Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A new configuration of the one-dimensional anionic Mo/S/Ag polymer, $\{[Ce(dmac)_7MeOH][Mo_3S_{12}Ag_3]\}_n$ (dmac is *N*,*N*-dimethylacetamide)

Yuan Cao, Jin-Fang Zhang 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 23 May 2007; accepted 4 June 2007

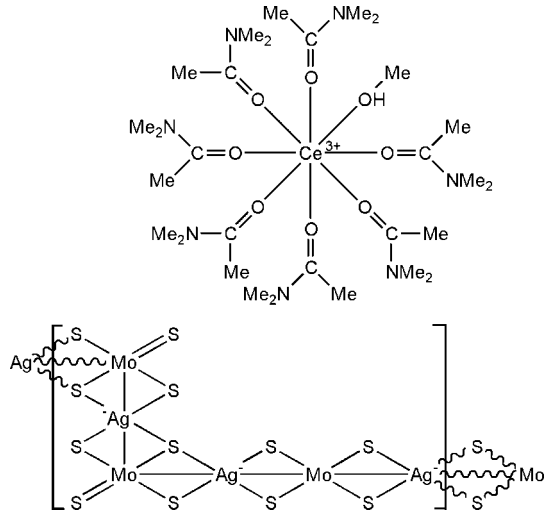
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.014 Å; disorder in main residue; R factor = 0.054; wR factor = 0.142; data-to-parameter ratio = 19.1.

The self-assembly of tetrathiomolybdate, silver iodide and cerium nitrate in *N*,*N*-dimethylacetamide (dmac) and methanol resulted in a one-dimensional anionic Mo/S/Ag polymer, catena-poly[heptakis(*N*,*N*-dimethylacetamide-κO)-(methanol-κO)cerium(III) [di-μ_3-sulfido-octa-μ_2-sulfido-disulfidotrisilver(I)trimolybdenum(VI)]], $\{[Ce(C_4H_9NO)_7(CH_4O)][Mo_3S_{12}Ag_3]\}_n$. The polymeric anion $\{[Mo_3S_{12}Ag_3]_n\}^{3n-}$ assumes a new configuration of a saw-tooth chain with the lengths of the sides in a 1:2 ratio. Such a configuration is intermediate between the polymeric anions in two reported compounds, *viz*. $\{[Ca(DMF)_6][Mo_2S_8Ag_2]\}_n$ and $\{[Ca(DMSO)_6]_2[W_4S_{16}Ag_4]\}_n$ (DMF is dimethylformamide and DMSO is dimethyl sulfoxide). The metal atoms in the chain are nearly coplanar. The central Ce in the solvent-coordinated cation has distorted square-antiprismatic coordination. Of the seven *N*,*N*-dimethylacetamide (dmac) molecules present, one is found to be disordered over two sites, with occupancy factors of 0.63 and 0.37. The overall structure can be viewed as consisting of staggered layers parallel to (010), which are formed by anionic chains propagating along the *a* axis and cations distributed in the spaces between the anionic chains. No notable interactions are found between cations and polymeric anions except for electrostatic attractions.

Related literature

The two most relevant known analogs of the title compound are $\{[Ca(DMF)_6][Mo_2S_8Ag_2]\}_n$ (Yu *et al.*, 1998) and $\{[Ca(DMSO)_6]_2[W_4S_{16}Ag_4]\}_n$ (Huang *et al.*, 1996) (DMF is dimethylformamide and DMSO is dimethyl sulfoxide), both also having saw-tooth-shaped polymeric anions but of different configurations, with the lengths of the sides in the ratio 1:1 and 1:3, respectively.

For related literature, see: Niu *et al.* (2004); Zhang *et al.* (2007).



Experimental

Crystal data

$[Ce(C_4H_9NO)_7(CH_4O)][Mo_3Ag_3S_{12}]$
M_r = 1777.28
Triclinic, $P\overline{1}$
a = 12.326 (3) Å
b = 15.089 (3) Å
c = 16.747 (3) Å
α = 96.10 (3)°
β = 98.01 (3)°
γ = 101.00 (3)°
V = 2999.3 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.77 mm^{-1}
T = 293 (2) K
0.25 × 0.20 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (*XCAD4*; Harms & Wocadlo, 1995)
T_{min} = 0.494, T_{max} = 0.610
12323 measured reflections
11741 independent reflections
8829 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
3 standard reflections
every 550 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.142
S = 1.00
11741 reflections
616 parameters
9 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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*.

Financial support from the National Natural Science Foundation of China (No. 50472048) and the Program for New Century Excellent Talents in Universities (NCET-05-0499) is acknowledged.

 doi:10.1107/S1600536807027389

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2044).

References

Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Huang, Q., Wu, X. T. & Lu, J. X. (1996). *Inorg. Chem.* **35**, 7445–7447.
Niu, Y. Y., Zheng, H. G., Hou, H. W. & Xin, X. Q. (2004). *Coord. Chem. Rev.* **248**, 169–183.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Yu, H., Zhang, W. J., Wu, X. T., Sheng, T. L., Wang, Q. M. & Lin, P. (1998). *Angew. Chem. Int. Ed.* **37**, 2520–2521.
Zhang, C., Song, Y. L. & Wang, X. (2007). *Coord. Chem. Rev.* **251**, 111–141.

supplementary materials

Acta Cryst. (2007). E**63**, m1987-m1988 [**doi:10.1107/S1600536807027389**]

A new configuration of the one-dimensional anionic Mo/S/Ag polymer, $\{[Ce(dmac)_7MeOH][Mo_3S_{12}Ag_3]\}_n$ (dmac is *N*,*N*-dimethylacetamide)

Y. Cao, J.-F. Zhang and C. Zhang

Comment

Heterothiometallic Mo(W)/S/Cu(Ag) polymers are of considerable interests for their structural richness (Niu *et al.*, 2004) and promising applications as third-order nonlinear optic (NLO) materials (Zhang *et al.*, 2007). The title compound represents a new configuration of 1-D Mo(W)/S/Ag polymers.

