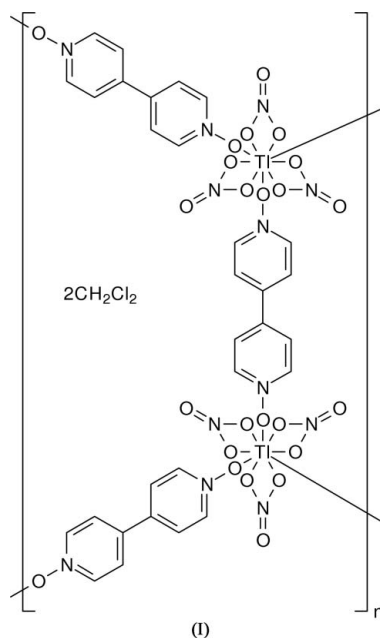
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, poly[[tris( $\mu_2$ -4,4'-bipyridine *N,N'*-dioxide)bis[trinitratothallium(III)]] dichloromethane disolvate],  $[\text{Tl}_2(\text{NO}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_3] \cdot 2\text{CH}_2\text{Cl}_2$ , forms a ladder polymer with channels which accommodate the  $\text{CH}_2\text{Cl}_2$  solvent molecules.

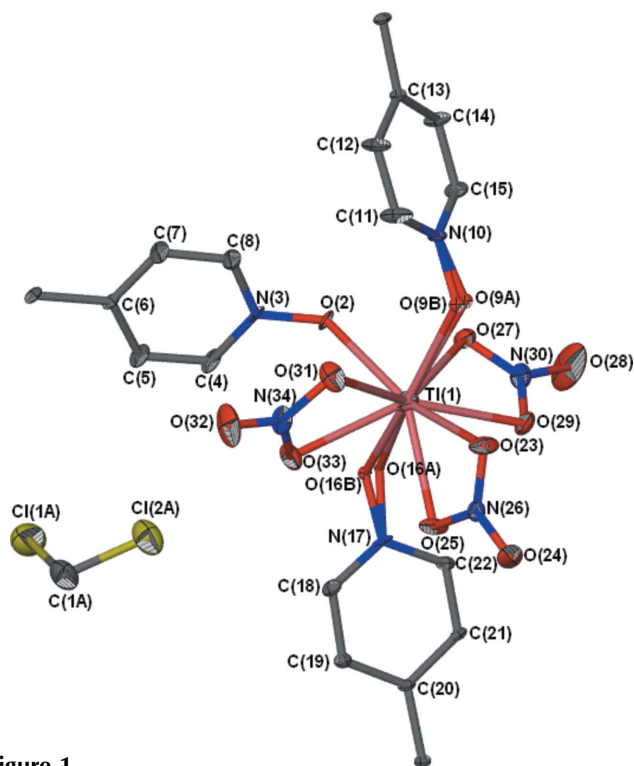
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### Comment

The construction of coordination polymers of different metals continues to be an area of special interest in crystal engineering. Recent examples have afforded interesting open-framework metal-organic structures (Biradha & Fujita, 2000; Eddaoudi *et al.*, 2001; Vujovic *et al.*, 2003). Various coordination polymers of bipyridyl ligands with lanthanides (Long *et al.*, 2002; Min & Lee, 2002; Dalgarno *et al.*, 2004; Dalgarno *et al.*, 2005) and transition metals (Aragoni *et al.*, 2005; Ghosh *et al.*, 2005; Ma *et al.*, 2005) have recently been reported. We report here the structure of a coordination polymer, (I), of  $\text{Tl}(\text{NO}_3)_3$  with 4,4'-bipyridine *N,N'*-dioxide (bpdo) as a bridging ligand; Fig. 1 shows the asymmetric unit. This structure is analogous to the terbium(III) compound reported by Long *et al.* (2002).



Compound (I) comprises a ladder-shaped coordination polymer (Fig. 2), forming channels which accommodate  $\text{CH}_2\text{Cl}_2$  guest molecules (Fig. 3). The guest position is stabilized by weak hydrogen bonds to polymer nitrate O atoms (Table 1), while the ladder-shaped polymer chains stack above



**Figure 1**

The asymmetric unit of the structure. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Both components are shown for the disordered atoms.

one another, also stabilized by C—H···O hydrogen bonds (Table 1). Bridging bpdpo ligands form both the uprights and the rungs of the ladder, while all nitrate ligands are bidentate, giving nine-coordinate Ti.

## Experimental

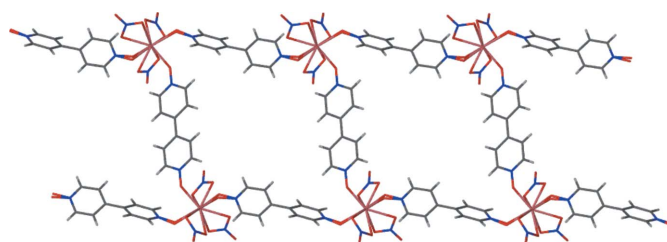
Compound (I) was prepared by layering an ethanol solution of 4,4'-bipyridine *N,N'*-dioxide (0.10 mmol) on top of a layer of CH<sub>2</sub>Cl<sub>2</sub> in which 0.05 mmol of Ti(NO<sub>3</sub>)<sub>3</sub> had been placed (but not fully dissolved). The layers mixed over several days at ambient temperature and crystals grew at the interface.

