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A Novel Triply Chromium(III)-Substituted Keggin Anion, $[A\text{-}\alpha\text{-SiO}_4W_9Cr_3(OH_2)_3O_{33}]^{7-}$

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Abstract

The structure determination of $K_3H_4[A\text{-}\alpha\text{-SiO}_4W_9\text{-}Cr_3(OH_2)_3O_{33}].11H_2O$, tripotassium tetrahydrogen triaquatrichromononatungstosilicate undecahydrate, represents the first X-ray analysis of a triply substituted Keggin anion containing low-valent heteroelements. The CrO_6 and WO_6 polyhedra are discussed on the basis of interatomic distances; for CrO_6 coordination an almost ideal octahedron is observed.

Comment

Recently, Liu *et al.* (1992) reported the synthesis and characterization of trimetallo derivatives of lacunary nonatungstosilicate heteropolyanions. In these anions, $[SiO_4W_9M_3(OH_2)_3O_{33}]^{n-}$, with the well known Keggin structure, main-group or low-valent 3*d* elements occupy a quarter of all the tungsten positions. Based on the structure of the precursor anion and ^{183}W NMR spectra (M = Al, Ga), it is expected, without any crystallographic evidence, that the MO_6 octahedra are corner-shared.

For the similar anion $[B\text{-}\alpha\text{-PO}_4W_9Ni_3(OH_2)_3O_{33}\text{-}WO_2(OH_2)]^{7-}$, the structure has been determined by Gómez-Garcia, Coronado & Ouahab (1992). However, in this case the triply substituted Keggin anion is additionally capped on the NiO_6 octahedra by a $WO_2(OH_2)$ group.

We shall now present the X-ray analysis of $K_3H_4[A\text{-}\alpha\text{-SiO}_4W_9Cr_3(OH_2)_3O_{33}].11H_2O$, which was synthesized by fixing three Cr^{3+} ions on vacant tungsten positions in $[A\text{-}\alpha\text{-SiO}_4W_9O_{30}]^{10-}$, which effectively constitutes the first ever structure of this type of triply substituted Keggin anion.

The compound was prepared following the procedure of Peng, Qu & Chen (1991), modified by us. After a few days, the repeatedly recrystallized potassium salt (water with some acetone, pH 5) yielded non-disordered crystals, stable in air and suitable for X-ray structural analysis. In the asymmetric unit, one Cr atom is placed in a general position with another in the mirror plane. The centrosymmetric unit of two anions with corner-shared CrO_6 octahedra is given in Fig. 1. The X-ray analysis characterizes the structure of the precursor anion $[A\text{-}\alpha\text{-SiO}_4W_9O_{30}]^{10-}$ in an indirect way. Until now, only the structure of the isomeric $[A\text{-}\beta\text{-SiO}_4\text{-}W_9O_{30}]^{10}$ anion has been determined (Robert & Tézé, 1981).

The close-bowl packing of the Keggin anion with 40 O atoms is not substantially affected by the tri-substitution. Most of the changes in the structure are related to the metal–oxygen and metal–metal bond distances. As evidenced from the data, the Cr atoms are located in an almost ideal octahedral O-atom environment, in contrast to all observed W-atom positions in polyoxometallate chemistry. The different formal oxidation states of Cr^{3+} and

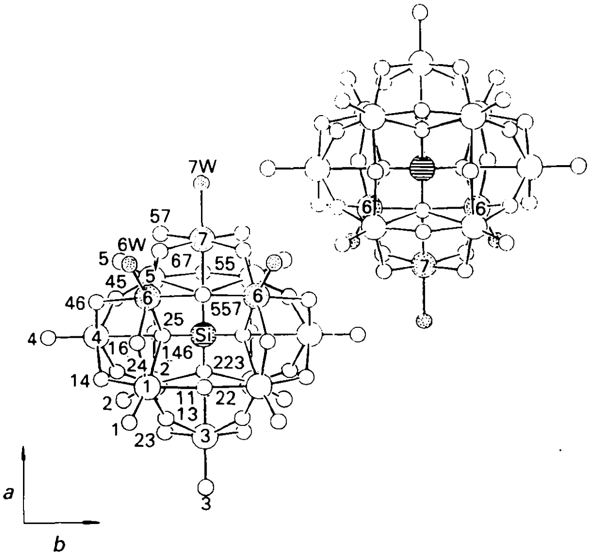

Fig. 1. *ORTEP* (Johnson, 1965) drawing of $[A\text{-}\alpha\text{-SiO}_4W_9Cr_3\text{-}(OH_2)_3O_{33}]^7$ showing the arrangement of the anions in centrosymmetric pairs. Large open circles represent W atoms, small open circles represent O atoms, and the large hatched circle represents Si. Aqua ligands attached to Cr atoms (large shaded circles) are indicated by small shaded circles.

W^{6+} might be responsible for this feature. The terminal O-atom position in each of the three CrO_6 octahedra is occupied by a water molecule, while between W and terminal O atoms the strongest covalent bonding (shortest distance) in tungsten polyanions was observed. A striking phenomenon is the surprisingly short Cr—W distances between edge-sharing CrO_6 and WO_6 octahedra, which are compensated for by the increased W—W distances between corner-sharing WO_6 octahedra. This impressively shows the scope for atom arrangement in Keggin anions.

