O2*A*—C1*A*—O1*A*	125.6 (8)	C9*D*—O7*D*—Ca	120.9 (7)
O2*A*—C1*A*—C2*A*	116.7 (8)	C11*D*—O8*D*—Ca	120.3 (5)
O1*A*—C1*A*—C2*A*	117.7 (6)	C13*D*—O9*D*—Ca	123.7 (5)
C3*A*—C2*A*—C7*A*	120.2 (8)	C10*D*—N3*D*—C12*D*	111 (1)
C3*A*—C2*A*—C1*A*	120.7 (7)	C10*D*—N3*D*—C8*D*	109 (1)
C7*A*—C2*A*—C1*A*	119.1 (7)	C12*D*—N3*D*—C8*D*	112 (1)
C2*A*—C3*A*—C4*A*	117.8 (8)	C9*D*—C8*D*—N3*D*	118.3 (9)
C5*A*—C4*A*—C3*A*	124.0 (8)	O7*D*—C9*D*—C8*D*	114 (1)
C5*A*—C4*A*—N1*A*	118.7 (8)	C11*D*—C10*D*—N3*D*	125 (1)
C3*A*—C4*A*—N1*A*	117.3 (8)	C10*D*—C11*D*—O8*D*	113.0 (8)
C6*A*—C5*A*—C4*A*	115.6 (8)	C13*D*—C12*D*—N3*D*	125 (1)
C5*A*—C6*A*—C7*A*	123.4 (8)	C12*D*—C13*D*—O9*D*	114.1 (9)
C5*A*—C6*A*—N2*A*	117.7 (8)		

C10*C*—N3*C*—C12*C*—C13*C*	159.5 (7)
C8*C*—N3*C*—C12*C*—C13*C*	−74.9 (9)
C8*C*—N3*C*—C10*C*—C11*C*	149.5 (8)
C10*C*—N3*C*—C8*C*—C9*C*	−79.4 (9)
C12*C*—N3*C*—C8*C*—C9*C*	156.3 (7)
C12*C*—N3*C*—C10*C*—C11*C*	−86.1 (9)
N3*C*—C8*C*—C9*C*—O7*C*	−59.7 (8)
N3*C*—C10*C*—C11*C*—O8*C*	−57.7 (10)
N3*C*—C12*C*—C13*C*—O9*C*	−63.8 (9)
C10*D*—N3*D*—C12*D*—C13*D*	99.6 (17)
C8*D*—N3*D*—C12*D*—C13*D*	−139.5 (15)
C8*D*—N3*D*—C10*D*—C11*D*	109.0 (14)
C10*D*—N3*D*—C8*D*—C9*D*	−136.7 (12)
C12*D*—N3*D*—C8*D*—C9*D*	101.3 (13)
C12*D*—N3*D*—C10*D*—C11*D*	−128.4 (14)
N3*D*—C8*D*—C9*D*—O7*D*	37.1 (15)
N3*D*—C10*D*—C11*D*—O8*D*	28.7 (17)
N3*D*—C12*D*—C13*D*—O9*D*	23 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O7*C*—H7*C*···O2*A*	1.89	2.661 (9)	155
O8*D*—H8*D*···O1*A*	1.66	2.695 (9)	151
O9*D*—H9*D*···O1*A*^{i}	1.78	2.704 (8)	163
O7*D*—H7*D*···O5*B*^{ii}	1.60	2.68 (1)	166
O9*C*—H9*C*···O6*B*^{ii}	1.72	2.83 (1)	164
O8*C*—H8*C*···O6*B*^{iii}	1.73	2.684 (8)	159

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

All H atoms were fixed geometrically except for the hydroxy H atoms which were located from a difference Fourier map. Weights were applied empirically so as to give no trends in $<w\Delta^2F>$ *versus* $<F_o>$ or $<\sin\theta/\lambda>$, using *PESOS* (Martinez-Ripoll & Cano, 1975).

