Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

catena-Poly[[tetrakis(hexamethylphosphoramide-κO)bis(nitrato-$\kappa^2 O,O'$)europium(III)] [silver(I)-di-μ-sulfido-tungstate(VI)(*Ag*—*W*)-di-μ-sulfido]]

Jinfang Zhang, Jun Qian, Yuan Cao and Chi Zhang*

Institute of Molecular Engineering and Advanced Materials, School of Chemical Engineering, Nanjing University of Science and Technology, 200 Xiaolingwei, Nanjing 210094, Jiangsu, People's Republic of China
Correspondence e-mail: chizhang@mail.njust.edu.cn

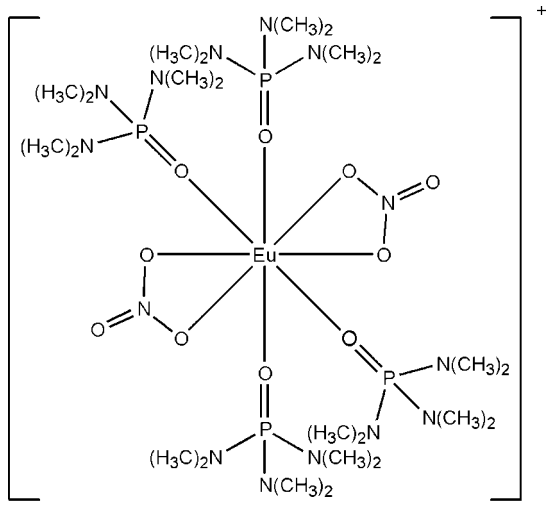
Received 31 July 2007; accepted 8 August 2007

Key indicators: single-crystal X-ray study; T = 153 K; mean σ(g–S) = 0.002 Å; R factor = 0.041; wR factor = 0.090; data-to-parameter ratio = 18.4.

Hexamethylphosphoramide (hmp), tetrathiotungstate, silver sulfide and europium nitrate were self-assembled to form a one-dimensional anionic $[AgWS_4]^-$ chain generated by the 2_1 symmetry operation, $\{[Eu(NO_3)_2(C_6H_{18}N_3OP)_4][WAgS_4]\}_n$. The central Eu in the cation is coordinated by eight O atoms from two nitrate and four hmp ligands, which gives rise to a distorted square-antiprismatic structure like those in the isostructural Yb and Y compounds. Parts of the dimethylamine groups from the hmp ligands have large librations. Together with the two nitrate ligands, the cation in the title compound is monovalent, which leads to the anionic chain having a monovalent repeat unit. This contrasts with solvent-coordinated rare-earth cations, which are trivalent and induce trivalent repeat units in the anionic chains. The polymeric anionic chain in the title compound, with W—Ag—W and Ag—W—Ag angles of 162.93 (2) and 154.250 (9)°, respectively, presents a distorted linear configuration, unlike those in $\{(\gamma\text{-MePyH})[WS_4Ag]\}_n$ and $\{[NH_3C(CH_2OH)_3][WS_4Ag]\text{-}(2DMF)\}_n$ (DMF is dimethylformamide), showing an ideal linear chain and a nearly linear chain, with W—Ag—W and Ag—W—Ag angles of 176.4 (5) and 176.4 (3)°, respectively. This fact suggests that cations with bigger bulk lead to more distorted anionic chains. At the same time, the anionic skeleton in the title compound is the same as those in $\{[M(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (M = Yb, Y), implying that different rare-earth cations with the same coordination environments have the same influence on the arrangement of their anionic skeletons.

Related literature

Examples of one-dimensional W/S/Ag anionic polymers with ideal and nearly linear configurations are $\{(\gamma\text{-MePyH})[WS_4Ag]\}_n$ (MePyH is protonated picoline; Lang *et al.*, 1993) and $\{[NH_3C(CH_2OH)_3][WS_4Ag](2DMF)\}_n$ (DMF is dimethylformamide; Huang *et al.*, 1997), respectively. Two more relevant analogs of the title compound are $\{[Yb(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Cao *et al.*, 2007) and $\{[Y(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Zhang, Cao *et al.*, 2007) (hmp is hexamethylphosphoramide), which have similar wave-like chains. $\{[Nd(DMF)_8][W_4S_{16}Ag_5]\}_n$ (Huang *et al.*, 1996) contains solvent-coordinated rare-earth cations leading to an anionic chain with a trivalent repeat unit. Polymeric Mo(W)/S/Ag(Cu) clusters have been reviewed by Niu *et al.* (2004, and references therein). The third-order nonlinear optical properties of Mo(W)/S/Ag(Cu) clusters are reviewed by Zhang, Song *et al.* (2007).



Experimental

Crystal data

$[Eu(NO_3)_2(C_6H_{18}N_3OP)_4][WAgS_4]$
M_r = 1412.79
Monoclinic, $P2_1/c$
a = 15.8182 (13) Å
b = 29.778 (2) Å
c = 11.4267 (9) Å
β = 90.934 (2)°
V = 5381.7 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.97 mm^{-1}
T = 153 (2) K
0.55 × 0.45 × 0.30 mm

Data collection

Rigaku Mercury CCD (2 × 2 bin mode) diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.139, T_{max} = 0.304
50038 measured reflections
9849 independent reflections
9106 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.090
S = 1.15
9849 reflections
535 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.99 e Å^{-3}

  doi:10.1107/S1600536807039293

Data collection: *CrystalClear* (Rigaku Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work is supported by the National Natural Science Foundation of China (No. 50472048) and the Program for New Century Excellent Talents in Universities (NCET-05-0499); JFZ thanks the Graduate Innovation Foundation of Jiangsu Province (No. xm04-46) and the Graduate Innovation Laboratory Center of Nanjing University of Science and Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2053).

