

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

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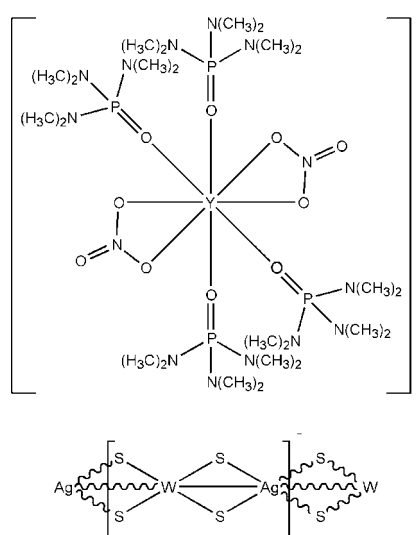
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Key indicators: single-crystal X-ray study; $T = 223$ K; mean $\sigma(\text{Ag-S}) = 0.002$ Å; R factor = 0.044; wR factor = 0.085; data-to-parameter ratio = 18.4.

The title salt of a one-dimensional anionic W/S/Ag polymer, $\{[\text{Y}(\text{NO}_3)_2(\text{C}_6\text{H}_{18}\text{N}_3\text{OP})_4][\text{WAgS}_4]\}_n$ was produced by the reaction of ammonium tetrathiotungstate(VI), silver(I) sulfide and yttrium(III) nitrate in hexamethylphosphoramide. The cation has the same structure as that in the isostructural Yb compound [Cao *et al.* (2007). *Acta Cryst.* E63, m2076–m2077]. Together with the two nitrate ligands, the cation 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 $\{[\text{WS}_4\text{Ag}]^{n-}\}_n$ anion, with W—Ag—W and Ag—W—Ag angles of 162.684 (19) and 153.833 (10)°, respectively, presents a distorted linear configuration the same as that of the anionic chain in the isostructural Yb compound, suggesting that different rare-earth cations with the same coordination environments have the same influence on the arrangement of their anionic chains.

Related literature

One example of a one-dimensional Mo/S/Ag anionic polymer with an almost ideal linear configuration is $\{(\gamma\text{-MePyH})[\text{MoS}_4\text{Ag}]\}_n$ (MePyH is protonated picoline) (Lang *et al.*, 1993). A more relevant analog of the title compound is $\{[\text{Yb}(\text{hmp})_4(\text{NO}_3)_2][\text{WS}_4\text{Ag}]\}_n$ (hmp = hexamethylphosphoramide) (Cao *et al.*, 2007), which has similar wave-like chains. For related literature, see: Huang *et al.* (1996); Niu *et al.* (2004) and references therein; Zhang *et al.* (2007).



Experimental

Crystal data

$[\text{Y}(\text{NO}_3)_2(\text{C}_6\text{H}_{18}\text{N}_3\text{OP})_4][\text{WAgS}_4]$	$V = 5352.3$ (18) Å ³
$M_r = 1349.74$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.789$ (3) Å	$\mu = 3.91$ mm ⁻¹
$b = 29.661$ (6) Å	$T = 223$ (2) K
$c = 11.430$ (2) Å	$0.50 \times 0.45 \times 0.32$ mm
$\beta = 90.83$ (3)°	

Data collection

Rigaku Mercury CCD diffractometer	49397 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	9804 independent reflections
$T_{\min} = 0.173$, $T_{\max} = 0.286$	9045 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	532 parameters
$wR(F^2) = 0.085$	H-atom parameters constrained
$S = 1.21$	$\Delta\rho_{\max} = 0.64$ e Å ⁻³
9804 reflections	$\Delta\rho_{\min} = -0.77$ e Å ⁻³

Data collection: *CrystalClear* (Rigaku, 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2050).

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supplementary materials

Acta Cryst. (2007). E63, m2248-m2249 [doi:10.1107/S1600536807036306]

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

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Comment

One-dimensional Mo(W)/S/Ag anionic polymers have attracted much attention for their configurational isomerism (Niu *et al.*, 2004) and potential applications, especially in third-order nonlinear optical (NLO) materials. (Zhang *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 $\{[Y(\text{hmp})_4(\text{NO}_3)_2][\text{WS}_4\text{Ag}]\}_n$ (hmp = hexamethylphosphoramidate) with a wave-like anionic chain was prepared by following such route using Y(III)-hmp complex as counterion.

In possession of two nitrate ligands, the cation in the title compound is univalent (Fig. 1), which leads to an anionic chain with a univalent repeat unit, unlike other solvent-coordinated rare-earth cations, in literature (Niu *et al.*, 2004), which are trivalent and induce trivalent repeat units. For example, $[\text{Nd}(\text{dmf})_8]^{3+}$ induces an anionic chain with a trivalent repeat unit $[\text{W}_4\text{S}_{16}\text{Ag}_5]^{3-}$ (Huang *et al.*, 1997).