Data collection: Philips PW1100 software. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *Xtal*3.2. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$\{Ca(OH_2)_3[Ca(DOTA)].7.7H_2O\}_n$

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Abstract

The octadentate ligand H_4DOTA (H_4DOTA = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) forms the most stable calcium complexes known. The overall solid-state structure of the title complex {poly[triaqua-μ-(1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetato)-dicalcium 7.7-hydrate], $[Ca_2(C_{16}H_{24}N_4O_8)(H_2O)_3].7.7H_2O$} contains two independent eight-coordinate Ca^{2+} ions on a twofold crystallographic axis with the Ca^{2+} ions bound to four of the eight O atoms [mean Ca—O = 2.45 (3) Å] and the four N atoms [mean Ca—N = 2.59 (2) Å] of the DOTA ligand. The coordination geometry of the Ca atom encapsulated by the DOTA ligand is distorted square antiprismatic. Carboxylate bridges link $[Ca(DOTA)]^{2-}$

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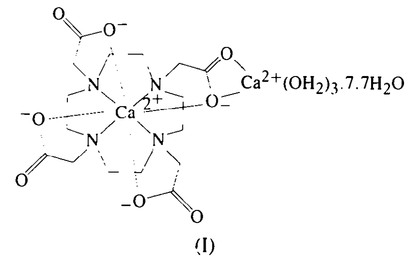
anions to $[\mathrm{Ca(OH_2)_3}]^{2+}$ counterions (on general positions related by the twofold symmetry) to form a neutral tetranuclear unit, which in turn bridges to surrounding units through a carboxylate O atom and generates a one-dimensional chain.

Comment

The DOTA ligand (1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetate) displays the highest stability constants for the 1:1 metal complexes of $\mathrm{Ca^{II}}$; $[ML]/[M][L] = 16.37\,(1)$ and $[MLH]/[ML][\mathrm{H}] = 3.60\,(4)$ (Clarke & Martell, 1991). This seems rather unusual when one considers that the $\mathrm{Ca^{II}}$ metal must bind to four N atoms in the DOTA ligand to fully utilize the octadentate coordination. Preorganization is one characteristic of the DOTA ligand that may prove beneficial to the overall stability of its metal complexes. As previously reported, the tetraazacyclododecane ring, which is the backbone of the DOTA ligand, has been shown to display the [3333] or square conformation (Reibenspies, 1992; Reibenspies & Anderson, 1991; Dale, 1980). Such a conformation is ideal for positioning the pendant carboxylate arms of the DOTA ligand on the same side of the tetraazacyclododecane ring, thus preorganizing the ligand for complexation.



(I)

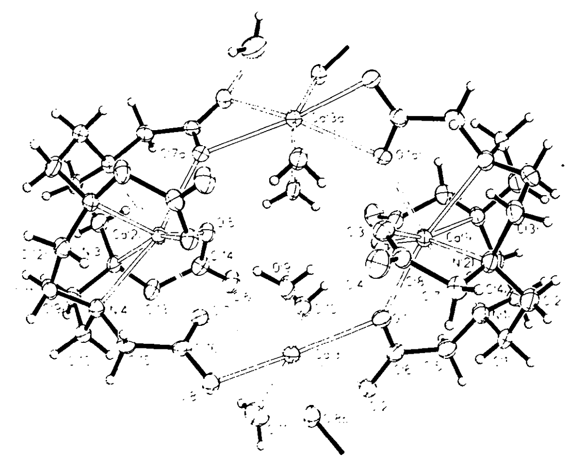


Fig. 1. View of the tetranuclear unit $\{\mathrm{Ca(OH_2)_3[Ca(DOTA)]}\}_2$ showing the displacement ellipsoids at 50% probability.

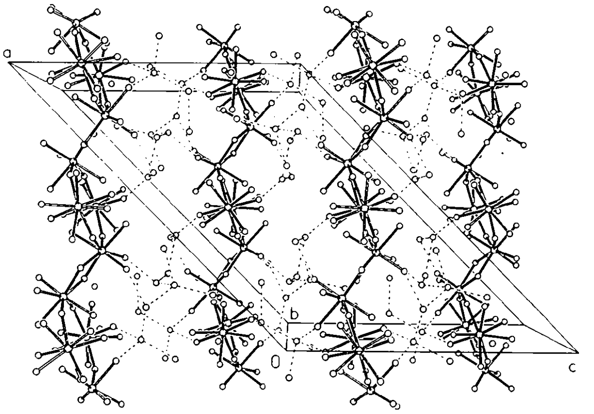


Fig. 2. Packing diagram for the title complex, viewed down the *b* axis. C and H atoms have been omitted for clarity.