References

Cao, Y., Zhang, J.-F., Qian, J. & Zhang, C. (2007). *Acta Cryst.* E**63**, m2076–m2077.
Huang, Q., Wu, X. T., Sheng, T. L., Wang, Q. M. & Lu, J. X. (1997). *Polyhedron* **16**, 217–222.
Huang, Q., Wu, X. T., Wang, Q. M., Sheng, T. L. & Lu, J. X. (1996). *Angew. Chem. Int. Ed.* **35**, 868–870.
Lang, J. P., Li, J. G., Bao, S. A., Xin, X. Q. & Yu, K. B. (1993). *Polyhedron*, **12**, 801–806.
Niu, Y. Y., Zheng, H. G., Hou, H. W. & Xin, X. Q. (2004). *Coord. Chem. Rev.* **248**, 169–183.
Rigaku Corporation (2000). *CrystalClear*. Version 1.3. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Zhang, C., Song, Y. L. & Wang, X. (2007). *Coord. Chem. Rev.* **251**, 111–141.
Zhang, J.-F., Cao, Y., Qian, J. & Zhang, C. (2007). *Acta Cryst.* E**63**, m2248–m2249.

supplementary materials

Acta Cryst. (2007). E**63**, m2386-m2387 [**doi:10.1107/S1600536807039293**]

catena-Poly[[tetrakis(hexamethylphosphoramide-κO)bis(nitrato-$\kappa^2 O,O'$)europium(III)] [silver(I)-di-μ-sulfido-tungstate(VI)(*Ag*-*W*)-di-μ-sulfido]]

J. Zhang, J. Qian, Y. Cao and C. Zhang

Comment

One-dimensional Mo(W)/S/Ag anionic polymers have attracted much attention for their configurational isomerism (Niu *et al.*, 2004) and unique properties as functional materials, such as third-order nonlinear optical (NLO) materials (Zhang, Song *et al.*, 2007, and references therein). Different solvent-coordinated rare-earth cations proved effective to obtain various configurations of anionic chains (Niu *et al.*, 2004). The title compound, $\{[Eu(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (hmp = hexamethylphosphoramide), with a wave-like anionic chain was prepared by following such route using Eu^{III}–hmp complex as counterion.

The cation in the title compound, where Eu^{3-} is coordinated by eight O atoms from two nitrate and four hmp ligands, has the same structure as those in the isostructural $\{[Yb(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Cao *et al.*, 2007) and $\{[Y(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Zhang, Cao *et al.*, 2007). Parts of dimethylamine groups from hmp ligands have large librations. In possession of two nitrate ligands, the cation in the title compound is monovalent (Fig. 1), which leads to an anionic chain with a monovalent repeat unit, unlike other solvent-coordinated rare-earth cations (Niu *et al.*, 2004), which are trivalent and induce trivalent repeat units. For example, $[Nd(dmf)_8]^{3+}$ induces an anionic chain with a trivalent repeat unit $[W_4S_{16}Ag_5]^{3-}$ (Huang *et al.*, 1996).

As illustrated in Fig. 2, the anionic chain in the title compound has a distorted linear configuration with W—Ag—W and Ag—W—Ag angles of 162.93 (2) and 154.250 (9)°, respectively, unlike those in $\{(\gamma\text{-MePyH})[WS_4Ag]\}_n$ (MePyH is protonated picoline; Lang *et al.*, 1993) and $\{[NH_3C(CH_2OH)_3][WS_4Ag](2DMF)\}_n$ (Huang *et al.*, 1997), showing an ideal linear chain and a nearly linear chain with W—Ag—W and Ag—W—Ag angles of 176.4 (5) and 176.4 (3)°, respectively. This fact suggests that cations with bigger bulk lead to more distorted anionic chains.

Similar angles of 160.81 (7) and 153.41 (7)° for W—Ag—W and Ag—W—Ag, respectively, are found in another two distorted linear chains in $\{[Yb(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Cao *et al.*, 2007) and $\{[Y(hmp)_4(NO_3)_2][WS_4Ag]\}_n$ (Zhang, Cao *et al.*, 2007), implying that different rare earth cations with the same coordination environments will result in the same anionic structures.

Experimental

1 mmol A g_2S was added to a solution of $[NH_4]_2WS_4$ (2 mmol in 30 mL h mp) with thorough stir for 12 h. The solution underwent an additional stir for one minute after 1 mmol $Eu(NO_3)_3{\cdot}6H_2O$ was added. After filtration the orange-red filtrate was carefully laid on the surface with 30 ml *i*-PrOH. Red block crystals were obtained after ten days. Yield: 1.291 g in pure form, 45.7% (based on W). Analysis calculated for $C_{24}H_{72}AgEuN_{14}O_{10}P_4S_4W$: C 20.40, H 5.14, N 13.88%; found: C 20.37, H 5.12, N 13.91%. IR: ν, cm^{-1}, 482.7 m, 446.6 s (W-μ_2-S).

Refinement

H atoms were positioned geometrically and refined with riding model, with $U_{iso} = 1.5U_{eq}$ for methyl H atoms and 0.98 Å for C—H bonds.