### Crystal data

[Ti <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> (C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub>	<i>Z</i> = 1
<i>M<sub>r</sub></i> = 1515.22	<i>D<sub>x</sub></i> = 2.121 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.0425 (16) Å	Cell parameters from 35318 reflections
<i>b</i> = 11.687 (2) Å	<i>θ</i> = 1.0–27.5°
<i>c</i> = 13.079 (3) Å	<i>μ</i> = 7.11 mm <sup>-1</sup>
<i>α</i> = 86.51 (3)°	<i>T</i> = 203 (2) K
<i>β</i> = 79.83 (3)°	Block, colorless
<i>γ</i> = 78.75 (3)°	0.15 × 0.10 × 0.08 mm
<i>V</i> = 1186.3 (4) Å <sup>3</sup>	

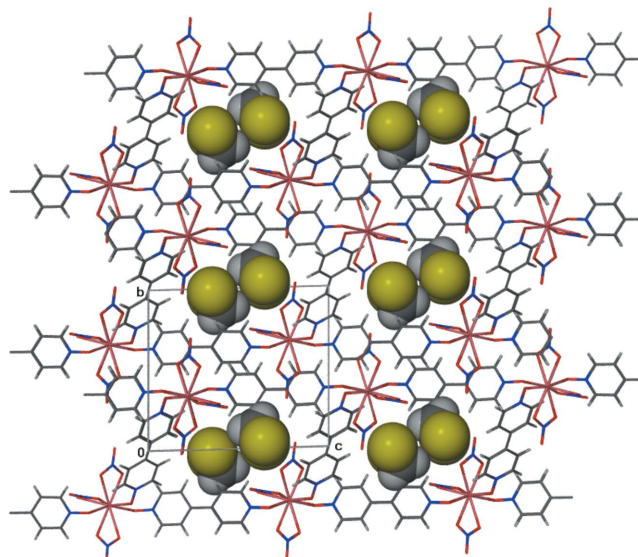
### Data collection

Nonius KappaCCD diffractometer	4847 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>ω</i> and <i>φ</i> scans	<i>R</i> <sub>int</sub> = 0.038
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	<i>θ</i> <sub>max</sub> = 27.5°
<i>T</i> <sub>min</sub> = 0.435, <i>T</i> <sub>max</sub> = 0.560	<i>h</i> = -10 → 10
35318 measured reflections	<i>k</i> = -15 → 15
5387 independent reflections	<i>l</i> = -16 → 16



**Figure 2**

The ladder polymeric structure. Solvent molecules are not shown.



**Figure 3**

The packing of compound (I), viewed along [100], showing guest molecules residing in the channels. CH<sub>2</sub>Cl<sub>2</sub> guests are represented by van der Waals radii.

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.107  
*S* = 1.06  
 5387 reflections  
 334 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 7.0981P]$$

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

$$(\Delta\sigma)_{\max} = 0.008$$

$$\Delta\rho_{\max} = 1.40 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.71 \text{ e } \text{Å}^{-3}$$

**Table 1**

Hydrogen-bond 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>
C1A—H1A···O28 <sup>i</sup>	0.98	2.46	3.292 (11)	143
C1A—H2A···O24 <sup>ii</sup>	0.98	2.52	3.148 (9)	122
C1A—H2A···O25 <sup>ii</sup>	0.98	2.58	3.362 (9)	137
C4—H13···O23 <sup>iii</sup>	0.94	2.42	3.100 (7)	129
C12—H16···O32 <sup>iv</sup>	0.94	2.55	3.119 (8)	120
C14—H18···O16A <sup>v</sup>	0.94	2.45	3.260 (17)	144

Symmetry codes: (i) *x* + 1, *y* - 1, *z*; (ii) -*x* + 1, -*y*, -*z* + 1; (iii) *x* + 1, *y*, *z*; (iv) -*x* + 1, -*y*, -*z*; (v) -*x* + 1, -*y* + 1, -*z*.

The pyridyl O atoms of one bpdpo ligand are disordered over two positions, with refined site-occupancy factors of 0.60:0.40 (12) and 0.60:0.40 (11); these disordered atoms were refined isotropically. H

atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.94 (aromatic) and 0.98 Å (solvent), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The largest residual electron-density peak is 0.44 Å from O9B, one of the disordered atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001) and *POV-RAY* (Persistence of Vision, 1999); software used to prepare material for publication: *SHELXL97*.

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## References

- Aragoni, M. C., Arca, M., Champness, N. R., De Pasquale, M., Devillanova, F. A., Isaia, F., Lippolis, V., Oxtoby, N. S. & Wilson, C. (2005). *CrystEngComm*, **7**, 363–369.
- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Biradha, K. & Fujita, M. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3805–3810.
- Dalgarno, S. J., Hardie, M. J., Atwood, J. L. & Raston, C. L. (2004). *Inorg. Chem.* **29**, 649–652.
- Dalgarno, S. J., Hardie, M. J., Atwood, J. L., Warren, J. E. & Raston, C. L. (2005). *New J. Chem.* **29**, 649–652.
- Eddaoudi, M., Kim, J., Wachter, J. B., Chae, H. K., O'Keeffe, M. & Yaghi, O. M. (2001). *J. Am. Chem. Soc.* **123**, 4368–4369.
- Ghosh, A. K., Ghoshai, D., Zangrando, E., Ribas, J. & Chaudhuri, N. R. (2005). *Inorg. Chem.* **44**, 1786–1793.
- Long, D.-L., Blake, A. J., Champness, N. R., Wilson, C. & Schröder, M. (2002). *Chem. Eur. J.* **8**, 2026–2033.
- Ma, B.-Q., Sun, H.-L. & Gao, S. (2005). *Inorg. Chem.* **44**, 837–839.
- Min, D. & Lee, S. W. (2002). *Bull. Korean Soc.* **23**, 948–952.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Persistence of Vision (1999). *POV-RAY*. Version 3.1e.watcom.win32. URL: <http://www.povray.org/>.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Vujovic, D., Raubenheimer, H. G. & Nassimbeni, L. R. (2003). *Dalton Trans.* pp. 631–637.