

# A novel polyoxometalate supramolecular compound: $[\text{La}(\text{H}_2\text{O})_9]_2[\text{V}_{10}\text{O}_{28}]\cdot 8\text{H}_2\text{O}$

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{La}-\text{O}) = 0.005\text{ \AA}$

Disorder in solvent or counterion

$R$  factor = 0.039

$wR$  factor = 0.124

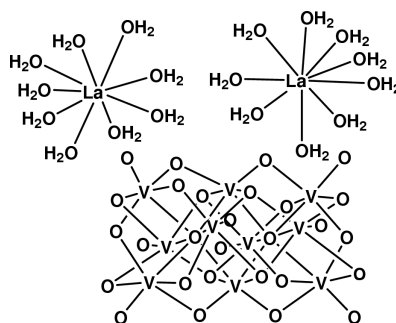
Data-to-parameter ratio = 12.4

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

The crystal structure of the novel polyoxometalate supramolecular compound bis[ennea-aqualanthanum(III)] octacosaoxododecavanadate(V) octahydrate is reported. The  $\text{V}_{10}$  cluster, with a 6− charge, plays a host role and  $[\text{La}(\text{H}_2\text{O})_9]^{3+}$  acts as a guest. The oxidation number of La is three and the oxidation number of V is five. There are four water molecules in the asymmetric unit, disordered over five sites. The corresponding site-occupation factors are 1.0, 0.54, 0.67, 0.85 and 0.94. Extensive intermolecular hydrogen-bonding interactions generate a three-dimensional supramolecular network structure. The polyoxovanadate anion has crystallographic inversion symmetry.

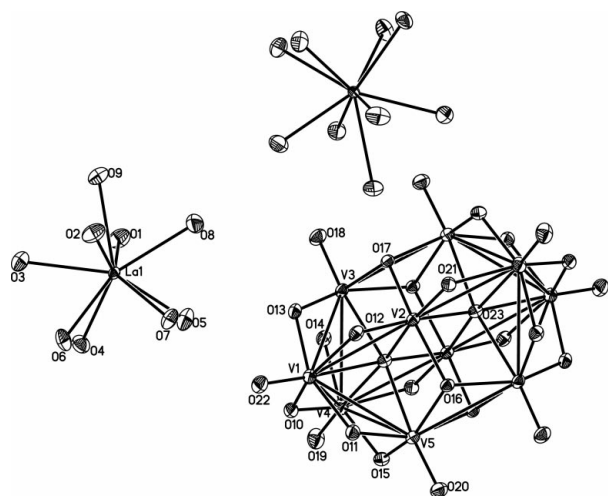
## Comment

Since the idea of supramolecular chemistry was advanced by Lehn (1988), polyacid supramolecular chemistry has developed fast, due to the fact that polyacid supramolecular compounds possess the ability to store electrons. Polyacids belong to a class of compound that can form a supramolecule with organic or inorganic ions, and possess electric, magnetic and non-linear optical properties. In order to investigate the relationship between the macroproperties and microproperties of polyacid supramolecular compounds, the novel title compound was synthesized.

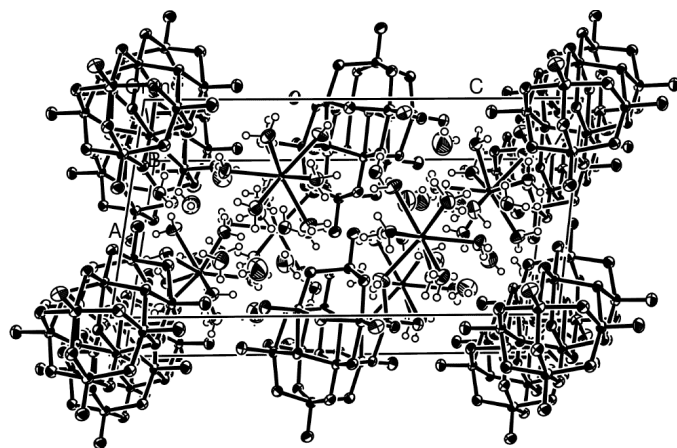


(I)