Figures

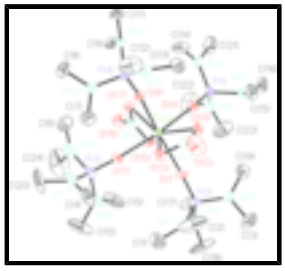


Fig. 1. The molecular structure of the cation in the title compound, with atom labels and 30% probability displacement ellipsoids. All H atoms have been omitted.

Fig. 2. The molecular structure of a portion of the anionic chain in the title compound, with atom labels and 30% probability displacement ellipsoids.

catena-Poly[[tetrakis(hexamethylphosphoramide-κ*O*)bis(nitrato-\ κ^2*O*,*O*')europium(III)] [silver(I)-di-μ-sulfido-tungstate(VI)(*Ag*—*W*)-di-μ-sulfido]]

Crystal data

$[Eu(NO_3)_2(C_6H_{18}N_3OP)_4][WAgS_4]$	$F_{000} = 2808.0$
$M_r = 1412.79$	$D_x = 1.744$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71070 Å
Hall symbol: -P 2ybc	Cell parameters from 20108 reflections
$a = 15.8182$ (13) Å	θ = 3.0–25.4º
$b = 29.778$ (2) Å	μ = 3.97 mm^{-1}
$c = 11.4267$ (9) Å	$T = 153$ (2) K
β = 90.934 (2)º	Block, red
$V = 5381.7$ (7) Å^3	0.55 × 0.45 × 0.30 mm
$Z = 4$	

Data collection

Rigaku Mercury CCD (2 × 2 bin mode) diffractometer	9849 independent reflections
Radiation source: fine-focus sealed tube	9106 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.047$
Detector resolution: 14.6306 pixels mm^{-1}	$\theta_{max} = 25.4$º
$T = 153(2)$ K	$\theta_{min} = 3.0$º
ω scans	$h = -18\rightarrow18$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -31\rightarrow35$

T_{min} = 0.139, T_{max} = 0.304
50038 measured reflections

l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.090
S = 1.15
9849 reflections
535 parameters
Primary atom site location: isomorphous structure methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 18.912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}
Extinction correction: none

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}
Eu1	0.237957 (17)	0.082979 (9)	0.83020 (2)	0.02536 (8)
P1	0.19588 (11)	−0.03010 (6)	0.69528 (15)	0.0405 (4)
P2	0.46094 (10)	0.09534 (6)	0.73359 (16)	0.0380 (4)
P3	0.29492 (13)	0.14797 (6)	1.10044 (16)	0.0499 (5)
P4	0.02042 (9)	0.13444 (6)	0.82420 (14)	0.0345 (4)
O1	0.3782 (2)	0.08073 (14)	0.7818 (4)	0.0410 (10)
O4	0.2074 (3)	0.01747 (13)	0.7293 (4)	0.0399 (10)
O8	0.1010 (2)	0.10817 (14)	0.8261 (4)	0.0344 (9)
O11	0.2732 (3)	0.12778 (14)	0.9851 (4)	0.0395 (10)
O12	0.2252 (5)	0.1724 (2)	0.5537 (5)	0.095 (2)
O13	0.2522 (3)	0.15902 (14)	0.7367 (4)	0.0436 (11)
O15	0.3007 (3)	0.02648 (15)	0.9710 (4)	0.0444 (11)
O16	0.2350 (4)	0.0010 (2)	1.1235 (5)	0.0717 (17)
O17	0.1680 (3)	0.04047 (15)	0.9930 (4)	0.0410 (10)
O19	0.2235 (3)	0.10444 (15)	0.6198 (4)	0.0454 (11)
N1	0.2603 (5)	−0.0660 (2)	0.7601 (6)	0.068 (2)

N2	0.2174 (4)	−0.0358 (2)	0.5567 (5)	0.0523 (15)
N3	0.1027 (5)	−0.0471 (3)	0.7327 (7)	0.081 (2)
N4	0.5348 (3)	0.0699 (2)	0.8040 (6)	0.067 (2)
N5	0.4855 (4)	0.1483 (2)	0.7383 (7)	0.071 (2)
N6	0.4597 (4)	0.0858 (3)	0.5925 (6)	0.071 (2)
N7	0.2770 (6)	0.2001 (2)	1.0988 (6)	0.083 (2)
N8	0.2390 (7)	0.1250 (3)	1.2012 (7)	0.103 (3)
N9	0.3937 (6)	0.1383 (3)	1.1331 (9)	0.115 (4)
N10	0.0224 (4)	0.1743 (2)	0.9212 (6)	0.0548 (16)
N11	0.0042 (4)	0.1578 (2)	0.6986 (5)	0.0588 (17)
N12	−0.0574 (3)	0.1001 (2)	0.8512 (5)	0.0414 (13)
N13	0.2340 (4)	0.1463 (2)	0.6344 (6)	0.0509 (15)
N14	0.2353 (4)	0.02194 (18)	1.0309 (5)	0.0451 (14)
C1	0.5132 (9)	0.1681 (4)	0.8488 (11)	0.147 (6)
H1A	0.5255	0.2001	0.8371	0.220*
H1B	0.5644	0.1528	0.8771	0.220*
H1C	0.4685	0.1649	0.9065	0.220*
C2	0.4540 (6)	0.1805 (4)	0.6513 (13)	0.137 (6)
H2A	0.4764	0.2105	0.6696	0.206*
H2B	0.3921	0.1813	0.6527	0.206*
H2C	0.4725	0.1715	0.5733	0.206*
C3	0.5320 (7)	0.0960 (6)	0.5201 (10)	0.140 (6)
H3A	0.5735	0.0717	0.5268	0.210*
H3B	0.5579	0.1242	0.5465	0.210*
H3C	0.5133	0.0990	0.4383	0.210*
C4	0.3065 (7)	0.2278 (3)	0.9985 (7)	0.074 (3)
H4A	0.2906	0.2592	1.0109	0.110*
H4B	0.2802	0.2168	0.9258	0.110*
H4C	0.3681	0.2255	0.9932	0.110*
C5	0.4336 (7)	0.0961 (4)	1.1182 (12)	0.120 (5)
H5A	0.4924	0.0979	1.1461	0.180*
H5B	0.4323	0.0880	1.0351	0.180*
H5C	0.4035	0.0732	1.1630	0.180*
C6	0.1481 (8)	0.1232 (5)	1.1876 (10)	0.115 (4)
H6A	0.1238	0.1088	1.2564	0.173*
H6B	0.1332	0.1058	1.1174	0.173*
H6C	0.1256	0.1537	1.1799	0.173*
C7	0.0897 (6)	0.2079 (3)	0.9205 (9)	0.080 (3)
H7A	0.0812	0.2293	0.9843	0.119*
H7B	0.0884	0.2239	0.8455	0.119*
H7C	0.1445	0.1931	0.9310	0.119*
C8	−0.0453 (5)	0.1845 (3)	1.0028 (8)	0.073 (2)
H8A	−0.0286	0.2100	1.0522	0.109*
H8B	−0.0556	0.1582	1.0523	0.109*
H8C	−0.0970	0.1920	0.9587	0.109*
C9	−0.0484 (4)	0.0666 (3)	0.9441 (7)	0.057 (2)
H9A	−0.1006	0.0490	0.9489	0.085*
H9B	−0.0376	0.0818	1.0190	0.085*
H9C	−0.0010	0.0466	0.9268	0.085*