The asymmetric unit of the title compound comprises one solvent-coordinated cation $[Ce(dmac)_7MeOH]^{3+}$ (dmac = *N*,*N*'-dimethylacetamide) and a repeat unit of the polymeric anion $[Mo_3S_{12}Ag_3]^{3-}$ (Fig. 1). The central Ce in the solvent-coordinated cation has distorted square antiprismatic coordination. Of the seven dmac molecules present, one is found to be disordered. The two components of the disordered dmac have occupancies of 0.63 and 0.37 (3). The Ce—O bond lengths between Ce and seven O atoms from dmac are similar but much shorter than that between Ce and O from methanol. The repeat unit in the anionic chains consists of two butterfly-shaped and one linear $[MoS_4Ag_2]$ sub-units joined together by shared silver atoms. The geometry of the sub-units is very similar to those in previous reported 1-D Mo(W)/S/Ag polymers, $\{[Ca(dmso)_6]_2[W_4S_{16}Ag_4]\}_n$ (Yu *et al.*, 1998) and $\{[Ca(dmf)_6][Mo_2S_8Ag_2]\}_n$ (Huang *et al.*, 1996) but they are differently arranged leading to different chain configurations(Fig. 2). The anionic chains in the title compound are saw-tooth-shaped with the lengths of the sides in the ratio 1:2, as against the ratios of 1:1 and 1:3 observed in the aforementioned reported compounds. All metals in the anionic chain of the title compound are nearly coplanar. The overall structure can be viewed as consisting of staggered layers parallel to (010), which are formed by anionic chains propagating along the *a* axis and cations distributed in the spaces of the anionic chains (Fig. 3).

Experimental

1 mmol AgI was added to a solution of $[NH_4]_2MoS_4$ (1 mmol in 10 mL dmac) with thorough stir for 10 minutes. The solution underwent an additional stir for one minute after 0.5 mmol $Ce(NO_3)_36H_2O$ was added. After filtration the black-red filtrate was carefully laid on the surface with 10 ml CH_3OH. Black-red prism crystals were obtained after two weeks. Yield: 0.377 g in pure form, 63.6% (based on Mo). Analysis calculated for $C_{29}H_{67}Ag_3CeMo_3N_7O_8S_{12}$: C 19.57, H 4.07, N 5.51%; found: C 19.32, H 3.86, N 5.72%. IR: ν, cm^{-1} 1604vs (C═O), 495*m*, 482s h (Mo—S_t), 451 s (Mo-μ_2-S) and 420s h (Mo-μ_3-S).

Refinement

One coordinated dmac molecule is disordered, with two distinct positions with partial occupancies except for the O atoms. The occupancy for the disordered parts was refined to be 0.63:0.37 (3). The minor component was restrained to obtain reasonable geometry. These disordered atoms were refined with anisotropic displacement parameters. H atoms were positioned geometrically and refined with a riding model, with $U_{iso} = 1.5U_{eq}$ for methyl H atoms. The –OH H atom of methanol cannot be located in difference Fourier maps so it is not included in the crystallographic data.

Figures

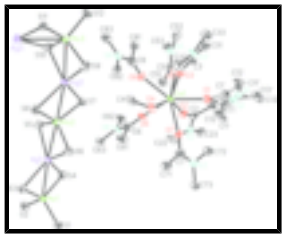


Fig. 1. The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids. All H atoms have been omitted.

Fig. 2. Different configurations of 1-D saw-tooth-shaped Mo(W)/S/Ag polymers.

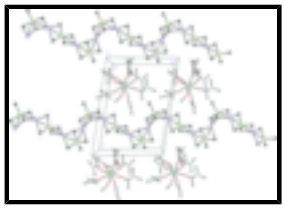


Fig. 3. The packing of the title compound, viewed down the *b* axis, only one layer of molecules shown for clarity. All H atoms have been omitted.

catena-poly[heptakis(*N*,*N*'-dimethylacetamide-κ*O*)(methanol-κ*O*)cerium(III) [di-μ$_3$-sulfido-octa-μ$_2$-sulfido-disulfidotrisilver(I)trimolybdenum(IV)]]

Crystal data

$[Ce(C_4H_9NO)_7(CH_4O)][Mo_3Ag_3S_{12}]$	$Z = 2$
$M_r = 1777.28$	$F_{000} = 1740$
Triclinic, $P\overline{1}$	$D_x = 1.968$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.326$ (3) Å	Cell parameters from 12323 reflections
$b = 15.089$ (3) Å	$\theta = 1.2$–26.0º
$c = 16.747$ (3) Å	$\mu = 2.77$ mm^{-1}
$\alpha = 96.10$ (3)º	$T = 293$ (2) K
$\beta = 98.01$ (3)º	Prism, black-red
$\gamma = 101.00$ (3)º	0.25 × 0.20 × 0.18 mm
$V = 2999.3$ (12) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.045$
Radiation source: sealed tube	$\theta_{max} = 26.0$º
Monochromator: graphite	$\theta_{min} = 1.2$º
$T = 293(2)$ K	$h = 0 \rightarrow 15$
ω scans	$k = -18 \rightarrow 18$
Absorption correction: ψ scan (XCAD4; Harms & Wocadlo, 1995)	$l = -20 \rightarrow 20$

