

# Synthesis, molecular structure and chemical properties of a new tungstosilicate with an open Wells–Dawson structure, $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup>

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Received (in Cambridge, UK) 26th June 2003, Accepted 28th July 2003

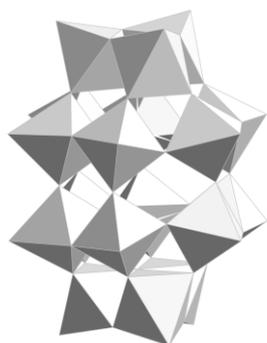
First published as an Advance Article on the web 12th August 2003

**Acidification of K<sub>10</sub>A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>] in aqueous solution leads to the formation of  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup>, built up from two A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>] subunits, which reacts with metal cations to form potassium and mixed potassium–transition metal complexes.**

Wells–Dawson polyoxometalates<sup>1</sup> are an important class of polyoxoanions constituted by the formal association of two fragments of Keggin type anions *via* condensation reactions (Fig. 1). From these  $\ll$  complete  $\gg$  anions, mono-,<sup>2</sup> di-,<sup>3</sup> tri-<sup>4</sup> and hexavacant<sup>5</sup> species can be obtained by selective hydrolysis reactions and are precursors of a very large number of derivatives with transition metal cations.<sup>6</sup> These complexes have attracted considerable attention over the past years as models of oxide surfaces, precursors for synthesis of organometallic derivatives,<sup>7</sup> for their magnetic properties<sup>8</sup> and as homogeneous catalysts<sup>9–10</sup> and electrocatalysts.<sup>11</sup> To date, Wells–Dawson anions [X<sub>2</sub>M<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> are known with M = Mo or W and X = P(v) or As(v)<sup>12</sup> in aqueous solution and S(vi)<sup>13</sup> in non aqueous solution. On the contrary, only Keggin type polyoxoanions are known with X = Si(iv)<sup>14</sup> even if *a priori* nothing precludes the formation of Wells–Dawson tungstosilicates. Here we report the synthesis, molecular structure and reactivity of  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup>, which is an intermediate between the monomer A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup> and the hypothetical  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>8-</sup> Wells–Dawson anion.

This new species has been obtained in the course of a study of the influence of the nature of the counter-ion, Na<sup>+</sup> or K<sup>+</sup>, on the reactivity of the A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup> anion. Acidification led to  $\alpha$ -[SiW<sub>11</sub>O<sub>39</sub>]<sup>8-</sup> with Na<sup>+</sup> but not with K<sup>+</sup>.

$\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup> has been obtained by acidification of K<sub>10</sub>A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>] $\cdot$ 13H<sub>2</sub>O in suspension in water (2 protons for one polyoxoanion).<sup>†</sup> Dissolution of the solid occurs during addition of the acid and single crystals of K<sub>16</sub> $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>] $\cdot$ 25H<sub>2</sub>O (**1**) could be grown from the clear solution within one day.<sup>‡</sup> The molecular anion comprises two A- $\alpha$ -[SiW<sub>9</sub>O<sub>34</sub>] subunits linked through two oxygen atoms (Fig. 2). The W atoms which participate to the two W–O–W bonds are linked by edge junctions in each half-anion.  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup> has thus the conformation  $\alpha\alpha E$ <sup>15</sup> as the  $\alpha$ -[X<sub>2</sub>M<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> Wells–Dawson oxoanion. The angle between the two half-

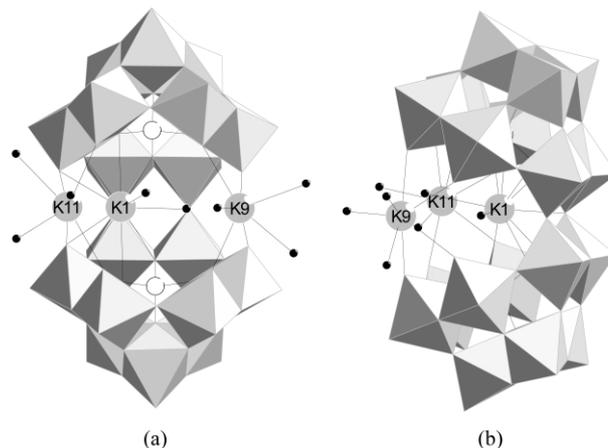


**Fig. 1** Polyhedral representation of the  $\alpha$ -[P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> Wells–Dawson oxoanion.

anions is 41° and the two W–O–W junction angles are 147–148°. The structure of  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup> can thus be described as an  $\ll$  open Wells–Dawson  $\gg$  structure, intermediate between the monomer and the closed framework of the classical  $\alpha$ -[X<sub>2</sub>M<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> anion.