C10	0.4501 (10)	0.1727 (6)	1.1869 (14)	0.185 (8)
H10A	0.5063	0.1598	1.2010	0.277*
H10B	0.4265	0.1827	1.2613	0.277*
H10C	0.4546	0.1985	1.1338	0.277*
C11	−0.1443 (4)	0.1096 (3)	0.8152 (7)	0.064 (2)
H11A	−0.1810	0.0850	0.8399	0.095*
H11B	−0.1476	0.1126	0.7298	0.095*
H11C	−0.1629	0.1377	0.8516	0.095*
C12	−0.0357 (6)	0.2023 (3)	0.6820 (10)	0.099 (4)
H12A	−0.0379	0.2096	0.5984	0.148*
H12B	−0.0024	0.2251	0.7240	0.148*
H12C	−0.0932	0.2016	0.7126	0.148*
C13	0.0173 (6)	0.1324 (4)	0.5934 (7)	0.097 (4)
H13A	0.0054	0.1514	0.5251	0.146*
H13B	−0.0207	0.1064	0.5921	0.146*
H13C	0.0761	0.1221	0.5915	0.146*
C14	0.0347 (5)	−0.0153 (3)	0.7535 (9)	0.082 (3)
H14A	−0.0162	−0.0317	0.7763	0.123*
H14B	0.0229	0.0018	0.6818	0.123*
H14C	0.0517	0.0053	0.8164	0.123*
C15	0.1975 (7)	−0.0008 (3)	0.4747 (7)	0.080 (3)
H15A	0.2153	−0.0098	0.3964	0.120*
H15B	0.2273	0.0268	0.4979	0.120*
H15C	0.1365	0.0047	0.4738	0.120*
C16	0.2237 (7)	−0.0813 (3)	0.5035 (8)	0.083 (3)
H16A	0.2376	−0.0784	0.4206	0.124*
H16B	0.1695	−0.0969	0.5107	0.124*
H16C	0.2681	−0.0984	0.5441	0.124*
C17	0.5220 (5)	0.0281 (3)	0.8643 (9)	0.085 (3)
H17A	0.5751	0.0187	0.9022	0.127*
H17B	0.5035	0.0051	0.8082	0.127*
H17C	0.4786	0.0321	0.9237	0.127*
C18	0.6243 (5)	0.0806 (5)	0.7837 (12)	0.144 (7)
H18A	0.6539	0.0844	0.8590	0.216*
H18B	0.6281	0.1085	0.7385	0.216*
H18C	0.6504	0.0560	0.7400	0.216*
C19	0.4087 (6)	0.0490 (4)	0.5441 (9)	0.087 (3)
H19A	0.4154	0.0479	0.4590	0.131*
H19B	0.3491	0.0540	0.5620	0.131*
H19C	0.4275	0.0205	0.5788	0.131*
C20	0.2500 (10)	0.2257 (4)	1.2042 (10)	0.136 (6)
H20A	0.2424	0.2574	1.1836	0.203*
H20B	0.2934	0.2231	1.2660	0.203*
H20C	0.1965	0.2135	1.2322	0.203*
C21	0.0789 (9)	−0.0953 (4)	0.7149 (11)	0.142 (6)
H21A	0.0215	−0.1002	0.7428	0.213*
H21B	0.1185	−0.1145	0.7587	0.213*
H21C	0.0813	−0.1026	0.6314	0.213*
C22	0.2524 (9)	−0.0824 (4)	0.8744 (11)	0.132 (5)