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 162.684 (19) and 153.833 (10) °, deviating significantly from the ideal 180 °, which is observed in the reported compound $\{(\gamma\text{-MePyH})[\text{MoS}_4\text{Ag}]\}_n$ (179.3 (2)–180.0 (1) °) (Lang *et al.*, 1993). Similar angles of 160.81 (7) and 153.41 (7) ° for W—Ag—W and Ag—W—Ag are found in another distorted linear chain in $\{[\text{Yb}(\text{hmp})_4(\text{NO}_3)_2][\text{WS}_4\text{Ag}]\}_n$ (Cao *et al.*, 2007), which suggests that different rare earth cations with the same coordination environments will result in the same anionic structures.

Experimental

1 mmol Ag_2S was added to a solution of $[\text{NH}_4]_2\text{WS}_4$ (2 mmol in 30 mL hmp) with thorough stir for 12 h. The solution underwent an additional stir for one minute after 1 mmol $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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: 1.138 g in pure form, 42.2% (based on W). Analysis calculated for $\text{C}_{24}\text{H}_{72}\text{AgN}_{14}\text{O}_{10}\text{P}_4\text{S}_4\text{WY}$: C 21.36, H 5.38, N 14.53%; found: C 21.39, H 5.40, N 14.49%. IR: ν , cm^{-1} , 478.9 m, 447.4 s (W- μ_2 -S).

Refinement

Some N and P atoms have low U_{eq} as compared to neighbors and a few C atoms have large ADP max/min ratio. Splitting these atoms to resolve disorder will cause the refinement unstable or ADP non positive definite, so no further treatments were applied to these atoms. H atoms were positioned geometrically and refined with riding model, with $U_{\text{iso}} = 1.5U_{\text{eq}}$ for methyl H atoms and 0.97 Å for C—H bonds.

Figures

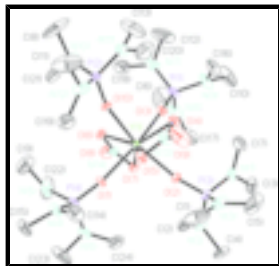


Fig. 1. The molecular structure of the cation in the title compound, with atom labels and 30% probability displacement ellipsoids. All H atoms have been omitted.



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

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Crystal data

[Y(NO₃)₂(C₆H₁₈N₃OP)₄][WAgS₄]

$M_r = 1349.74$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 15.789$ (3) Å

$b = 29.661$ (6) Å

$c = 11.430$ (2) Å

$\beta = 90.83$ (3)°

$V = 5352.3$ (18) Å³

$Z = 4$

$F_{000} = 2712.0$

$D_x = 1.675$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 18559 reflections

$\theta = 3.0$ – 25.4 °

$\mu = 3.91$ mm⁻¹

$T = 223$ (2) K

Block, red

$0.50 \times 0.45 \times 0.32$ mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 14.6306 pixels mm⁻¹

$T = 223$ (2) K

ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.173$, $T_{\max} = 0.286$

49397 measured reflections

9804 independent reflections

9045 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 25.4$ °

$\theta_{\text{min}} = 3.0$ °

$h = -19 \rightarrow 18$

$k = -35 \rightarrow 34$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 15.0729P]$
$S = 1.21$	where $P = (F_o^2 + 2F_c^2)/3$
9783 reflections	$(\Delta/\sigma)_{\max} = 0.001$
532 parameters	$\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$
	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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Y1	0.76115 (3)	0.082921 (16)	0.17150 (4)	0.02278 (12)
P1	0.70695 (12)	0.14734 (5)	-0.09585 (14)	0.0438 (4)
P2	0.54106 (9)	0.09577 (5)	0.26801 (14)	0.0342 (3)
P3	0.97701 (9)	0.13288 (5)	0.17952 (13)	0.0338 (3)
P4	0.80120 (10)	-0.02977 (5)	0.30019 (13)	0.0353 (4)
O1	0.7919 (2)	0.01860 (11)	0.2690 (3)	0.0339 (9)
O2	0.8953 (2)	0.10728 (12)	0.1756 (3)	0.0322 (9)
O3	0.7269 (2)	0.12720 (13)	0.0200 (3)	0.0371 (9)
O4	0.7473 (2)	0.15830 (12)	0.2613 (4)	0.0377 (9)
O5	0.7751 (2)	0.10306 (12)	0.3780 (3)	0.0369 (9)
O6	0.6976 (2)	0.02732 (13)	0.0357 (4)	0.0381 (9)
O7	0.8304 (2)	0.04127 (13)	0.0125 (3)	0.0372 (9)
O8	0.7633 (3)	0.00110 (17)	-0.1173 (4)	0.0650 (14)
O9	0.7713 (4)	0.17139 (17)	0.4459 (4)	0.0830 (19)
O10	0.6240 (2)	0.08090 (12)	0.2196 (3)	0.0338 (9)
N1	0.9766 (3)	0.17387 (18)	0.0847 (5)	0.0561 (15)
N2	1.0543 (3)	0.09826 (18)	0.1512 (4)	0.0399 (12)
N3	0.9927 (3)	0.1554 (2)	0.3074 (5)	0.0628 (18)