The magnetic properties of the compound are influenced mostly by the magnetic interactions between Cr atoms belonging to the same anion. Information about the contribution from magnetic interactions (dipole–dipole) between adjacent polyanions could be inferred by their orientation in the cell. The closest approach of these paramagnetic centres to one another is observed in a centrosymmetric pair (Cr6—Cr6 = 5.28, Cr6—Cr7 = 5.78 Å). As part of a comprehensive investigation of the magnetic behaviour, further ESR and magnetic measurements (4–300 K) are underway.

Experimental

Crystal data

$K_3H_4[SiO_4W_9Cr_3(OH_2)_3O_{33}].11H_2O$
$M_r = 2804.25$
Orthorhombic
Pnma
$a = 25.365$ (3) Å
$b = 14.985$ (2) Å
$c = 12.315$ (2) Å
$V = 4680.9$ (9) $Å^3$
$Z = 4$
$D_x = 3.909$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 88 reflections
$\theta = 5-12.5°$
$\mu = 24.43$ mm^{-1}
$T = 292$ K
Needles
0.5 × 0.15 × 0.15 mm
Green

Data collection

Stoe-4 diffractometer
ω scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.85$, $T_{max} = 1.28$
5278 measured reflections
4759 independent reflections
3335 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.143$
$\theta_{max} = 27°$
$h = -32 \rightarrow 0$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 90 min
intensity variation: 3%

Refinement

Refinement on F
$R = 0.063$
$wR = 0.063$
$S = 1.019$
3335 reflections
193 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 7.2$ e $Å^{-3}$
$\Delta\rho_{min} = -6.7$ e $Å^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
W1	0.68319 (5)	0.62499 (9)	0.9098 (1)	0.0082 (3)
W2	0.67919 (5)	0.63737 (9)	0.3209 (1)	0.0076 (3)
W3	0.75040 (7)	3/4	0.1315 (1)	0.0079 (5)
W4	0.61224 (5)	0.51136 (8)	1.0993 (3)	0.0080 (3)
W5	0.53221 (5)	0.63738 (9)	1.30685 (9)	0.0071 (3)
Cr6	0.5586 (2)	0.6292 (4)	0.9183 (4)	0.006 (1)
Cr7	0.4819 (3)	3/4	1.1159 (6)	0.004 (2)
Si	0.6110 (5)	3/4	1.110 (1)	0.009 (3)
K1	0.4418 (6)	3/4	0.825 (1)	0.034 (4)
K2	0.7364 (4)	0.5126 (8)	0.6201 (7)	0.037 (3)
O1	0.729 (1)	0.583 (2)	0.825 (3)	0.019 (5)
O11	0.685 (1)	3/4	0.872 (3)	0.009 (6)
O13	0.7265 (8)	0.664 (1)	1.034 (2)	0.004 (4)
O14	0.671 (1)	0.520 (2)	0.999 (2)	0.019 (6)
O146	0.6125 (8)	0.661 (1)	1.032 (2)	0.005 (4)
O16	0.6227 (9)	0.607 (2)	0.835 (2)	0.011 (5)
O2	0.700 (1)	0.566 (2)	0.418 (2)	0.023 (6)
O22	0.693 (1)	3/4	0.394 (3)	0.013 (7)
O223	0.663 (1)	3/4	1.188 (2)	0.002 (5)
O23	0.7464 (8)	0.663 (1)	1.250 (2)	0.004 (4)
O24	0.6630 (8)	0.557 (1)	1.205 (2)	0.005 (4)
O25	0.6069 (9)	0.646 (1)	1.349 (2)	0.008 (4)
O3	0.819 (2)	3/4	1.115 (3)	0.028 (9)
O4	0.614 (1)	0.402 (2)	1.127 (2)	0.015 (5)
O45	0.5589 (8)	0.554 (1)	1.199 (2)	0.003 (4)
O46	0.5646 (9)	0.512 (2)	0.987 (2)	0.011 (5)
O5	0.5092 (8)	0.565 (1)	1.406 (2)	0.009 (4)
O55	0.525 (2)	3/4	1.392 (3)	0.024 (8)
O557	0.553 (1)	3/4	1.177 (3)	0.013 (7)
O57	0.4742 (8)	0.659 (1)	1.229 (2)	0.003 (4)
O6*W*	0.514 (1)	0.586 (2)	0.797 (2)	0.016 (5)
O66	0.557 (1)	3/4	0.853 (3)	0.014 (7)
O67	0.4953 (9)	0.656 (2)	1.005 (2)	0.012 (5)
O7*W*	0.406 (1)	3/4	1.079 (3)	0.013 (7)
O100†	0.633 (2)	0.452 (3)	0.653 (3)	0.060 (1)
O200	0.661 (2)	0.375 (3)	0.861 (3)	0.050 (1)
O300	0.563 (1)	0.588 (2)	0.607 (3)	0.043 (8)
O400	0.601 (3)	3/4	0.575 (6)	0.090 (2)
O500	0.861 (3)	0.610 (6)	0.902 (7)	0.180 (3)
O600	0.580 (4)	1/4	0.566 (8)	0.170 (3)
O700	0.826 (6)	3/4	0.80 (1)	0.170 (6)

† O100–O700: water of crystallization.

Computer programs: *SHELXS*86 (Sheldrick, 1985); *Xtal* (Hall & Stewart, 1988).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71563 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1029]

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