T_{min} = 0.494, T_{max} = 0.610
12323 measured reflections
11741 independent reflections
8829 reflections with $I > 2\sigma(I)$

3 standard reflections
every . reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.142$
$S = 1.00$
11741 reflections
616 parameters
9 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.30$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}
Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ce1	0.25569 (4)	0.25542 (3)	0.26384 (3)	0.03690 (12)	
Mo3	−0.21526 (6)	0.30112 (5)	0.57263 (4)	0.03952 (16)	
Mo1	0.66703 (5)	0.23209 (5)	0.89485 (4)	0.03867 (16)	
Mo2	0.22670 (6)	0.25434 (5)	0.71991 (4)	0.03925 (16)	
Ag2	0.01230 (5)	0.27838 (4)	0.63464 (4)	0.04257 (15)	
Ag1	0.44028 (5)	0.23634 (5)	0.81193 (4)	0.04697 (16)	
Ag3	−0.26820 (6)	0.27206 (4)	0.73640 (4)	0.04776 (16)	
S7	0.16012 (18)	0.20197 (16)	0.59142 (13)	0.0483 (5)	
S11	−0.31129 (18)	0.38494 (15)	0.64026 (13)	0.0456 (4)	
S10	−0.18108 (19)	0.18235 (15)	0.63386 (15)	0.0521 (5)	
S6	0.38461 (19)	0.35212 (15)	0.72524 (15)	0.0542 (5)	
S5	0.24748 (19)	0.13581 (15)	0.78314 (16)	0.0533 (5)	
S4	0.58495 (19)	0.14711 (14)	0.77510 (14)	0.0503 (5)	
S12	−0.3167 (2)	0.24885 (18)	0.45738 (14)	0.0579 (6)	
S3	0.5513 (2)	0.30032 (17)	0.95274 (14)	0.0543 (5)	
S8	0.1154 (2)	0.32516 (16)	0.78014 (14)	0.0532 (5)	
S9	−0.0618 (2)	0.39019 (16)	0.55104 (15)	0.0543 (5)	
S2	0.7228 (2)	0.14308 (16)	0.97578 (15)	0.0552 (5)	
S1	0.8153 (2)	0.33502 (18)	0.88300 (15)	0.0600 (6)	
O1	0.2916 (6)	0.3164 (4)	0.1362 (4)	0.0565 (15)	
N1	0.2963 (10)	0.3762 (10)	0.0245 (10)	0.053 (4)	0.63 (3)
C1	0.3137 (15)	0.3835 (15)	0.1020 (13)	0.062 (5)	0.63 (3)
C11	0.373 (2)	0.4798 (16)	0.1453 (11)	0.042 (5)	0.63 (3)
H11A	0.3805	0.4802	0.2031	0.064*	0.63 (3)
H11B	0.3289	0.5231	0.1294	0.064*	0.63 (3)

H11C	0.4455	0.4958	0.1301	0.064*	0.63 (3)
C12	0.244 (2)	0.2814 (19)	−0.0182 (19)	0.055 (8)	0.63 (3)
H12A	0.2288	0.2412	0.0216	0.083*	0.63 (3)
H12B	0.2940	0.2601	−0.0509	0.083*	0.63 (3)
H12C	0.1748	0.2825	−0.0523	0.083*	0.63 (3)
C13	0.323 (2)	0.4524 (15)	−0.0244 (16)	0.051 (5)	0.63 (3)
H13A	0.3429	0.5094	0.0111	0.077*	0.63 (3)
H13B	0.2591	0.4525	−0.0641	0.077*	0.63 (3)
H13C	0.3851	0.4444	−0.0515	0.077*	0.63 (3)
N1'	0.3063 (19)	0.4207 (14)	0.0662 (14)	0.051 (7)	0.37 (3)
C1'	0.282 (2)	0.3342 (13)	0.0651 (10)	0.050 (8)	0.37 (3)
C11'	0.275 (4)	0.275 (3)	−0.016 (2)	0.044 (10)	0.37 (3)
H11D	0.2680	0.3115	−0.0592	0.066*	0.37 (3)
H11E	0.2107	0.2260	−0.0234	0.066*	0.37 (3)
H11F	0.3415	0.2511	−0.0156	0.066*	0.37 (3)
C12'	0.338 (4)	0.478 (3)	0.149 (2)	0.072 (18)	0.37 (3)
H12D	0.3259	0.4397	0.1904	0.109*	0.37 (3)
H12E	0.2921	0.5228	0.1521	0.109*	0.37 (3)
H12F	0.4152	0.5081	0.1568	0.109*	0.37 (3)
C13'	0.303 (4)	0.469 (3)	−0.0072 (18)	0.056 (12)	0.37 (3)
H13D	0.3256	0.5339	0.0096	0.084*	0.37 (3)
H13E	0.2285	0.4553	−0.0374	0.084*	0.37 (3)
H13F	0.3536	0.4501	−0.0410	0.084*	0.37 (3)
O2	0.3846 (5)	0.1674 (4)	0.2114 (4)	0.0525 (15)	
N2	0.5164 (6)	0.0950 (5)	0.1864 (5)	0.0509 (17)	
C2	0.4278 (7)	0.1245 (6)	0.1617 (5)	0.049 (2)	
C21	0.3960 (7)	0.1166 (7)	0.0700 (6)	0.055 (2)	
H21A	0.3323	0.1436	0.0572	0.083*	
H21B	0.3777	0.0535	0.0470	0.083*	
H21C	0.4578	0.1478	0.0477	0.083*	
C22	0.5481 (9)	0.1043 (7)	0.2779 (6)	0.069 (3)	
H22A	0.5020	0.1396	0.3032	0.104*	
H22B	0.6254	0.1343	0.2936	0.104*	
H22C	0.5371	0.0449	0.2949	0.104*	
C23	0.5706 (8)	0.0382 (7)	0.1323 (6)	0.063 (2)	
H23A	0.5422	0.0410	0.0764	0.094*	
H23B	0.5541	−0.0239	0.1428	0.094*	
H23C	0.6502	0.0608	0.1427	0.094*	
O3	0.1029 (5)	0.3306 (5)	0.2131 (4)	0.0573 (16)	
N3	−0.0014 (7)	0.4207 (5)	0.1652 (4)	0.0559 (19)	
C3	0.0411 (8)	0.3489 (6)	0.1572 (6)	0.056 (2)	
C31	−0.0048 (8)	0.2886 (7)	0.0780 (6)	0.063 (3)	
H31A	0.0301	0.2369	0.0752	0.094*	
H31B	0.0103	0.3221	0.0337	0.094*	
H31C	−0.0843	0.2681	0.0742	0.094*	
C32	0.0317 (10)	0.4821 (7)	0.2463 (6)	0.067 (3)	
H32A	0.0839	0.4583	0.2817	0.101*	
H32B	−0.0338	0.4845	0.2708	0.101*	
H32C	0.0659	0.5423	0.2378	0.101*	