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N4	0.7792 (3)	-0.03569 (17)	0.4397 (4)	0.0460 (13)
N5	0.7355 (4)	-0.06513 (17)	0.2348 (5)	0.0560 (15)
N6	0.8944 (4)	-0.0475 (2)	0.2622 (5)	0.0624 (17)
N7	0.6078 (5)	0.1388 (2)	-0.1297 (7)	0.091 (3)
N8	0.7640 (5)	0.1249 (2)	-0.1959 (5)	0.081 (2)
N9	0.7263 (5)	0.20028 (18)	-0.0935 (5)	0.0643 (18)
N10	0.4665 (3)	0.0697 (2)	0.1992 (5)	0.0626 (18)
N11	0.5156 (4)	0.14856 (19)	0.2598 (6)	0.0631 (17)
N12	0.5426 (4)	0.0871 (2)	0.4099 (5)	0.0603 (16)
N13	0.7646 (3)	0.14517 (17)	0.3638 (5)	0.0454 (13)
N14	0.7637 (3)	0.02239 (16)	-0.0259 (4)	0.0376 (12)
C1	0.9801 (5)	0.1285 (4)	0.4099 (7)	0.101 (4)
H1A	0.9527	0.1004	0.3880	0.151*
H1B	0.9446	0.1449	0.4640	0.151*
H1C	1.0344	0.1222	0.4470	0.151*
C2	1.0456 (4)	0.0655 (2)	0.0564 (6)	0.0548 (18)
H2A	0.9861	0.0614	0.0370	0.082*
H2B	1.0698	0.0369	0.0810	0.082*
H2C	1.0752	0.0765	-0.0118	0.082*
C3	1.0453 (5)	0.1839 (3)	0.0046 (7)	0.072 (2)
H3A	1.0869	0.1598	0.0082	0.107*
H3B	1.0719	0.2121	0.0270	0.107*
H3C	1.0227	0.1863	-0.0745	0.107*
C4	1.1419 (4)	0.1073 (3)	0.1885 (7)	0.065 (2)
H4A	1.1422	0.1294	0.2512	0.098*
H4B	1.1734	0.1190	0.1229	0.098*
H4C	1.1680	0.0796	0.2161	0.098*
C5	1.0340 (6)	0.1992 (4)	0.3275 (10)	0.122 (4)
H5A	1.0400	0.2148	0.2535	0.183*
H5B	1.0895	0.1945	0.3629	0.183*
H5C	0.9997	0.2173	0.3795	0.183*
C6	0.7278 (10)	0.1079 (5)	-0.3074 (8)	0.170 (7)
H6A	0.6667	0.1112	-0.3069	0.255*
H6B	0.7422	0.0763	-0.3163	0.255*
H6C	0.7507	0.1249	-0.3720	0.255*
C7	0.9100 (5)	0.2080 (3)	0.0883 (9)	0.082 (3)
H7A	0.8670	0.1988	0.1432	0.123*
H7B	0.8846	0.2114	0.0111	0.123*
H7C	0.9342	0.2366	0.1132	0.123*
C8	0.3773 (5)	0.0796 (4)	0.2200 (10)	0.144 (6)
H8A	0.3728	0.1080	0.2618	0.216*
H8B	0.3529	0.0557	0.2664	0.216*
H8C	0.3471	0.0818	0.1457	0.216*
C9	0.6478 (6)	-0.0669 (4)	0.2665 (10)	0.104 (3)
H9A	0.6414	-0.0552	0.3452	0.155*
H9B	0.6282	-0.0979	0.2636	0.155*
H9C	0.6145	-0.0488	0.2122	0.155*
C10	0.7551 (8)	0.2262 (3)	-0.1959 (8)	0.112 (4)
H10A	0.7741	0.2055	-0.2558	0.168*