H22A	0.2995	−0.1028	0.8925	0.198*
H22B	0.1988	−0.0987	0.8810	0.198*
H22C	0.2535	−0.0573	0.9297	0.198*
C23	0.3489 (7)	−0.0687 (5)	0.7285 (13)	0.136 (5)
H23A	0.3820	−0.0477	0.7770	0.204*
H23B	0.3547	−0.0607	0.6458	0.204*
H23C	0.3695	−0.0993	0.7415	0.204*
C24	0.2820 (13)	0.1085 (6)	1.3115 (10)	0.200 (9)
H24A	0.2396	0.0960	1.3640	0.300*
H24B	0.3111	0.1336	1.3503	0.300*
H24C	0.3231	0.0852	1.2919	0.300*
W1	0.715479 (15)	0.228140 (8)	0.474607 (19)	0.02705 (7)
Ag1	0.71643 (4)	0.235706 (19)	0.21504 (4)	0.04964 (15)
S1	0.82933 (11)	0.21256 (7)	0.37402 (14)	0.0474 (4)
S2	0.60182 (11)	0.21406 (7)	0.36870 (14)	0.0475 (4)
S3	0.71359 (11)	0.18439 (5)	0.62998 (13)	0.0401 (4)
S4	0.71643 (13)	0.30024 (5)	0.51802 (14)	0.0461 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.02305 (15)	0.01944 (14)	0.03358 (16)	0.00003 (11)	0.00043 (11)	−0.00040 (11)
P1	0.0537 (10)	0.0286 (9)	0.0396 (9)	−0.0101 (8)	0.0113 (8)	−0.0095 (7)
P2	0.0238 (8)	0.0393 (9)	0.0510 (10)	−0.0004 (7)	0.0053 (7)	0.0072 (8)
P3	0.0700 (13)	0.0395 (10)	0.0395 (10)	−0.0077 (9)	−0.0207 (9)	−0.0011 (8)
P4	0.0258 (8)	0.0404 (9)	0.0371 (9)	0.0061 (7)	−0.0010 (6)	0.0072 (7)
O1	0.027 (2)	0.040 (3)	0.056 (3)	−0.0019 (19)	0.0067 (19)	0.008 (2)
O4	0.046 (3)	0.021 (2)	0.053 (3)	−0.0020 (19)	−0.003 (2)	−0.0099 (19)
O8	0.025 (2)	0.037 (2)	0.041 (2)	0.0064 (18)	−0.0011 (17)	−0.0017 (19)
O11	0.042 (2)	0.038 (2)	0.039 (2)	−0.0014 (19)	−0.0094 (19)	−0.0048 (19)
O12	0.160 (7)	0.057 (4)	0.066 (4)	−0.029 (4)	−0.023 (4)	0.037 (3)
O13	0.053 (3)	0.029 (2)	0.049 (3)	−0.007 (2)	−0.002 (2)	0.002 (2)
O15	0.034 (2)	0.039 (3)	0.061 (3)	0.001 (2)	−0.002 (2)	0.009 (2)
O16	0.076 (4)	0.077 (4)	0.062 (4)	−0.004 (3)	−0.007 (3)	0.043 (3)
O17	0.037 (2)	0.042 (3)	0.044 (3)	0.001 (2)	−0.002 (2)	0.011 (2)
O19	0.059 (3)	0.038 (3)	0.039 (3)	−0.004 (2)	0.005 (2)	−0.002 (2)
N1	0.108 (6)	0.028 (3)	0.069 (5)	0.014 (3)	0.020 (4)	0.004 (3)
N2	0.075 (4)	0.043 (3)	0.039 (3)	−0.013 (3)	0.009 (3)	−0.009 (3)
N3	0.073 (5)	0.080 (5)	0.092 (6)	−0.041 (4)	0.038 (4)	−0.045 (4)
N4	0.026 (3)	0.094 (5)	0.080 (5)	0.006 (3)	0.008 (3)	0.055 (4)
N5	0.054 (4)	0.051 (4)	0.107 (6)	−0.011 (3)	0.015 (4)	0.015 (4)
N6	0.046 (4)	0.112 (6)	0.055 (4)	−0.014 (4)	0.011 (3)	0.014 (4)
N7	0.159 (8)	0.040 (4)	0.050 (4)	−0.009 (4)	−0.001 (4)	−0.007 (3)
N8	0.178 (10)	0.079 (6)	0.050 (5)	−0.040 (6)	−0.009 (5)	0.010 (4)
N9	0.118 (7)	0.075 (6)	0.148 (9)	−0.004 (5)	−0.094 (7)	−0.024 (6)
N10	0.046 (3)	0.046 (4)	0.072 (4)	0.006 (3)	0.010 (3)	−0.011 (3)
N11	0.041 (3)	0.086 (5)	0.049 (4)	0.003 (3)	−0.006 (3)	0.029 (3)
N12	0.026 (3)	0.057 (4)	0.042 (3)	−0.001 (2)	0.001 (2)	0.006 (3)