C33	−0.0857 (9)	0.4431 (8)	0.1035 (7)	0.066 (3)
H33A	−0.1028	0.3969	0.0570	0.099*
H33B	−0.0566	0.5010	0.0873	0.099*
H33C	−0.1526	0.4462	0.1261	0.099*
O5	0.1308 (6)	0.1204 (4)	0.1755 (4)	0.0599 (17)
N5	0.0311 (7)	−0.0145 (5)	0.1339 (5)	0.061 (2)
C5	0.1202 (10)	0.0364 (8)	0.1709 (6)	0.069 (3)
C51	0.2056 (9)	−0.0116 (6)	0.2111 (6)	0.067 (3)
H51A	0.2697	0.0328	0.2393	0.101*
H51B	0.2284	−0.0507	0.1704	0.101*
H51C	0.1731	−0.0474	0.2492	0.101*
C52	−0.0618 (9)	0.0308 (6)	0.1024 (7)	0.060 (2)
H52A	−0.0365	0.0958	0.1136	0.090*
H52B	−0.1253	0.0126	0.1288	0.090*
H52C	−0.0830	0.0130	0.0447	0.090*
C53	0.0090 (8)	−0.1155 (7)	0.1205 (6)	0.060 (2)
H53A	0.0732	−0.1359	0.1452	0.090*
H53B	−0.0057	−0.1366	0.0631	0.090*
H53C	−0.0549	−0.1395	0.1444	0.090*
O6	0.3340 (5)	0.1890 (4)	0.3810 (4)	0.0477 (14)
N6	0.3873 (6)	0.1322 (5)	0.4908 (4)	0.0523 (18)
C6	0.3731 (8)	0.1975 (6)	0.4534 (6)	0.053 (2)
C61	0.4061 (8)	0.2932 (6)	0.5061 (6)	0.064 (3)
H61A	0.3902	0.3388	0.4730	0.096*
H61B	0.4846	0.3061	0.5278	0.096*
H61C	0.3637	0.2936	0.5501	0.096*
C62	0.3572 (9)	0.0382 (6)	0.4430 (6)	0.061 (3)
H62A	0.3241	0.0415	0.3882	0.092*
H62B	0.3048	−0.0006	0.4680	0.092*
H62C	0.4236	0.0139	0.4421	0.092*
C63	0.4383 (8)	0.1383 (7)	0.5773 (5)	0.058 (2)
H63A	0.4560	0.2008	0.6020	0.086*
H63B	0.5056	0.1147	0.5804	0.086*
H63C	0.3864	0.1032	0.6056	0.086*
O7	0.4431 (5)	0.3621 (4)	0.3000 (4)	0.0526 (15)
N7	0.6201 (7)	0.3994 (6)	0.2894 (5)	0.061 (2)
C7	0.5409 (8)	0.4003 (7)	0.3275 (6)	0.059 (2)
C71	0.5676 (9)	0.4684 (7)	0.4077 (6)	0.063 (3)
H71A	0.4996	0.4708	0.4289	0.094*
H71B	0.6005	0.5279	0.3967	0.094*
H71C	0.6191	0.4485	0.4469	0.094*
C72	0.5890 (9)	0.3481 (7)	0.2047 (6)	0.063 (3)
H72A	0.5102	0.3221	0.1941	0.094*
H72B	0.6303	0.3004	0.1999	0.094*
H72C	0.6068	0.3891	0.1661	0.094*
C73	0.7404 (8)	0.4434 (7)	0.3211 (6)	0.057 (2)
H73A	0.7463	0.4767	0.3742	0.086*
H73B	0.7678	0.4844	0.2848	0.086*
H73C	0.7842	0.3972	0.3245	0.086*