H10B	0.8015	0.2458	-0.1725	0.168*
H10C	0.7086	0.2442	-0.2265	0.168*
C11	0.4713 (6)	0.0980 (5)	0.4814 (8)	0.131 (5)
H11A	0.4399	0.1227	0.4460	0.196*
H11B	0.4912	0.1068	0.5587	0.196*
H11C	0.4348	0.0719	0.4876	0.196*
C12	0.5528 (8)	0.1728 (4)	-0.1864 (12)	0.160 (6)
H12A	0.5838	0.2009	-0.1940	0.239*
H12B	0.5032	0.1778	-0.1391	0.239*
H12C	0.5354	0.1622	-0.2634	0.239*
C13	0.4851 (8)	0.1680 (4)	0.1525 (10)	0.140 (5)
H13A	0.4653	0.1443	0.1005	0.210*
H13B	0.5305	0.1845	0.1156	0.210*
H13C	0.4387	0.1885	0.1688	0.210*
C14	0.8032 (5)	-0.0008 (3)	0.5217 (6)	0.068 (2)
H14A	0.8055	0.0279	0.4814	0.102*
H14B	0.8584	-0.0077	0.5554	0.102*
H14C	0.7617	0.0008	0.5833	0.102*
C15	0.7738 (5)	-0.0808 (2)	0.4921 (6)	0.066 (2)
H15A	0.7577	-0.1025	0.4322	0.099*
H15B	0.7317	-0.0807	0.5530	0.099*
H15C	0.8284	-0.0891	0.5255	0.099*
C16	0.6951 (6)	0.2277 (2)	0.0057 (6)	0.069 (2)
H16A	0.6776	0.2079	0.0684	0.103*
H16B	0.6472	0.2458	-0.0204	0.103*
H16C	0.7400	0.2474	0.0339	0.103*
C17	0.8541 (7)	0.1225 (3)	-0.1835 (8)	0.100 (3)
H17A	0.8712	0.1346	-0.1079	0.151*
H17B	0.8802	0.1400	-0.2450	0.151*
H17C	0.8720	0.0913	-0.1891	0.151*
C18	0.5672 (6)	0.0961 (3)	-0.1161 (10)	0.107 (4)
H18A	0.6065	0.0751	-0.0796	0.160*
H18B	0.5497	0.0847	-0.1922	0.160*
H18C	0.5179	0.0996	-0.0672	0.160*
C19	0.5932 (5)	0.0498 (3)	0.4575 (7)	0.074 (2)
H19A	0.6407	0.0440	0.4067	0.111*
H19B	0.5583	0.0229	0.4623	0.111*
H19C	0.6141	0.0577	0.5350	0.111*
C20	0.5465 (6)	0.1826 (3)	0.3437 (12)	0.140 (6)
H20A	0.5670	0.1678	0.4142	0.210*
H20B	0.5007	0.2029	0.3631	0.210*
H20C	0.5923	0.1996	0.3091	0.210*
C21	0.4794 (5)	0.0279 (3)	0.1376 (8)	0.079 (3)
H21A	0.5396	0.0231	0.1266	0.118*
H21B	0.4509	0.0292	0.0619	0.118*
H21C	0.4564	0.0032	0.1827	0.118*
C22	0.7468 (7)	-0.0825 (3)	0.1202 (8)	0.105 (4)
H22A	0.8064	-0.0812	0.1007	0.158*
H22B	0.7143	-0.0646	0.0645	0.158*