For the structure reported here (Figs. 1 and 2) the DOTA ligand is seen to encapsulate the $\mathrm{Ca^{II}}$ atoms completely in a manner similar to that seen for the $\mathrm{Na^{I}}$ and $\mathrm{K^{I}}$ complexes of 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (Groth, 1983) and the $\mathrm{Eu^{III}}$ complex of DOTA [sodium aqua(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato)europate(III) tetrahydrate] (Spirlet, Rebizant, Desreux & Loncin, 1984). The encapsulated Ca atoms are eight-coordinate with the metal ligated to the four N atoms and four carboxylate groups of the DOTA ligand. The coordination geometry is best described as distorted antiprismatic, with four O atoms occupying the top corners and four N atoms the bottom corners of the antiprism. The coordination geometry is similar to that seen for the calcium complex of the macrotetrolide ionophore nonactin (Vishwanath, Shamala, Easwaran, & Vijayan, 1983). The Ca atom of each independent Ca(DOTA) complex is displaced toward the plane of the ligated O atoms [1.094 (3) for Ca1 and 1.075 (3) Å for Ca2] and away from the plane of the ligated N atoms [1.548 (4) for Ca1 and 1.509 (4) Å for Ca2].

The tetraazacyclododecane backbone of the DOTA ligand displays the [3333] square conformation. The unencapsulated Ca counterion in turn binds to the O atoms from three water molecules and to five carboxylate O atoms from adjacent $\mathrm{Ca[DOTA]^{2-}}$ ions in such a way as to form a one-dimensional chain which runs parallel to the diagonal of the *ac* plane. One-half of two unique $\mathrm{Ca(DOTA)^{2-}}$ ions are seen in the asymmetric unit, with the remaining halves generated by the inherent symmetry.

A total of ten sites in the asymmetric unit were assigned to uncoordinated water molecules. Seven of these sites were found to be completely occupied (five general sites and two special positions). Examination of the three remaining sites (O16, O19 and O19′) indicated that the intermolecular distances O16···O19′ [2.06 (1) Å] and O19···O19′ [1.78 (1) Å] were much shorter than the expected hydrogen-bonding distance; however, the O16···O19 distance [2.72 (1) Å] is well within the expected range for hydrogen-bond distances between water molecules. It is concluded that O16 and O19 are disordered with O19′ in such a fashion as to allow either O16 and O19 to be present or to allow only O19′ to be present. The site-occupation factors for the three molecules were tied in such a manner as to allow the occupation of O16 and O19 to refine together and to allow O19′ to be the complement of this factor. The occupation factor of O16/O19 refined to 0.7. The total of the uncoordinated water content of the asymmetric unit is therefore 7.7 water molecules.

Experimental

$Ca(OH_2)_3[Ca(DOTA)].7.7H_2O$ was synthesized by neutralizing 47 mg of $[H_6DOTA]Cl_2.5H_2O$ in 0.5 ml of aqueous solution with 0.2 ml of 1*M* NaOH followed by addition of 15 mg of reagent grade $Ca(OH)_2$. The resulting solution was stirred at room temperature until the solid dissolved. Small needles of $Ca(OH_2)_3[Ca(DOTA)].7.7H_2O$ grew upon addition of 0.5 ml of acetone and slow cooling. The $[H_6DOTA]Cl_2.5H_2O$ was obtained by a literature method (Hay & Norman, 1979; Desreux, 1980) and recrystallized by slow cooling from a supersaturated aqueous solution.