O8	0.0996 (5)	0.1932 (4)	0.3294 (4)	0.0537 (15)
N8	−0.0321 (6)	0.0976 (5)	0.3725 (5)	0.0524 (18)
C8	0.0026 (9)	0.1720 (7)	0.3435 (6)	0.058 (2)
C81	−0.0862 (8)	0.2282 (6)	0.3240 (5)	0.052 (2)
H81A	−0.0531	0.2823	0.3035	0.079*
H81B	−0.1150	0.2449	0.3725	0.079*
H81C	−0.1461	0.1928	0.2837	0.079*
C82	0.0511 (8)	0.0383 (6)	0.3886 (6)	0.054 (2)
H82A	0.1198	0.0641	0.3710	0.081*
H82B	0.0215	−0.0216	0.3592	0.081*
H82C	0.0653	0.0345	0.4458	0.081*
C83	−0.1457 (9)	0.0642 (7)	0.3895 (7)	0.064 (3)
H83A	−0.1923	0.1061	0.3749	0.096*
H83B	−0.1421	0.0593	0.4465	0.096*
H83C	−0.1766	0.0054	0.3584	0.096*
O4	0.2456 (5)	0.3896 (4)	0.3731 (4)	0.0509 (14)
C4	0.1747 (8)	0.3940 (7)	0.4364 (6)	0.060 (2)
H4A	0.1950	0.4534	0.4679	0.089*
H4B	0.1854	0.3488	0.4713	0.089*
H4C	0.0976	0.3826	0.4114	0.089*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.0382 (2)	0.0364 (2)	0.0348 (2)	0.00785 (17)	0.00085 (17)	0.00563 (16)
Mo3	0.0361 (3)	0.0395 (3)	0.0415 (4)	0.0063 (3)	0.0031 (3)	0.0064 (3)
Mo1	0.0342 (3)	0.0453 (4)	0.0355 (3)	0.0067 (3)	0.0006 (3)	0.0104 (3)
Mo2	0.0373 (3)	0.0391 (3)	0.0422 (4)	0.0133 (3)	0.0006 (3)	0.0072 (3)
Ag2	0.0357 (3)	0.0480 (3)	0.0421 (3)	0.0071 (2)	−0.0015 (2)	0.0111 (3)
Ag1	0.0406 (3)	0.0527 (4)	0.0433 (3)	0.0049 (3)	−0.0012 (3)	0.0067 (3)
Ag3	0.0602 (4)	0.0394 (3)	0.0421 (3)	0.0030 (3)	0.0119 (3)	0.0071 (3)
S7	0.0436 (11)	0.0579 (12)	0.0402 (10)	0.0112 (9)	0.0006 (9)	−0.0013 (9)
S11	0.0428 (11)	0.0491 (11)	0.0458 (11)	0.0138 (9)	0.0041 (9)	0.0068 (9)
S10	0.0461 (12)	0.0503 (12)	0.0623 (13)	0.0139 (10)	0.0130 (10)	0.0061 (10)
S6	0.0483 (12)	0.0475 (11)	0.0576 (13)	0.0021 (9)	−0.0120 (10)	0.0082 (10)
S5	0.0481 (12)	0.0448 (11)	0.0677 (14)	0.0115 (9)	0.0109 (11)	0.0062 (10)
S4	0.0487 (12)	0.0408 (10)	0.0573 (13)	0.0034 (9)	0.0056 (10)	0.0033 (9)
S12	0.0554 (13)	0.0649 (14)	0.0452 (12)	0.0118 (11)	−0.0065 (10)	−0.0078 (10)
S3	0.0498 (12)	0.0637 (14)	0.0489 (12)	0.0083 (10)	0.0146 (10)	0.0035 (10)
S8	0.0546 (13)	0.0562 (13)	0.0496 (12)	0.0159 (10)	0.0071 (10)	0.0053 (10)
S9	0.0486 (12)	0.0553 (13)	0.0605 (13)	0.0117 (10)	0.0138 (10)	0.0072 (10)
S2	0.0637 (14)	0.0487 (12)	0.0533 (12)	0.0141 (11)	0.0026 (11)	0.0116 (10)
S1	0.0501 (13)	0.0661 (14)	0.0557 (13)	−0.0089 (11)	0.0026 (10)	0.0181 (11)
O1	0.062 (4)	0.051 (4)	0.053 (4)	0.007 (3)	0.006 (3)	0.005 (3)
N1	0.042 (7)	0.052 (9)	0.059 (9)	0.003 (6)	−0.005 (6)	0.009 (7)
C1	0.047 (9)	0.069 (14)	0.069 (13)	0.019 (9)	−0.001 (9)	0.009 (11)
C11	0.036 (14)	0.050 (10)	0.036 (8)	0.004 (8)	−0.008 (6)	0.009 (7)
C12	0.032 (16)	0.048 (10)	0.076 (14)	0.011 (9)	−0.018 (10)	−0.005 (8)