The crystal structure of the title compound shows that the  $\text{V}_{10}$  cluster plays a host role with a 6− charge and  $[\text{La}(\text{H}_2\text{O})_9]^{3+}$  acts as a guest in the polyacid supramolecular compound. The oxidation number of La is three and the oxidation number of V is five. All the coordination polyhedra of V are distorted octahedra. The O atoms, acting as terminal and bridging ligands, coordinate to V in four modes: (i) end-coordinated (O18, O19, O20 and O22), with V—O distances in the range 1.604 (5)–1.620 (4) Å; (ii) bridged coordination (O10, O11, O12, O13, O14, O15 and O21), with V—O

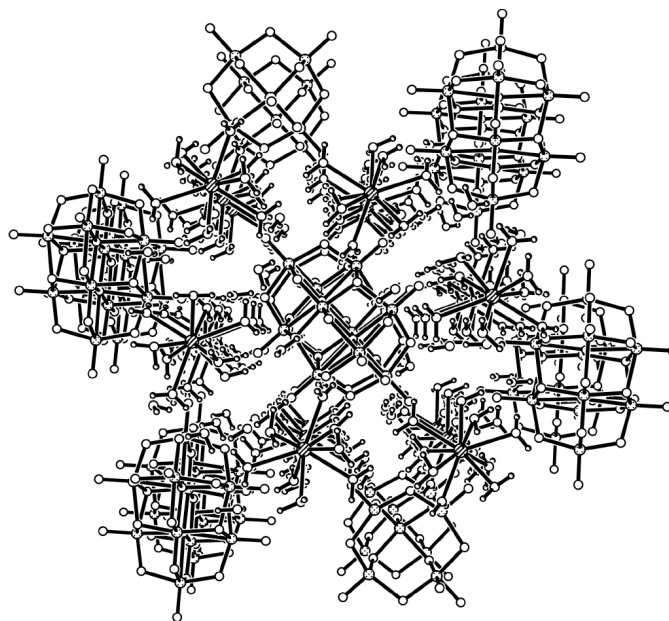


**Figure 1**  
View of the title compound (30% probability ellipsoids), without the uncoordinated water molecules. All H atoms have also been omitted.



**Figure 2**  
A view of the packing in the crystal of the title compound.

distances in the range 1.677 (4)–2.037 (4) Å; (iii) triply bridging coordination (O16 and O17), with V–O distances in the range 1.927 (4)–1.935 (4) Å; and (iv) sixfold bridged coordination (O23), with V–O distances in the range 2.098 (4)–2.308 (4) Å. The bridged V···V distances are in the range 3.0563 (16)–3.1093 (16) Å, the O–V–O bond angles are in the ranges 74.09 (15)–106.9 (2) and 154.02 (19)–174.2 (2)°, where the first range is for *cis* angles (around 90°) and the second range is for *trans* angles (around 180°), and the V–O–V bond angles are in the ranges 82.95 (14)–114.2 (2)° (around 90°) and 169.5 (2)–171.0 (2)° (around 180°) for *cis* and *trans* angles. The  $[\text{La}(\text{H}_2\text{O})_9]^{3+}$  cations are arranged as pillars (see Fig. 3) along the *a* axis, with La–O distances in the range 2.414 (5)–2.540 (5) Å. There are 35 discrete hydrogen bonds (Table 1), with O···O distances in the range 2.58 (2)–3.606 (7) Å, forming a three-dimensional network.



**Figure 3**  
The  $\text{La}(\text{H}_2\text{O})_9$  cations, arranged as pillars along the *a* axis.

## Experimental

The title compound was prepared as follows:  $\text{NaV}_{10}\text{O}_{28} \cdot 12\text{H}_2\text{O}$  (1 mmol),  $\text{La}(\text{NO}_3)_3$  (2 mmol) and distilled water (100 ml) were mixed to form an aqueous solution with stirring and the pH was adjusted to 4.0. The mixture was stirred for 4 h and placed in an ice-box at 277 K for a few weeks. Red crystals, suitable for diffraction studies, were obtained.