N13	0.055 (4)	0.040 (3)	0.059 (4)	−0.005 (3)	0.004 (3)	0.015 (3)
N14	0.048 (3)	0.037 (3)	0.049 (4)	−0.006 (3)	−0.012 (3)	0.006 (3)
C1	0.201 (15)	0.121 (11)	0.119 (11)	−0.100 (11)	0.055 (10)	−0.052 (9)
C2	0.066 (6)	0.083 (8)	0.263 (17)	0.007 (6)	0.025 (8)	0.097 (10)
C3	0.103 (9)	0.246 (18)	0.073 (7)	−0.061 (10)	0.036 (7)	0.003 (9)
C4	0.130 (8)	0.037 (4)	0.053 (5)	−0.013 (5)	0.000 (5)	−0.003 (4)
C5	0.091 (8)	0.084 (8)	0.183 (13)	0.008 (6)	−0.082 (8)	−0.003 (8)
C6	0.110 (9)	0.145 (12)	0.093 (8)	−0.038 (9)	0.043 (7)	−0.004 (8)
C7	0.074 (6)	0.051 (5)	0.114 (8)	−0.009 (5)	0.015 (5)	−0.022 (5)
C8	0.066 (5)	0.070 (6)	0.082 (6)	0.020 (5)	0.021 (5)	−0.010 (5)
C9	0.041 (4)	0.069 (5)	0.062 (5)	−0.001 (4)	0.008 (3)	0.017 (4)
C10	0.164 (14)	0.200 (17)	0.187 (16)	−0.088 (13)	−0.102 (12)	−0.009 (13)
C11	0.031 (4)	0.095 (7)	0.065 (5)	−0.007 (4)	−0.008 (3)	0.011 (5)
C12	0.081 (7)	0.091 (8)	0.124 (9)	0.018 (6)	−0.021 (6)	0.067 (7)
C13	0.074 (6)	0.174 (12)	0.044 (5)	−0.018 (7)	−0.014 (4)	0.000 (6)
C14	0.042 (5)	0.094 (7)	0.110 (8)	−0.008 (5)	−0.011 (5)	0.020 (6)
C15	0.111 (8)	0.081 (7)	0.048 (5)	−0.006 (6)	0.001 (5)	−0.002 (5)
C16	0.113 (8)	0.064 (6)	0.071 (6)	−0.020 (5)	0.033 (5)	−0.037 (5)
C17	0.052 (5)	0.068 (6)	0.133 (9)	0.006 (4)	0.004 (5)	0.047 (6)
C18	0.028 (4)	0.224 (15)	0.180 (12)	0.010 (6)	0.011 (6)	0.147 (12)
C19	0.074 (6)	0.108 (8)	0.079 (7)	−0.007 (6)	0.002 (5)	−0.029 (6)
C20	0.260 (18)	0.074 (8)	0.074 (8)	−0.013 (9)	0.031 (9)	−0.042 (6)
C21	0.186 (13)	0.098 (9)	0.145 (11)	−0.102 (9)	0.100 (10)	−0.067 (8)
C22	0.169 (13)	0.108 (10)	0.121 (10)	0.066 (9)	0.030 (9)	0.049 (8)
C23	0.079 (8)	0.158 (13)	0.171 (14)	0.041 (8)	0.008 (8)	0.042 (11)
C24	0.36 (3)	0.188 (17)	0.049 (7)	−0.002 (17)	−0.003 (11)	0.062 (9)
W1	0.03451 (14)	0.02849 (13)	0.01806 (12)	−0.00325 (10)	−0.00220 (9)	0.00184 (9)
Ag1	0.0782 (4)	0.0500 (3)	0.0207 (2)	0.0004 (3)	−0.0006 (2)	0.0025 (2)
S1	0.0401 (9)	0.0705 (12)	0.0317 (9)	0.0070 (9)	0.0016 (7)	0.0033 (8)
S2	0.0410 (9)	0.0703 (12)	0.0309 (9)	−0.0158 (9)	−0.0070 (7)	0.0041 (8)
S3	0.0620 (10)	0.0313 (8)	0.0270 (8)	0.0004 (7)	0.0005 (7)	0.0069 (6)
S4	0.0782 (12)	0.0280 (8)	0.0321 (8)	−0.0066 (8)	−0.0006 (8)	0.0034 (7)

Geometric parameters (Å, °)

Eu1—O11	2.279 (4)	N2—C15	1.434 (10)
Eu1—O8	2.292 (4)	N2—C16	1.487 (9)
Eu1—O1	2.296 (4)	N3—C14	1.455 (11)
Eu1—O4	2.313 (4)	N3—C21	1.496 (11)
Eu1—O19	2.494 (4)	N4—C17	1.439 (10)
Eu1—O13	2.515 (4)	N4—C18	1.473 (10)
Eu1—O15	2.520 (4)	N5—C1	1.455 (13)
Eu1—O17	2.521 (4)	N5—C2	1.464 (12)
P1—O4	1.479 (4)	N6—C3	1.454 (11)
P1—N3	1.622 (7)	N6—C19	1.463 (11)
P1—N2	1.634 (6)	N7—C4	1.492 (10)
P1—N1	1.645 (7)	N7—C20	1.495 (11)
P2—O1	1.493 (4)	N8—C6	1.444 (14)
P2—N4	1.598 (6)	N8—C24	1.505 (14)