Crystal data

$[Ca_2(C_{16}H_{24}N_4O_8)(H_2O)_3]$.-
$7.7H_2O$
$M_r = 673.1$
Monoclinic
$C2/c$
$a = 25.109\ (2)$ Å
$b = 18.557\ (4)$ Å
$c = 18.436\ (7)$ Å
$\beta = 134.85\ (2)°$
$V = 6090\ (3)$ Å^3
$Z = 8$
$D_x = 1.468$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.1–22.3°$
$\mu = 0.457$ mm^{-1}
$T = 153\ (2)$ K
Needle
0.20 × 0.02 × 0.02 mm
Colorless

Data collection

Siemens *R*3*m*/*E* diffractometer
$\theta–2\theta$ scans
Absorption correction: none
4509 measured reflections
4364 independent reflections
3108 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.048$
$\theta_{\rm max} = 25.06°$
$h = -29 \rightarrow 18$
$k = -6 \rightarrow 20$
$l = -5 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0681$
$wR(F^2) = 0.1999$
$S = 1.483$
4364 reflections
386 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0918P)^2 + 12.0614P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.148$
$\Delta\rho_{\rm max} = 0.844$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.615$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ca1	0	0.9742 (1)	1/4	0.0230 (4)
Ca2	0	0.5959 (1)	1/4	0.0196 (4)
Ca3	0.1665 (1)	0.78707 (7)	0.3566 (1)	0.0233 (3)
O1	0.1159 (2)	0.9152 (2)	0.3269 (3)	0.025 (1)
O2	0.1971 (2)	0.8977 (2)	0.3159 (3)	0.027 (1)
O3	0.0320 (2)	0.9154 (2)	0.3945 (3)	0.028 (1)
O4	0.1137 (3)	0.9068 (3)	0.5648 (4)	0.041 (1)
O5	−0.0453 (2)	0.6528 (2)	0.0995 (3)	0.025 (1)
O6	−0.0003 (3)	0.6815 (2)	0.0345 (4)	0.034 (1)
O7	0.1146 (2)	0.6550 (2)	0.3185 (3)	0.023 (1)
O8	0.2263 (2)	0.6796 (2)	0.4719 (3)	0.029 (1)
O9	0.0985 (3)	0.7832 (2)	0.4000 (4)	0.037 (1)
O10	0.0650 (2)	0.7987 (2)	0.1732 (3)	0.031 (1)
O11	0.2328 (3)	0.7336 (3)	0.3221 (5)	0.052 (2)
O12	0	0.2858 (3)	1/4	0.022 (1)
O13	−0.1268 (3)	0.7646 (3)	−0.1140 (4)	0.044 (1)
O14	−0.2676 (3)	0.9220 (4)	−0.2425 (5)	0.078 (2)
O15	0.2053 (4)	0.4329 (4)	0.2032 (5)	0.077 (2)
O16†	0.0687 (6)	0.2877 (4)	0.4708 (8)	0.062 (3)
O17	−0.2054 (4)	0.6941 (5)	−0.2848 (6)	0.110 (3)
O18	0.1572 (6)	0.8238 (6)	0.1254 (8)	0.052 (3)
O19†	0.2163 (7)	0.6743 (8)	0.1123 (1)	0.150 (8)
O19′†	0.1497 (13)	0.6757 (14)	0.1197 (22)	0.11 (1)
O20	0.1771 (10)	0.2860 (6)	0.3993 (12)	0.201 (7)
N1	0.0951 (3)	1.0577 (3)	0.2735 (4)	0.030 (1)
N2	0.0697 (3)	1.0575 (3)	0.4080 (4)	0.029 (1)
N3	0.0074 (3)	0.5148 (3)	0.1444 (4)	0.023 (1)
N4	0.1168 (3)	0.5141 (3)	0.3686 (4)	0.023 (1)
C1	0.1500 (4)	1.0868 (3)	0.3793 (5)	0.031 (2)
C2	0.1124 (4)	1.1152 (4)	0.4114 (6)	0.033 (2)
C3	0.0154 (4)	1.0891 (4)	0.4089 (5)	0.033 (2)
C4	0.0552 (4)	1.1158 (4)	0.1966 (5)	0.034 (2)
C5	0.1361 (4)	1.0113 (4)	0.2613 (6)	0.033 (2)
C6	0.1516 (3)	0.9361 (3)	0.3054 (5)	0.025 (1)
C7	0.1219 (4)	1.0110 (3)	0.4989 (5)	0.031 (2)
C8	0.0861 (4)	0.9383 (3)	0.4853 (5)	0.027 (2)
C9	0.0651 (4)	0.4570 (3)	0.2078 (5)	0.027 (1)
C10	0.1344 (3)	0.4837 (3)	0.3132 (5)	0.028 (2)
C11	0.1068 (4)	0.4563 (3)	0.4135 (5)	0.027 (2)
C12	0.0677 (3)	0.4839 (3)	0.4434 (5)	0.027 (1)
C13	0.0297 (4)	0.5656 (4)	0.1080 (5)	0.031 (2)
C14	−0.0088 (4)	0.6385 (3)	0.0778 (5)	0.024 (1)
C15	0.1786 (3)	0.5631 (3)	0.4500 (5)	0.027 (1)
C16	0.1724 (3)	0.6371 (3)	0.4099 (5)	0.021 (1)