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H22C	0.7275	-0.1135	0.1171	0.158*
C23	0.9172 (7)	-0.0953 (3)	0.2798 (9)	0.113 (4)
H23A	0.8661	-0.1130	0.2890	0.169*
H23B	0.9526	-0.0982	0.3495	0.169*
H23C	0.9480	-0.1061	0.2125	0.169*
C24	0.9634 (5)	-0.0158 (3)	0.2480 (8)	0.076 (2)
H24A	0.9407	0.0143	0.2373	0.114*
H24B	0.9960	-0.0241	0.1800	0.114*
H24C	0.9998	-0.0164	0.3171	0.114*
W1	0.283016 (14)	0.227680 (7)	0.528018 (18)	0.02567 (7)
Ag1	0.28194 (4)	0.264566 (17)	0.28785 (4)	0.04883 (14)
S1	0.28226 (11)	0.30025 (5)	0.48562 (13)	0.0427 (4)
S2	0.28502 (11)	0.18418 (5)	0.37165 (12)	0.0391 (4)
S3	0.16900 (10)	0.21196 (6)	0.62861 (13)	0.0434 (4)
S4	0.39682 (10)	0.21320 (6)	0.63391 (13)	0.0458 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Y1	0.0208 (3)	0.0182 (2)	0.0293 (3)	0.0000 (2)	0.0008 (2)	0.0008 (2)
P1	0.0625 (11)	0.0335 (8)	0.0348 (9)	0.0083 (8)	-0.0171 (8)	0.0021 (7)
P2	0.0214 (7)	0.0355 (8)	0.0458 (9)	0.0016 (6)	0.0059 (6)	-0.0069 (7)
P3	0.0229 (7)	0.0428 (9)	0.0358 (8)	-0.0074 (6)	-0.0004 (6)	-0.0078 (7)
P4	0.0449 (9)	0.0235 (7)	0.0378 (8)	0.0080 (7)	0.0110 (7)	0.0088 (6)
O1	0.040 (2)	0.0202 (18)	0.042 (2)	0.0036 (17)	-0.0010 (17)	0.0057 (17)
O2	0.0229 (19)	0.035 (2)	0.039 (2)	-0.0053 (16)	-0.0012 (16)	-0.0013 (17)
O3	0.040 (2)	0.034 (2)	0.036 (2)	-0.0008 (18)	-0.0110 (18)	0.0082 (18)
O4	0.045 (2)	0.026 (2)	0.042 (2)	0.0064 (18)	-0.0023 (19)	-0.0024 (18)
O5	0.048 (2)	0.028 (2)	0.035 (2)	0.0040 (18)	0.0047 (18)	-0.0005 (17)
O6	0.031 (2)	0.033 (2)	0.050 (3)	-0.0012 (17)	-0.0020 (19)	-0.0081 (19)
O7	0.030 (2)	0.037 (2)	0.044 (2)	-0.0006 (18)	0.0008 (18)	-0.0082 (19)
O8	0.067 (3)	0.071 (3)	0.056 (3)	0.005 (3)	-0.004 (2)	-0.041 (3)
O9	0.149 (6)	0.050 (3)	0.049 (3)	0.020 (3)	-0.019 (3)	-0.028 (3)
O10	0.0194 (19)	0.033 (2)	0.049 (2)	0.0011 (16)	0.0035 (16)	-0.0067 (18)
N1	0.045 (3)	0.044 (3)	0.080 (4)	-0.012 (3)	0.013 (3)	0.011 (3)
N2	0.025 (3)	0.058 (3)	0.037 (3)	-0.001 (2)	-0.001 (2)	-0.011 (2)
N3	0.041 (3)	0.097 (5)	0.050 (4)	0.002 (3)	-0.010 (3)	-0.034 (3)
N4	0.062 (4)	0.038 (3)	0.039 (3)	0.007 (3)	0.009 (3)	0.012 (2)
N5	0.082 (4)	0.030 (3)	0.057 (4)	-0.011 (3)	0.018 (3)	-0.005 (3)
N6	0.058 (4)	0.055 (4)	0.075 (4)	0.026 (3)	0.025 (3)	0.029 (3)
N7	0.094 (6)	0.061 (4)	0.115 (6)	0.010 (4)	-0.068 (5)	0.018 (4)
N8	0.127 (7)	0.068 (4)	0.048 (4)	0.033 (4)	0.000 (4)	-0.007 (3)
N9	0.119 (6)	0.037 (3)	0.038 (3)	0.006 (3)	0.002 (3)	0.012 (3)
N10	0.027 (3)	0.081 (4)	0.080 (4)	-0.004 (3)	0.006 (3)	-0.045 (4)
N11	0.048 (4)	0.041 (3)	0.100 (5)	0.012 (3)	0.013 (3)	-0.003 (3)
N12	0.046 (3)	0.087 (5)	0.048 (3)	0.014 (3)	0.011 (3)	-0.010 (3)
N13	0.055 (3)	0.038 (3)	0.043 (3)	0.006 (3)	0.001 (3)	-0.009 (3)
N14	0.040 (3)	0.031 (3)	0.042 (3)	0.006 (2)	-0.002 (2)	-0.006 (2)