P2—N5	1.625 (7)	N9—C5	1.418 (13)
P2—N6	1.637 (7)	N9—C10	1.485 (13)
P3—O11	1.484 (4)	N10—C7	1.460 (10)
P3—N7	1.578 (7)	N10—C8	1.463 (9)
P3—N8	1.615 (9)	N11—C13	1.439 (11)
P3—N9	1.626 (9)	N11—C12	1.476 (11)
P4—O8	1.496 (4)	N12—C11	1.457 (8)
P4—N11	1.612 (6)	N12—C9	1.462 (9)
P4—N10	1.625 (6)	W1—S2	2.1913 (16)
P4—N12	1.633 (5)	W1—S1	2.2016 (17)
O12—N13	1.212 (7)	W1—S3	2.2028 (15)
O13—N13	1.258 (7)	W1—S4	2.2036 (16)
O15—N14	1.257 (7)	W1—Ag1^{i}	2.9506 (6)
O16—N14	1.227 (7)	W1—Ag1	2.9748 (6)
O17—N14	1.268 (7)	Ag1—S4^{ii}	2.4929 (17)
O19—N13	1.267 (7)	Ag1—S3^{ii}	2.5704 (17)
N1—C22	1.402 (13)	Ag1—S1	2.6190 (18)
N1—C23	1.455 (12)	Ag1—S2	2.6245 (18)
O11—Eu1—O8	92.50 (15)	N13—O13—Eu1	95.9 (3)
O11—Eu1—O1	88.80 (16)	N14—O15—Eu1	95.8 (3)
O8—Eu1—O1	157.08 (15)	N14—O17—Eu1	95.5 (3)
O11—Eu1—O4	158.04 (16)	N13—O19—Eu1	96.6 (4)
O8—Eu1—O4	94.37 (15)	C22—N1—C23	108.2 (9)
O1—Eu1—O4	92.88 (15)	C22—N1—P1	125.6 (7)
O11—Eu1—O19	128.04 (15)	C23—N1—P1	121.0 (7)
O8—Eu1—O19	79.91 (15)	C15—N2—C16	114.2 (7)
O1—Eu1—O19	81.31 (15)	C15—N2—P1	120.7 (5)
O4—Eu1—O19	73.78 (15)	C16—N2—P1	120.5 (5)
O11—Eu1—O13	77.32 (15)	C14—N3—C21	117.4 (8)
O8—Eu1—O13	77.74 (15)	C14—N3—P1	121.2 (6)
O1—Eu1—O13	80.24 (15)	C21—N3—P1	119.4 (7)
O4—Eu1—O13	124.54 (15)	C17—N4—C18	113.9 (7)
O19—Eu1—O13	50.76 (15)	C17—N4—P2	122.9 (5)
O11—Eu1—O15	78.82 (15)	C18—N4—P2	121.0 (5)
O8—Eu1—O15	126.42 (14)	C1—N5—C2	114.7 (10)
O1—Eu1—O15	76.26 (15)	C1—N5—P2	119.4 (7)
O4—Eu1—O15	80.32 (15)	C2—N5—P2	122.4 (8)
O19—Eu1—O15	144.60 (15)	C3—N6—C19	112.0 (8)
O13—Eu1—O15	146.63 (15)	C3—N6—P2	121.8 (7)
O11—Eu1—O17	79.94 (15)	C19—N6—P2	120.0 (6)
O8—Eu1—O17	75.74 (14)	C4—N7—C20	115.7 (7)
O1—Eu1—O17	126.90 (14)	C4—N7—P3	119.6 (6)
O4—Eu1—O17	81.59 (15)	C20—N7—P3	123.1 (7)
O19—Eu1—O17	143.68 (14)	C6—N8—C24	120.8 (11)
O13—Eu1—O17	143.99 (15)	C6—N8—P3	119.7 (7)
O15—Eu1—O17	50.69 (14)	C24—N8—P3	119.3 (10)
O11—Eu1—N13	102.65 (17)	C5—N9—C10	113.4 (10)
O8—Eu1—N13	76.40 (16)	C5—N9—P3	123.8 (6)

O1—Eu1—N13	80.99 (16)	C10—N9—P3	122.7 (10)
O4—Eu1—N13	99.23 (17)	C7—N10—C8	113.8 (7)
O19—Eu1—N13	25.48 (16)	C7—N10—P4	120.2 (5)
O13—Eu1—N13	25.34 (15)	C8—N10—P4	125.4 (6)
O15—Eu1—N13	157.18 (16)	C13—N11—C12	115.6 (8)
O17—Eu1—N13	152.10 (15)	C13—N11—P4	119.6 (7)
O11—Eu1—N14	76.19 (15)	C12—N11—P4	124.3 (7)
O8—Eu1—N14	101.16 (16)	C11—N12—C9	114.7 (5)
O1—Eu1—N14	101.36 (16)	C11—N12—P4	122.4 (5)
O4—Eu1—N14	82.03 (15)	C9—N12—P4	120.0 (4)
O19—Eu1—N14	155.78 (15)	O12—N13—O13	122.3 (6)
O13—Eu1—N14	153.41 (15)	O12—N13—O19	121.2 (7)
O15—Eu1—N14	25.30 (14)	O13—N13—O19	116.5 (5)
O17—Eu1—N14	25.55 (14)	O16—N14—O15	122.6 (6)
N13—Eu1—N14	177.30 (17)	O16—N14—O17	120.0 (6)
O4—P1—N3	109.8 (3)	O15—N14—O17	117.4 (5)
O4—P1—N2	109.1 (3)	S2—W1—S1	110.00 (7)
N3—P1—N2	115.3 (4)	S2—W1—S3	108.07 (7)
O4—P1—N1	115.6 (3)	S1—W1—S3	108.55 (7)
N3—P1—N1	103.7 (4)	S2—W1—S4	108.26 (7)
N2—P1—N1	103.4 (3)	S1—W1—S4	108.68 (7)
O1—P2—N4	108.3 (3)	S3—W1—S4	113.26 (6)
O1—P2—N5	118.7 (3)	$Ag1^{i}$—W1—Ag1	154.250 (9)
N4—P2—N5	105.7 (4)	$S4^{ii}$—Ag1—$S3^{ii}$	93.23 (5)
O1—P2—N6	108.4 (3)	$S4^{ii}$—Ag1—S1	120.22 (6)
N4—P2—N6	114.2 (4)	$S3^{ii}$—Ag1—S1	120.89 (6)
N5—P2—N6	101.5 (4)	$S4^{ii}$—Ag1—S2	120.59 (6)
O11—P3—N7	110.4 (3)	$S3^{ii}$—Ag1—S2	118.18 (6)
O11—P3—N8	109.9 (4)	S1—Ag1—S2	86.67 (5)
N7—P3—N8	108.9 (5)	$S4^{ii}$—Ag1—$W1^{ii}$	46.83 (4)
O11—P3—N9	109.9 (4)	$S3^{ii}$—Ag1—$W1^{ii}$	46.40 (3)
N7—P3—N9	110.4 (5)	S1—Ag1—$W1^{ii}$	137.30 (4)
N8—P3—N9	107.3 (6)	S2—Ag1—$W1^{ii}$	136.01 (4)
O8—P4—N11	111.2 (3)	$S4^{ii}$—Ag1—W1	150.22 (4)
O8—P4—N10	111.4 (3)	$S3^{ii}$—Ag1—W1	116.54 (4)
N11—P4—N10	107.0 (4)	S1—Ag1—W1	45.81 (4)
O8—P4—N12	108.3 (3)	S2—Ag1—W1	45.55 (4)
N11—P4—N12	109.2 (3)	$W1^{ii}$—Ag1—W1	162.93 (2)
N10—P4—N12	109.6 (3)	W1—S1—Ag1	75.66 (5)
P2—O1—Eu1	159.5 (3)	W1—S2—Ag1	75.70 (5)
P1—O4—Eu1	164.2 (3)	W1—S3—$Ag1^{i}$	75.93 (5)
P4—O8—Eu1	167.6 (3)	W1—S4—$Ag1^{i}$	77.57 (5)
P3—O11—Eu1	167.8 (3)		