† Occupancy factors: 0.7 for O16 and O19, 0.3 for O19′.

Table 2. *Selected geometric parameters (Å, °)*

Ca1—O1	2.420 (4)	Ca1—O1^{i}	2.420 (4)
Ca1—O3	2.433 (4)	Ca1—O3^{i}	2.433 (4)
Ca1—N2	2.597 (6)	Ca1—N2^{i}	2.597 (6)
Ca1—N1^{i}	2.613 (5)	Ca1—N1	2.613 (5)
Ca2—O5^{i}	2.379 (4)	Ca2—O5	2.379 (4)
Ca2—O7^{i}	2.441 (4)	Ca2—O7	2.441 (4)
Ca2—N3	2.567 (5)	Ca2—N3^{i}	2.567 (5)
Ca2—N4	2.577 (5)	Ca2—N4^{i}	2.577 (5)
Ca3—O9	2.342 (4)	Ca3—O8^{ii}	2.371 (5)
Ca3—O11	2.378 (5)	Ca3—O10	2.413 (5)
Ca3—O2	2.486 (4)	Ca3—O8	2.498 (5)
Ca3—O1	2.566 (4)	Ca3—O7	2.628 (4)
O1^{i}—Ca1—O1	126.2 (2)	O1^{i}—Ca1—O3^{i}	79.8 (1)
O1—Ca1—O3^{i}	76.7 (2)	O1—Ca1—N2	91.8 (2)
O1^{i}—Ca1—N2	120.5 (2)	O3—Ca1—N2	66.3 (2)
O3^{i}—Ca1—N2	159.5 (2)	O1—Ca1—N2^{i}	120.5 (2)
N2—Ca1—N2^{i}	107.0 (2)	O1^{i}—Ca1—N1	161.1 (2)
O1^{i}—Ca1—N1^{i}	65.9 (2)	O3^{i}—Ca1—N1	90.3 (2)
O3^{i}—Ca1—N1^{i}	121.8 (2)	N2^{i}—Ca1—N1	69.3 (2)
N2^{i}—Ca1—N1^{i}	69.4 (2)	O1—Ca1—N1	65.9 (2)
N1—Ca1—N1^{i}	107.3 (2)	O5^{i}—Ca2—O5	127.2 (2)
O5^{i}—Ca2—O7^{i}	79.8 (2)	O5—Ca2—O7^{i}	77.2 (1)