C1	0.066 (6)	0.195 (12)	0.040 (5)	0.022 (6)	-0.013 (4)	-0.003 (6)
C2	0.038 (4)	0.071 (5)	0.056 (4)	0.000 (3)	0.012 (3)	-0.019 (4)
C3	0.070 (5)	0.066 (5)	0.080 (6)	-0.022 (4)	0.020 (4)	0.006 (4)
C4	0.024 (3)	0.104 (6)	0.067 (5)	0.006 (4)	-0.007 (3)	-0.016 (4)
C5	0.091 (7)	0.118 (9)	0.157 (11)	-0.026 (6)	-0.025 (7)	-0.093 (8)
C6	0.31 (2)	0.169 (13)	0.037 (5)	-0.011 (13)	0.000 (8)	-0.049 (7)
C7	0.073 (6)	0.051 (5)	0.124 (8)	0.008 (4)	0.019 (5)	0.024 (5)
C8	0.028 (4)	0.221 (13)	0.183 (11)	-0.013 (6)	0.015 (5)	-0.156 (11)
C9	0.069 (6)	0.115 (8)	0.127 (9)	-0.025 (6)	-0.005 (6)	-0.027 (7)
C10	0.213 (13)	0.063 (6)	0.060 (6)	0.018 (7)	0.027 (7)	0.033 (5)
C11	0.095 (8)	0.240 (15)	0.059 (6)	0.075 (9)	0.027 (5)	-0.009 (7)
C12	0.164 (12)	0.129 (10)	0.182 (13)	0.066 (9)	-0.107 (10)	0.007 (9)
C13	0.195 (13)	0.109 (9)	0.119 (9)	0.094 (9)	0.057 (9)	0.044 (7)
C14	0.096 (6)	0.068 (5)	0.041 (4)	0.006 (5)	-0.005 (4)	0.002 (4)
C15	0.094 (6)	0.051 (4)	0.054 (4)	0.013 (4)	0.027 (4)	0.029 (4)
C16	0.121 (7)	0.033 (4)	0.053 (5)	0.010 (4)	0.003 (4)	-0.001 (3)
C17	0.112 (8)	0.107 (8)	0.085 (7)	0.043 (7)	0.043 (6)	0.011 (6)
C18	0.082 (7)	0.081 (7)	0.155 (10)	-0.008 (5)	-0.074 (7)	-0.001 (7)
C19	0.061 (5)	0.097 (7)	0.063 (5)	0.002 (5)	0.000 (4)	0.017 (5)
C20	0.069 (6)	0.070 (6)	0.281 (17)	-0.003 (5)	0.012 (8)	-0.098 (9)
C21	0.041 (4)	0.069 (5)	0.127 (8)	-0.010 (4)	0.016 (4)	-0.053 (5)
C22	0.135 (9)	0.086 (7)	0.095 (7)	-0.047 (6)	0.032 (6)	-0.040 (6)
C23	0.143 (9)	0.083 (7)	0.115 (8)	0.081 (7)	0.070 (7)	0.049 (6)
C24	0.039 (4)	0.079 (6)	0.110 (7)	0.004 (4)	-0.006 (4)	-0.014 (5)
W1	0.03217 (13)	0.02568 (12)	0.01909 (11)	0.00287 (9)	-0.00250 (8)	-0.00114 (9)
Ag1	0.0780 (4)	0.0470 (3)	0.0214 (2)	0.0006 (3)	-0.0012 (2)	0.0028 (2)
S1	0.0713 (11)	0.0254 (7)	0.0312 (8)	0.0047 (7)	0.0005 (7)	-0.0022 (6)
S2	0.0597 (10)	0.0293 (7)	0.0283 (7)	-0.0007 (7)	-0.0002 (7)	-0.0057 (6)
S3	0.0385 (9)	0.0605 (10)	0.0314 (8)	-0.0081 (8)	0.0016 (6)	-0.0014 (7)
S4	0.0395 (9)	0.0649 (11)	0.0328 (8)	0.0174 (8)	-0.0084 (7)	-0.0053 (8)

Geometric parameters (Å, °)

Y1—O3	2.233 (4)	N2—C2	1.460 (8)
Y1—O2	2.238 (3)	N2—C4	1.466 (7)
Y1—O10	2.243 (3)	N3—C1	1.432 (11)
Y1—O1	2.259 (3)	N3—C5	1.472 (10)
Y1—O5	2.441 (4)	N4—C14	1.443 (9)
Y1—O7	2.466 (4)	N4—C15	1.470 (8)
Y1—O6	2.468 (4)	N5—C22	1.421 (10)
Y1—O4	2.471 (4)	N5—C9	1.438 (10)
P1—O3	1.483 (4)	N6—C24	1.449 (9)
P1—N9	1.600 (6)	N6—C23	1.477 (9)
P1—N8	1.610 (7)	N7—C18	1.428 (11)
P1—N7	1.627 (7)	N7—C12	1.476 (10)
P2—O10	1.495 (4)	N8—C17	1.429 (11)
P2—N10	1.605 (5)	N8—C6	1.479 (11)
P2—N11	1.619 (6)	N9—C10	1.477 (9)
P2—N12	1.642 (6)	N9—C16	1.486 (9)