C13	0.053 (12)	0.047 (9)	0.052 (13)	0.011 (8)	0.005 (9)	0.000 (10)
N1'	0.043 (12)	0.050 (15)	0.044 (15)	−0.012 (10)	−0.006 (10)	−0.014 (12)
C1'	0.054 (15)	0.051 (15)	0.028 (13)	−0.014 (12)	−0.009 (10)	−0.011 (12)
C11'	0.02 (2)	0.06 (2)	0.044 (17)	0.012 (14)	0.009 (14)	0.000 (14)
C12'	0.04 (3)	0.06 (2)	0.10 (3)	−0.025 (19)	−0.004 (18)	0.001 (18)
C13'	0.06 (2)	0.08 (3)	0.026 (14)	0.029 (17)	0.002 (12)	−0.023 (14)
O2	0.051 (3)	0.049 (3)	0.059 (4)	0.012 (3)	0.023 (3)	−0.005 (3)
N2	0.053 (4)	0.046 (4)	0.056 (4)	0.013 (3)	0.005 (3)	0.017 (3)
C2	0.045 (5)	0.048 (5)	0.049 (5)	−0.002 (4)	0.006 (4)	0.009 (4)
C21	0.041 (5)	0.061 (5)	0.062 (6)	0.011 (4)	−0.007 (4)	0.017 (4)
C22	0.077 (7)	0.055 (5)	0.063 (6)	0.023 (5)	−0.031 (5)	−0.008 (5)
C23	0.056 (6)	0.064 (6)	0.067 (6)	0.004 (5)	0.020 (5)	0.004 (5)
O3	0.051 (4)	0.066 (4)	0.049 (3)	0.011 (3)	−0.001 (3)	−0.003 (3)
N3	0.061 (5)	0.058 (4)	0.044 (4)	0.014 (4)	−0.015 (3)	0.012 (3)
C3	0.059 (5)	0.056 (5)	0.045 (5)	0.013 (4)	−0.006 (4)	−0.007 (4)
C31	0.047 (5)	0.061 (6)	0.071 (6)	0.005 (4)	0.003 (5)	−0.013 (5)
C32	0.080 (7)	0.049 (5)	0.067 (6)	0.011 (5)	−0.005 (5)	0.007 (5)
C33	0.058 (6)	0.075 (7)	0.068 (6)	0.023 (5)	0.001 (5)	0.021 (5)
O5	0.060 (4)	0.052 (4)	0.058 (4)	0.007 (3)	−0.002 (3)	−0.015 (3)
N5	0.073 (5)	0.040 (4)	0.064 (5)	0.000 (4)	0.012 (4)	−0.004 (3)
C5	0.070 (7)	0.068 (7)	0.055 (6)	−0.011 (5)	−0.006 (5)	0.010 (5)
C51	0.079 (7)	0.048 (5)	0.065 (6)	−0.006 (5)	−0.010 (5)	0.027 (5)
C52	0.073 (6)	0.040 (4)	0.078 (7)	0.024 (4)	0.030 (5)	0.016 (4)
C53	0.040 (5)	0.064 (6)	0.066 (6)	−0.010 (4)	0.015 (4)	−0.009 (5)
O6	0.041 (3)	0.045 (3)	0.051 (3)	0.008 (2)	−0.017 (3)	0.011 (3)
N6	0.057 (4)	0.058 (4)	0.038 (4)	0.024 (4)	−0.014 (3)	−0.003 (3)
C6	0.049 (5)	0.043 (4)	0.064 (6)	0.012 (4)	−0.006 (4)	0.010 (4)
C61	0.057 (6)	0.046 (5)	0.079 (7)	0.005 (4)	−0.027 (5)	0.027 (5)
C62	0.074 (6)	0.043 (5)	0.056 (5)	0.001 (4)	−0.020 (5)	0.021 (4)
C63	0.050 (5)	0.069 (6)	0.049 (5)	0.010 (4)	−0.004 (4)	0.010 (4)
O7	0.048 (3)	0.051 (3)	0.047 (3)	−0.013 (3)	0.009 (3)	−0.007 (3)
N7	0.053 (5)	0.062 (5)	0.062 (5)	0.005 (4)	0.003 (4)	0.007 (4)
C7	0.048 (5)	0.054 (5)	0.066 (6)	−0.003 (4)	0.003 (5)	0.007 (5)
C71	0.058 (6)	0.053 (5)	0.068 (6)	−0.001 (4)	0.003 (5)	−0.007 (5)
C72	0.064 (6)	0.056 (5)	0.055 (5)	−0.006 (5)	0.000 (5)	−0.004 (4)
C73	0.057 (5)	0.061 (5)	0.045 (5)	−0.003 (4)	0.002 (4)	0.001 (4)
O8	0.050 (4)	0.062 (4)	0.051 (3)	0.010 (3)	0.018 (3)	0.010 (3)
N8	0.046 (4)	0.065 (5)	0.049 (4)	0.019 (4)	0.010 (3)	0.008 (4)
C8	0.063 (6)	0.054 (5)	0.058 (5)	0.013 (5)	0.003 (5)	0.012 (4)
C81	0.061 (5)	0.044 (5)	0.049 (5)	0.002 (4)	0.007 (4)	0.014 (4)
C82	0.048 (5)	0.051 (5)	0.060 (5)	0.004 (4)	0.013 (4)	0.008 (4)
C83	0.066 (6)	0.053 (5)	0.068 (6)	0.011 (5)	−0.003 (5)	0.014 (5)
O4	0.062 (4)	0.039 (3)	0.048 (3)	0.012 (3)	0.002 (3)	−0.002 (2)
C4	0.066 (6)	0.066 (6)	0.045 (5)	0.024 (5)	−0.008 (4)	0.003 (4)

Geometric parameters (Å, °)

Ce1—O8	2.430 (6)	O1—C1	1.22 (2)
Ce1—O2	2.450 (6)	O1—C1'	1.242 (15)