O7—Ca2—O7$^{\rm i}$	126.6 (2)	O5$^{\rm i}$—Ca2—N3	156.1 (2)
O5—Ca2—N3	66.8 (2)	O7$^{\rm i}$—Ca2—N3	124.1 (2)
O7—Ca2—N3	88.1 (1)	N3—Ca2—N3$^{\rm i}$	108.3 (2)
O5$^{\rm i}$—Ca2—N4	87.2 (2)	O5$^{\rm i}$—Ca2—N4$^{\rm i}$	124.9 (1)
O7—Ca2—N4$^{\rm i}$	157.7 (1)	O7—Ca2—N4	66.7 (1)
N3—Ca2—N4	69.6 (2)	N3$^{\rm i}$—Ca2—N4	70.1 (2)
N4$^{\rm i}$—Ca2—N4	107.9 (2)	O9—Ca3—O8$^{\rm ii}$	88.2 (2)
O9—Ca3—O11	153.5 (2)	O8$^{\rm ii}$—Ca3—O11	96.6 (2)
O9—Ca3—O10	100.2 (2)	O8$^{\rm ii}$—Ca3—O10	158.4 (2)
O11—Ca3—O10	84.8 (2)	O9—Ca3—O2	125.7 (2)
O8$^{\rm ii}$—Ca3—O2	83.4 (2)	O11—Ca3—O2	80.8 (2)
O10—Ca3—O2	75.5 (2)	O9—Ca3—O8	80.3 (2)
O8$^{\rm ii}$—Ca3—O8	68.8 (2)	O11—Ca3—O8	77.3 (2)
O10—Ca3—O8	132.1 (2)	O2—Ca3—O8	142.0 (2)
O9—Ca3—O1	74.4 (1)	O8$^{\rm ii}$—Ca3—O1	88.2 (1)
O11—Ca3—O1	131.6 (2)	O10—Ca3—O1	75.1 (1)
O2—Ca3—O1	51.9 (1)	O8—Ca3—O1	146.2 (1)
O9—Ca3—O7	73.7 (1)	O8$^{\rm ii}$—Ca3—O7	118.8 (2)
O11—Ca3—O7	81.2 (2)	O10—Ca3—O7	82.7 (1)
O2—Ca3—O7	152.8 (1)	O8—Ca3—O7	51.0 (1)
O1—Ca3—O7	136.8 (1)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

Table 3. *Contact distances (Å)*

O9···O5$^{\rm i}$	2.77 (1)	O10···O3$^{\rm i}$	2.81 (1)
O11···O13$^{\rm ii}$	2.82 (1)	O11···O19′	2.92 (1)
O12···O20$^{\rm i}$	3.07 (2)	O13···O4$^{\rm i}$	2.74 (1)
O13···O6	2.77 (1)	O13···O17	2.59 (1)
O14···O4$^{\rm i}$	2.81 (1)	O14···O15$^{\rm iii}$	2.78 (1)
O14···O19′$^{\rm iii}$	2.58 (1)	O15···O2$^{\rm vi}$	2.79 (1)
O15···O17$^{\rm iv}$	2.80 (1)	O16···O6$^{\rm v}$	2.75 (1)
O16···O19$^{\rm v}$	2.72 (1)	O17···O18$^{\rm iii}$	2.58 (1)
O17···O20$^{\rm iv}$	2.69 (1)	O18···O19′	2.75 (1)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $-x, 1 - y, -z$; (v) $x, 1 - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Unfortunately, the crystal was lost due to icing with approximately 500 reflections to collect; consequently no azimuthal data were collected. C-bound H atoms were placed in idealized positions [C—H = 0.96 Å, U(H) = 0.08 Å^2(fixed)] and all O-bound H atoms, except for those of O12 and O20, were located in a difference Fourier map. H atom parameters were not refined. The H atoms bound to O12 and O20 were not included in the list of atomic coordinates.

Data collection: *P*3 (Siemens, 1982*a*). Data reduction: *XTAPE* (Siemens, 1982*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990).

The Siemens *R*3*m*/*E* X-ray diffractometer and crystallographic computing system at Colorado State University were purchased with funds provided by the US National Science Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Polymeric Cluster Complex $\{[(CH_3CH_2)_3NH][WAgS_4].(DMF)\}_n$

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Abstract

The structure of the anion in *catena*-poly[triethylammonium [tungsten-di-μ-sulfido-silver-di-μ-sulfido] *N*,*N*′-dimethylformamide solvate], $\{(C_6H_{16}N)[WAgS_4].(C_3H_7NO)\}_n$, can be viewed as a polymeric chain composed of extended fragments of AgS_2W, which are alternately almost perpendicular to each other. Each metal atom displays approximate tetrahedral coordination with four μ-S atoms. Hydrogen-bond interactions exist between the DMF molecule and the $[(CH_3CH_2)_3NH]^+$ cation.

Comment

Early in 1983, Müller and co-workers proposed the polymeric structure of $[(C_6H_5)_4P][AgMoS_4]$ from the strong absorption in the Mo—S absorption bands in its resonance Raman spectrum (Müller, Jaegermann & Hellmann, 1983; Müller & Hellmann, 1985). The crystal structure of this kind of complex, however, was not reported until 1993 (Lang, Li, Bao & Xin, 1993). The