supplementary materials

P3—O2	1.497 (4)	N10—C21	1.442 (8)
P3—N3	1.622 (5)	N10—C8	1.462 (9)
P3—N1	1.628 (6)	N11—C13	1.432 (12)
P3—N2	1.631 (5)	N11—C20	1.472 (11)
P4—O1	1.485 (4)	N12—C11	1.436 (9)
P4—N6	1.628 (6)	N12—C19	1.466 (9)
P4—N4	1.646 (5)	W1—S4	2.1943 (16)
P4—N5	1.647 (6)	W1—S3	2.2000 (16)
O4—N13	1.260 (6)	W1—S2	2.2050 (14)
O5—N13	1.270 (6)	W1—S1	2.2063 (15)
O6—N14	1.275 (6)	W1—Ag1	2.9549 (7)
O7—N14	1.266 (6)	W1—Ag1 ⁱ	2.9791 (7)
O8—N14	1.221 (6)	Ag1—S1	2.4960 (16)
O9—N13	1.222 (6)	Ag1—S2	2.5698 (16)
N1—C3	1.460 (8)	Ag1—S3 ⁱⁱ	2.6236 (17)
N1—C7	1.462 (9)	Ag1—S4 ⁱⁱ	2.6293 (18)
O3—Y1—O2	92.57 (14)	N13—O5—Y1	96.2 (3)
O3—Y1—O10	88.97 (14)	N14—O6—Y1	95.5 (3)
O2—Y1—O10	157.01 (13)	N14—O7—Y1	95.8 (3)
O3—Y1—O1	157.99 (14)	P2—O10—Y1	159.5 (2)
O2—Y1—O1	93.76 (14)	C3—N1—C7	114.7 (6)
O10—Y1—O1	93.32 (14)	C3—N1—P3	125.0 (5)
O3—Y1—O5	128.53 (13)	C7—N1—P3	119.7 (5)
O2—Y1—O5	80.13 (14)	C2—N2—C4	114.6 (5)
O10—Y1—O5	81.00 (14)	C2—N2—P3	120.2 (4)
O1—Y1—O5	73.37 (13)	C4—N2—P3	122.1 (5)
O3—Y1—O7	80.11 (14)	C1—N3—C5	115.4 (7)
O2—Y1—O7	75.36 (13)	C1—N3—P3	119.2 (6)
O10—Y1—O7	127.40 (13)	C5—N3—P3	124.5 (7)
O1—Y1—O7	81.14 (13)	C14—N4—C15	113.9 (6)
O5—Y1—O7	143.13 (13)	C14—N4—P4	119.7 (5)
O3—Y1—O6	79.26 (14)	C15—N4—P4	120.4 (4)
O2—Y1—O6	127.21 (13)	C22—N5—C9	110.7 (7)
O10—Y1—O6	75.60 (13)	C22—N5—P4	124.2 (5)
O1—Y1—O6	80.13 (13)	C9—N5—P4	120.8 (5)
O5—Y1—O6	143.31 (13)	C24—N6—C23	117.1 (7)
O7—Y1—O6	51.85 (13)	C24—N6—P4	120.3 (5)
O3—Y1—O4	76.59 (14)	C23—N6—P4	119.5 (5)
O2—Y1—O4	77.82 (13)	C18—N7—C12	113.1 (8)
O10—Y1—O4	80.25 (13)	C18—N7—P1	123.0 (5)
O1—Y1—O4	125.37 (13)	C12—N7—P1	123.7 (7)
O5—Y1—O4	52.00 (12)	C17—N8—C6	116.1 (9)
O7—Y1—O4	143.34 (13)	C17—N8—P1	121.1 (6)
O6—Y1—O4	145.91 (13)	C6—N8—P1	122.7 (8)
O3—Y1—N13	102.53 (15)	C10—N9—C16	115.4 (6)
O2—Y1—N13	76.64 (15)	C10—N9—P1	123.9 (5)
O10—Y1—N13	80.63 (15)	C16—N9—P1	119.0 (5)
O1—Y1—N13	99.44 (15)	C21—N10—C8	113.3 (6)

O5—Y1—N13	26.10 (13)	C21—N10—P2	123.1 (5)
O7—Y1—N13	151.97 (14)	C8—N10—P2	121.6 (5)
O6—Y1—N13	156.14 (14)	C13—N11—C20	112.7 (8)
O4—Y1—N13	25.94 (13)	C13—N11—P2	121.3 (6)
O3—Y1—N14	76.44 (14)	C20—N11—P2	123.1 (7)
O2—Y1—N14	101.15 (14)	C11—N12—C19	112.7 (7)
O10—Y1—N14	101.51 (14)	C11—N12—P2	121.7 (6)
O1—Y1—N14	81.66 (14)	C19—N12—P2	119.0 (5)
O5—Y1—N14	155.02 (13)	O9—N13—O4	122.1 (5)
O7—Y1—N14	25.90 (12)	O9—N13—O5	121.2 (5)
O6—Y1—N14	26.11 (13)	O4—N13—O5	116.7 (5)
O4—Y1—N14	152.93 (13)	O8—N14—O7	121.3 (5)
N13—Y1—N14	177.56 (15)	O8—N14—O6	122.5 (5)
O3—P1—N9	110.0 (3)	O7—N14—O6	116.2 (4)
O3—P1—N8	110.8 (3)	S4—W1—S3	109.87 (6)
N9—P1—N8	108.0 (4)	S4—W1—S2	108.14 (6)
O3—P1—N7	109.9 (3)	S3—W1—S2	108.73 (6)
N9—P1—N7	109.9 (4)	S4—W1—S1	108.29 (7)
N8—P1—N7	108.3 (4)	S3—W1—S1	108.65 (7)
O10—P2—N10	108.4 (2)	S2—W1—S1	113.14 (6)
O10—P2—N11	118.8 (3)	Ag1—W1—Ag1 ⁱ	153.833 (10)
N10—P2—N11	105.0 (3)	S1—Ag1—S2	93.22 (5)
O10—P2—N12	108.6 (3)	S1—Ag1—S3 ⁱⁱ	120.54 (6)
N10—P2—N12	114.1 (3)	S2—Ag1—S3 ⁱⁱ	120.92 (6)
N11—P2—N12	102.1 (3)	S1—Ag1—S4 ⁱⁱ	120.49 (6)
O2—P3—N3	110.9 (3)	S2—Ag1—S4 ⁱⁱ	118.21 (6)
O2—P3—N1	111.3 (3)	S3 ⁱⁱ —Ag1—S4 ⁱⁱ	86.43 (5)
N3—P3—N1	107.0 (3)	S1—Ag1—W1	46.82 (4)
O2—P3—N2	108.7 (2)	S2—Ag1—W1	46.40 (3)
N3—P3—N2	109.4 (3)	S3 ⁱⁱ —Ag1—W1	137.51 (4)
N1—P3—N2	109.5 (3)	S4 ⁱⁱ —Ag1—W1	136.04 (4)
O1—P4—N6	109.5 (3)	S1—Ag1—W1 ⁱⁱ	150.48 (4)
O1—P4—N4	108.3 (2)	S2—Ag1—W1 ⁱⁱ	116.29 (4)
N6—P4—N4	115.4 (3)	S3 ⁱⁱ —Ag1—W1 ⁱⁱ	45.70 (4)
O1—P4—N5	116.6 (3)	S4 ⁱⁱ —Ag1—W1 ⁱⁱ	45.54 (4)
N6—P4—N5	103.8 (3)	W1—Ag1—W1 ⁱⁱ	162.684 (19)
N4—P4—N5	103.4 (3)	W1—S1—Ag1	77.59 (5)
P4—O1—Y1	162.6 (2)	W1—S2—Ag1	76.04 (5)
P3—O2—Y1	168.3 (2)	W1—S3—Ag1 ⁱ	75.71 (5)
P1—O3—Y1	167.3 (3)	W1—S4—Ag1 ⁱ	75.68 (5)
N13—O4—Y1	95.0 (3)		