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

Fig. 1

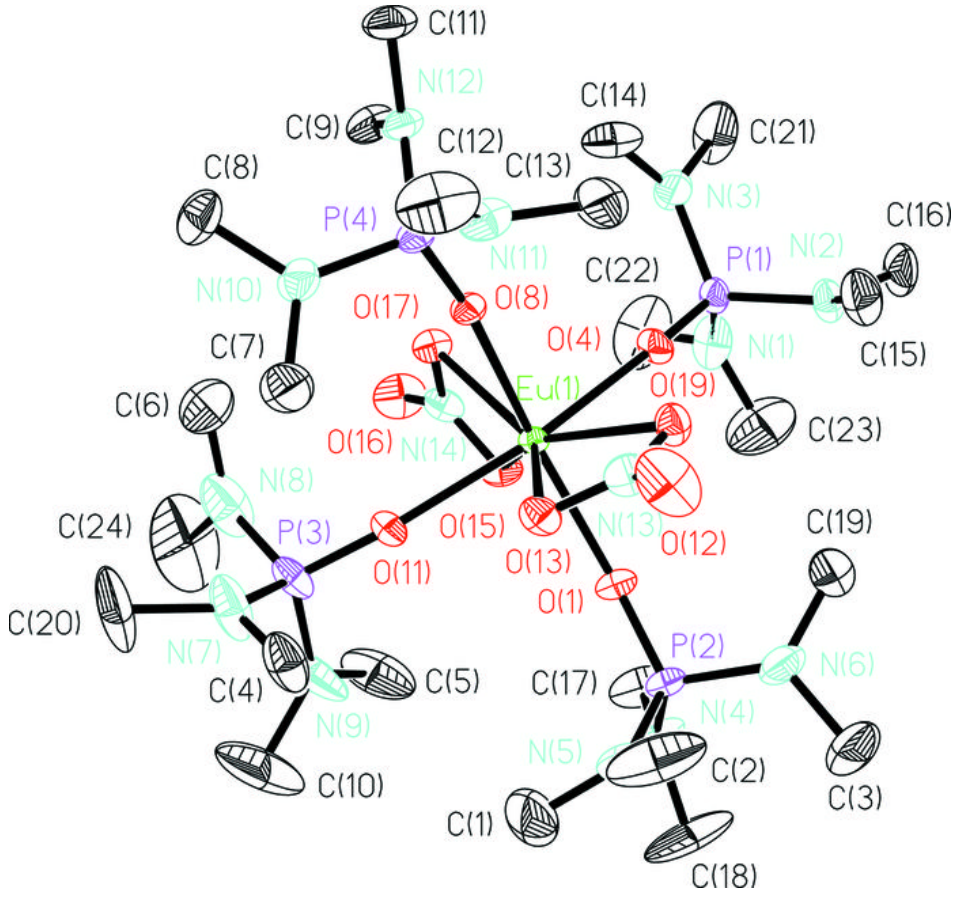

C(11)
N(12)
C(9)
C(12)
C(14)
C(21)
C(8)
C(13)
N(3)
C(16)
P(4)
N(11)
C(22)
P(1)
N(2)
N(10)
O(17)
O(8)
O(4)
N(1)
C(15)
C(7)
Eu(1)
O(19)
C(6)
O(16)
N(14)
C(23)
N(8)
C(24)
P(3)
O(15)
N(13)
O(12)
C(19)
O(11)
O(13)
O(1)
C(20)
N(7)
P(2)
N(6)
C(4)
C(5)
C(17)
N(4)
N(9)
N(5)
C(2)
C(3)
C(10)
C(1)
C(18)

Fig. 2