Ce1—O6	2.458 (5)	N1—C1	1.28 (3)
Ce1—O3	2.476 (7)	N1—C13	1.49 (2)
Ce1—O1	2.478 (6)	N1—C12	1.51 (3)
Ce1—O5	2.497 (6)	C1—C11	1.55 (3)
Ce1—O7	2.506 (6)	N1'—C1'	1.28 (2)
Ce1—O4	2.615 (6)	N1'—C13'	1.50 (2)
Mo3—S12	2.131 (2)	N1'—C12'	1.51 (2)
Mo3—S9	2.199 (3)	C1'—C11'	1.52 (2)
Mo3—S11	2.219 (2)	O2—C2	1.240 (10)
Mo3—S10	2.236 (2)	N2—C2	1.288 (11)
Mo3—Ag2	2.9487 (12)	N2—C23	1.491 (12)
Mo3—Ag3	2.9641 (11)	N2—C22	1.512 (12)
Mo1—S2	2.143 (2)	C2—C21	1.518 (12)
Mo1—S3	2.183 (3)	O3—C3	1.213 (11)
Mo1—S1	2.208 (2)	N3—C3	1.291 (12)
Mo1—S4	2.254 (3)	N3—C33	1.474 (11)
Mo1—Ag1	2.9579 (12)	N3—C32	1.518 (12)
Mo1—Ag3^{i}	2.9646 (11)	C3—C31	1.500 (12)
Mo2—S8	2.181 (2)	O5—C5	1.243 (13)
Mo2—S6	2.191 (3)	N5—C5	1.252 (13)
Mo2—S7	2.197 (2)	N5—C53	1.483 (12)
Mo2—S5	2.211 (2)	N5—C52	1.505 (13)
Mo2—Ag2	2.9290 (12)	C5—C51	1.511 (15)
Mo2—Ag1	2.9343 (12)	O6—C6	1.225 (11)
Ag2—S7	2.483 (2)	N6—C6	1.248 (11)
Ag2—S9	2.525 (3)	N6—C63	1.484 (10)
Ag2—S10	2.540 (3)	N6—C62	1.505 (11)
Ag2—S8	2.545 (3)	C6—C61	1.561 (13)
Ag1—S5	2.516 (3)	O7—C7	1.234 (11)
Ag1—S6	2.520 (2)	N7—C7	1.239 (13)
Ag1—S4	2.534 (3)	N7—C73	1.500 (12)
Ag1—S3	2.545 (3)	N7—C72	1.503 (12)
Ag3—S1^{ii}	2.533 (3)	C7—C71	1.557 (14)
Ag3—S11	2.543 (2)	O8—C8	1.239 (12)
Ag3—S10	2.551 (2)	N8—C8	1.291 (12)
Ag3—S4^{ii}	2.556 (2)	N8—C83	1.473 (13)
Ag3—Mo1^{ii}	2.9646 (11)	N8—C82	1.500 (12)
S4—Ag3^{i}	2.556 (2)	C8—C81	1.530 (13)
S1—Ag3^{i}	2.533 (3)	O4—C4	1.467 (12)
O8—Ce1—O2	124.7 (2)	S8—Mo2—S6	107.53 (10)
O8—Ce1—O6	73.1 (2)	S8—Mo2—S7	113.29 (9)
O2—Ce1—O6	75.0 (2)	S6—Mo2—S7	108.06 (10)
O8—Ce1—O3	75.1 (2)	S8—Mo2—S5	107.83 (10)
O2—Ce1—O3	139.8 (2)	S6—Mo2—S5	113.00 (9)
O6—Ce1—O3	143.4 (2)	S7—Mo2—S5	107.24 (10)
O8—Ce1—O1	139.9 (2)	Ag2—Mo2—Ag1	177.26 (3)
O2—Ce1—O1	75.7 (2)	S7—Ag2—S9	120.29 (8)

O6—Ce1—O1	145.6 (2)	S7—Ag2—S10	118.75 (8)
O3—Ce1—O1	70.1 (2)	S9—Ag2—S10	93.70 (8)
O8—Ce1—O5	69.2 (2)	S7—Ag2—S8	93.32 (8)
O2—Ce1—O5	75.6 (2)	S9—Ag2—S8	122.38 (8)
O6—Ce1—O5	103.0 (2)	S10—Ag2—S8	110.11 (9)
O3—Ce1—O5	81.9 (2)	Mo2—Ag2—Mo3	171.36 (3)
O1—Ce1—O5	86.6 (2)	S5—Ag1—S6	93.59 (8)
O8—Ce1—O7	139.1 (2)	S5—Ag1—S4	110.62 (8)
O2—Ce1—O7	76.0 (2)	S6—Ag1—S4	120.53 (9)
O6—Ce1—O7	81.0 (2)	S5—Ag1—S3	125.48 (9)
O3—Ce1—O7	113.3 (2)	S6—Ag1—S3	115.81 (8)
O1—Ce1—O7	74.8 (2)	S4—Ag1—S3	93.18 (8)
O5—Ce1—O7	149.2 (2)	Mo2—Ag1—Mo1	174.07 (3)
O8—Ce1—O4	76.1 (2)	S1^{ii}—Ag3—S11	117.64 (8)
O2—Ce1—O4	142.9 (2)	S1^{ii}—Ag3—S10	127.35 (9)
O6—Ce1—O4	84.62 (19)	S11—Ag3—S10	93.57 (8)
O3—Ce1—O4	70.5 (2)	S1^{ii}—Ag3—S4^{ii}	93.65 (8)
O1—Ce1—O4	109.1 (2)	S11—Ag3—S4^{ii}	124.63 (8)
O5—Ce1—O4	140.1 (2)	S10—Ag3—S4^{ii}	102.10 (8)
O7—Ce1—O4	70.3 (2)	Mo2—S7—Ag2	77.22 (7)
S12—Mo3—S9	107.79 (11)	Mo3—S11—Ag3	76.66 (7)
S12—Mo3—S11	106.54 (9)	Mo3—S10—Ag2	75.96 (8)
S9—Mo3—S11	108.80 (9)	Mo3—S10—Ag3	76.20 (7)
S12—Mo3—S10	107.68 (10)	Ag2—S10—Ag3	105.48 (9)
S9—Mo3—S10	112.83 (9)	Mo2—S6—Ag1	76.70 (8)
S11—Mo3—S10	112.89 (9)	Mo2—S5—Ag1	76.44 (8)
Ag2—Mo3—Ag3	86.51 (4)	Mo1—S4—Ag1	76.06 (8)
S2—Mo1—S3	107.19 (10)	Mo1—S4—Ag3^{i}	75.79 (7)
S2—Mo1—S1	107.36 (10)	Ag1—S4—Ag3^{i}	101.22 (8)
S3—Mo1—S1	108.89 (11)	Mo1—S3—Ag1	77.02 (8)
S2—Mo1—S4	108.10 (9)	Mo2—S8—Ag2	76.15 (8)
S3—Mo1—S4	112.48 (9)	Mo3—S9—Ag2	76.90 (8)
S1—Mo1—S4	112.55 (10)	Mo1—S1—Ag3^{i}	77.08 (8)
Ag1—Mo1—Ag3^{i}	83.24 (3)		