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

Fig. 1

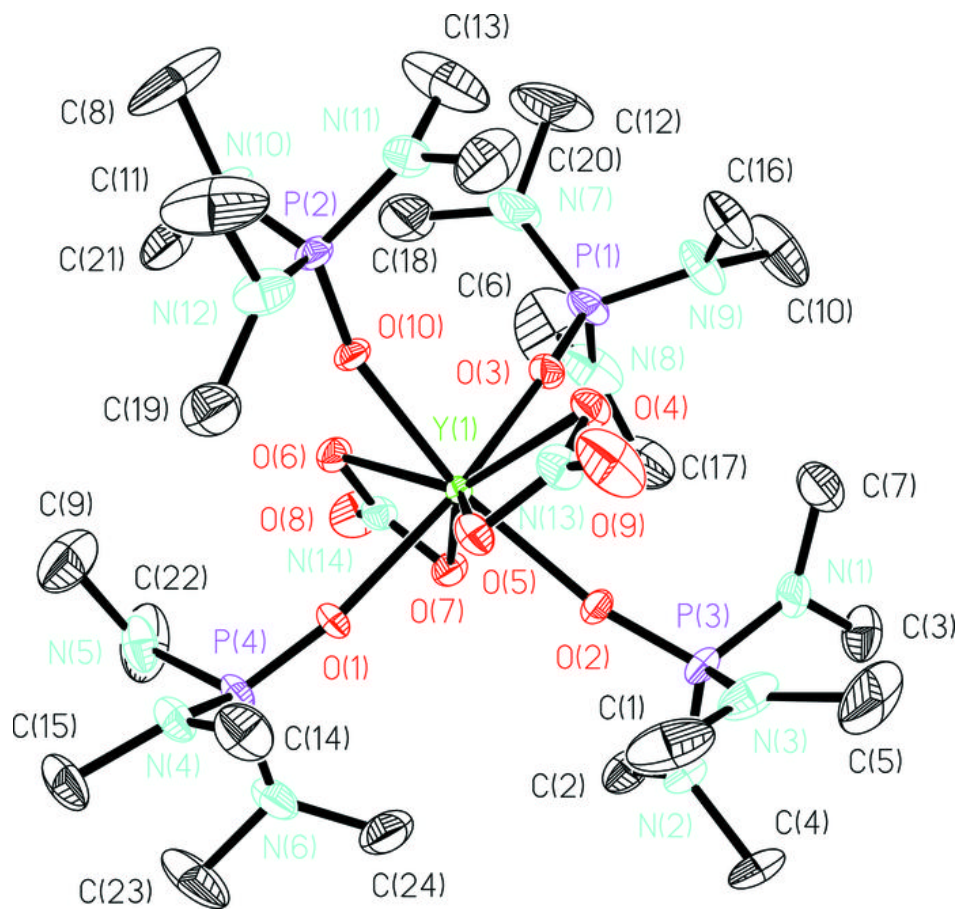


Fig. 2