### Crystal data

$[\text{La}(\text{H}_2\text{O})_9]_2[\text{V}_{10}\text{O}_{28}] \cdot 8\text{H}_2\text{O}$   
 $M_r = 1703.64$   
 Monoclinic,  $P2_1/c$   
 $a = 9.818$  (2) Å  
 $b = 11.935$  (2) Å  
 $c = 19.514$  (4) Å  
 $\beta = 98.42$  (3)°  
 $V = 2262.0$  (8) Å<sup>3</sup>  
 $Z = 2$

$D_x = 2.501$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 15.1$ – $15.9$ °  
 $\mu = 3.94$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, red  
 $0.30 \times 0.20 \times 0.20$  mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.403$ ,  $T_{\max} = 0.456$   
 4226 measured reflections  
 3979 independent reflections  
 3460 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 14$   
 $l = 0 \rightarrow 23$   
 5 standard reflections every 300 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.124$   
 $S = 1.07$   
 3979 reflections  
 322 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 0.7084P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.79$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.79$  e Å<sup>-3</sup>

**Table 1**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1B···O9	0.82	2.31	2.712 (7)	111
O1—H1A···O4W	0.96	1.88	2.737 (8)	147
O2W—H2WA···O3W	0.85	2.02	2.58 (2)	123
O4W—H4WB···O2O	0.85	2.01	2.855 (8)	180
O5W—H5WB···O2W	0.85	2.53	3.019 (18)	118
O1W—H1WB···O11 <sup>i</sup>	0.85	2.26	2.781 (7)	120
O5W—H5WB···O11 <sup>i</sup>	0.85	2.44	3.020 (8)	126
O2—H2B···O20 <sup>i</sup>	0.96	2.51	3.363 (7)	148
O7—H7A···O16 <sup>i</sup>	0.85	1.92	2.689 (6)	151
O1W—H1WA···O12 <sup>ii</sup>	0.85	2.31	3.013 (7)	140
O2W—H2WA···O21 <sup>ii</sup>	0.85	2.16	2.838 (14)	137
O3W—H3WB···O21 <sup>ii</sup>	0.85	2.61	3.185 (9)	126
O4W—H4WA···O18 <sup>ii</sup>	0.85	2.32	3.128 (8)	159
O5—H5B···O22 <sup>ii</sup>	0.96	2.39	3.220 (7)	145
O7—H7B···O22 <sup>ii</sup>	0.85	2.12	2.971 (6)	174
O8—H8B···O13 <sup>ii</sup>	0.96	2.65	3.606 (7)	173
O3W—H3WA···O6 <sup>iii</sup>	0.85	2.45	2.991 (9)	122
O3W—H3WA···O4 <sup>iii</sup>	0.85	2.61	3.202 (10)	128
O3W—H3WB···O19 <sup>iv</sup>	0.85	2.37	3.190 (10)	162
O4W—H4WA···O5W <sup>v</sup>	0.85	2.53	2.944 (9)	111
O5W—H5WA···O18 <sup>vi</sup>	0.85	2.39	2.912 (8)	120
O1—H1B···O1W <sup>v</sup>	0.82	2.09	2.841 (7)	153
O3—H3B···O19 <sup>v</sup>	0.96	2.59	3.339 (8)	135
O4—H4A···O10 <sup>v</sup>	0.85	2.36	2.792 (6)	112
O6—H6B···O19 <sup>v</sup>	0.85	2.09	2.814 (7)	143
O8—H8A···O5W <sup>v</sup>	0.96	2.15	2.899 (9)	134
O8—H8A···O2W <sup>v</sup>	0.96	2.35	3.087 (15)	134
O3—H3B···O20 <sup>vii</sup>	0.96	2.30	2.814 (7)	112
O3—H3A···O18 <sup>viii</sup>	0.96	2.50	3.198 (7)	130
O4—H4A···O2W <sup>ix</sup>	0.85	2.48	3.016 (14)	122
O4—H4B···O3W <sup>ix</sup>	0.85	2.23	2.837 (9)	128
O5—H5A···O3W <sup>ix</sup>	0.96	1.80	2.748 (10)	171
O6—H6A···O14 <sup>x</sup>	0.85	2.00	2.731 (6)	144
O9—H9A···O17 <sup>viii</sup>	0.82	2.02	2.761 (6)	150
O9—H9B···O21 <sup>viii</sup>	0.96	2.57	3.140 (7)	118

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

The positions of all H atoms were fixed geometrically, with O—H = 0.82–0.96 Å. The site-occupation factors of the five water O-atom positions were refined, constraining their sum to 4.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 SDP/VAX* (Enraf–Nonius, 1989); data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

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