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

Fig. 1

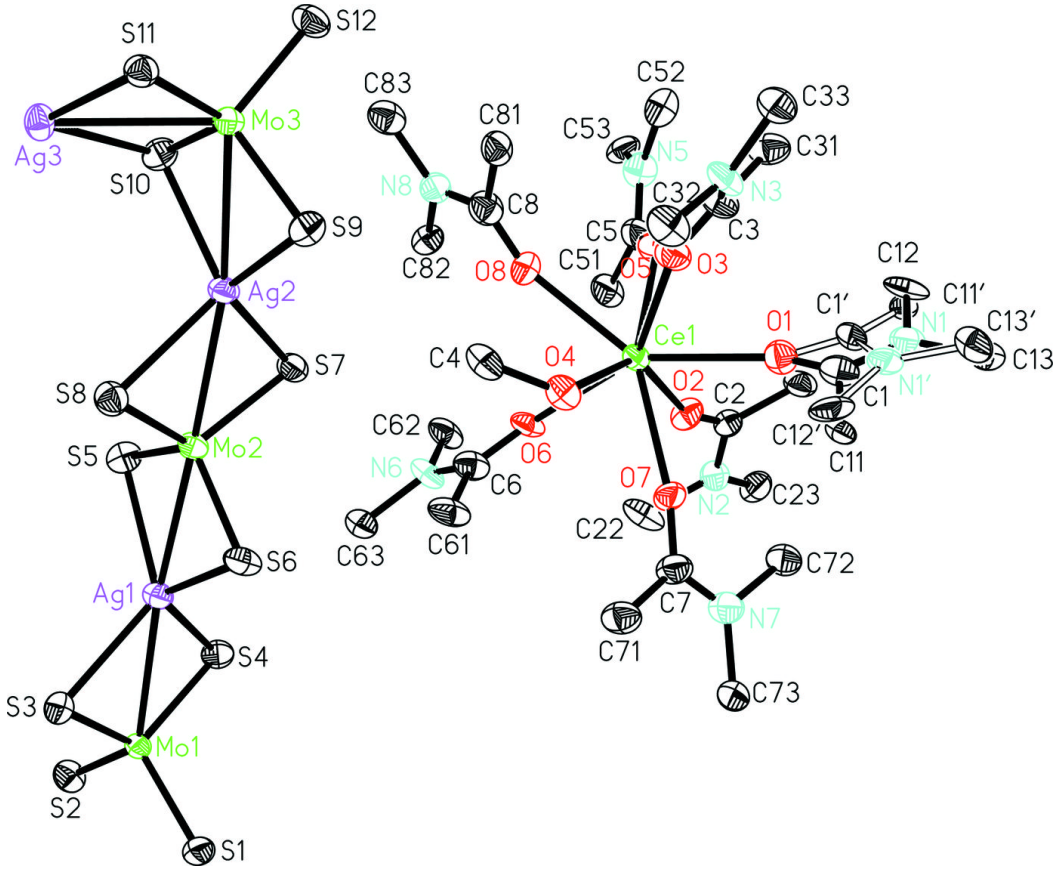

S11
S12
Mo3
Ag3
S10
S9
Ag2
S7
S8
Mo2
S5
S6
Ag1
S4
S3
Mo1
S2
S1
C83
C81
C52
C33
C53
N5
C31
N8
C8
C32
N3
C82
C5
C3
O8
C51
O5
O3
C12
C1′
C11′
O1
N1
C13′
Ce1
C4
O4
C13
N1′
O2
C2
C1
C62
O6
C12′
C11
N6
C6
O7
N2
C23
C22
C63
C61
C72
C7
N7
C71
C73

Fig. 2

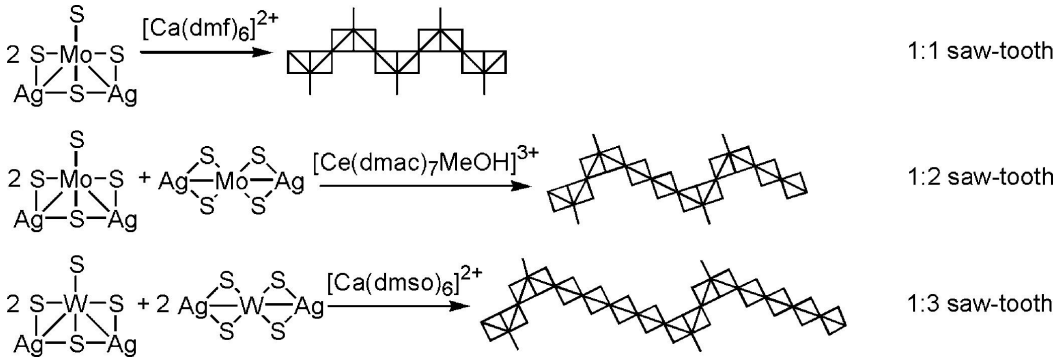

[Ca(dmf)6]2+
1:1 saw-tooth
[Ce(dmac)7MeOH]3+
1:2 saw-tooth
[Ca(dmso)6]2+
1:3 saw-tooth

Fig. 3