The pocket between the two half-anions is surrounded by eight terminal oxygen atoms, four on each subunit, and the two junction oxygen atoms, which constitute donor sites for metal cations. Actually, in the crystal structure of the potassium salt, the pocket is filled by three potassium cations and the polyanion could be written  $\alpha$ -[K(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>[K(H<sub>2</sub>O)<sub>2</sub>](Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>)<sup>13-</sup>. K1 is localized inside the pocket, bridges the two half-anions and locks up the framework. It is bound to only one of the two junction oxygen atoms and is thus shifted to one side of the pocket (Fig. 2). In this position K1 has the highest coordination number since it is bound to nine oxygen atoms of the polyanion (in each subunit, two are shared with the SiO<sub>4</sub> tetrahedron and two are terminal oxygen atoms) with bond lengths in the range 2.76–3.22 Å. The coordination sphere of K1 is completed by two water molecules. If it was not shifted to one side but localized in the middle of the pocket it would be in strong interaction with only four oxygen atoms of the polyanion. Due to this shift the ideal symmetry of  $\alpha$ -[Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>16-</sup> which would be C<sub>2v</sub>, decreases to C<sub>s</sub>. The two other potassium cations K9 and K11 bridge also the two half-anions through terminal oxygen atoms and are thus localized at the periphery of the pocket. Their coordination sphere is completed by three water molecules which are bound to other potassium cations so that they participate to the linkage between the polyanions in the lattice. The K–O bond lengths are in the range 2.67–3.05 Å and 2.72–3.09 Å for K9 and K11, respectively.

Titration of **1** by Co<sup>2+</sup> or VO<sup>2+</sup> cations, monitored by visible spectroscopy, shows the formation of metal/polyanion 2/1 complexes. Addition of MCl<sub>2</sub> salts (M = Co, Ni, Zn) to the solution obtained after acidification of K<sub>10</sub>[SiW<sub>9</sub>O<sub>34</sub>] in

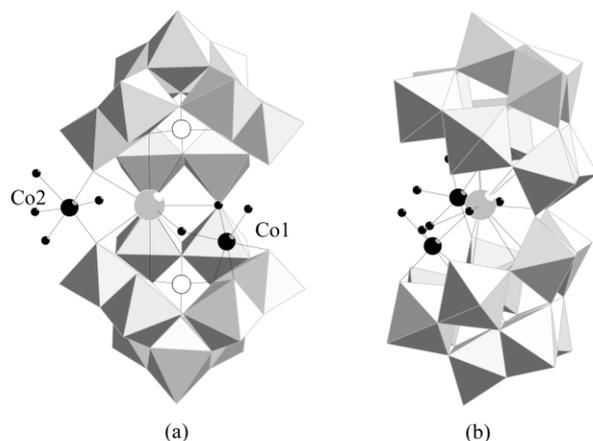


**Fig. 2** Polyhedral representation of the molecular structure of  $\alpha$ -[K(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>[K(H<sub>2</sub>O)<sub>2</sub>](Si<sub>2</sub>W<sub>18</sub>O<sub>66</sub>)<sup>13-</sup> showing potassium (light grey ball) and oxygen of water molecules (small black); front view (a) side view (b).

suspension in water produces diffraction quality crystals of  $K_{11}\{[M(H_2O)]\}\{M(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})\cdot 30H_2O$ . The structure of the anion in the cobalt complex **2**§ is the same as in **1** and the angle between the two half-anions is also  $41^\circ$  (Fig. 3).

The pocket between the two subunits is filled by one  $K^+$  and two  $Co^{2+}$  cations. K1 occupies exactly the same position as in **1** with the same mode of coordination. The cobalt Co1 is coordinated to only one half-anion through three oxygen atoms (one O56 is shared with the  $SiO_4$  tetrahedron and two are terminal oxygen atoms of the subunit) and its coordination sphere is completed by three water ligands. Actually, two of them are shared with K1 and correspond to the two water molecules bound to K1 in **1**. The Co1–O56 bond length, 2.23 Å, is slightly longer than the other distances which are in the normal range 2.05–2.13 Å. The cobalt atom Co2 links the two subunits through two *cis* M–O bonds involving one terminal oxygen atom of each half-anion. Its coordination sphere is completed by four water molecules. The difference between the modes of coordination of the two cobalt atoms is clearly due to the asymmetric position of K1 in the pocket which push Co2 away. The distance between the two  $Co^{2+}$  is 6.84 Å. These results show that K9 and K11 in **1** are labile and can be easily substituted by divalent transition metal cations in solution. This is not the case of K1 which very likely plays an important role in the stabilization of **1** in solution.

In conclusion, the  $[Si_2W_{18}O_{66}]^{16-}$  anion is an intermediate species in the formation of the Wells–Dawson tungstosilicate, not known at the present time. It has an open structure, is stabilized by inclusion of a potassium cation, and closing of the



**Fig. 3** Polyhedral representation of the cobalt complex  $\{[Co(H_2O)]\}\{Co(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})\}^{12-}$  showing potassium (light grey ball), cobalt (black) and oxygen of water molecules (small black); front view (a) side view (b).

structure needs elimination of this cation. It constitutes a new type of inorganic ligand. Usually, ligand behaviour of polyoxometalates in solution results from the elimination of oxo-tungsten fragments of a complete structure. Here it is a consequence of the opening of the complete structure, which generates terminal oxygen atoms in such a manner that they define a coordination site very reactive towards alkali and transition metal cations. Topology and size of this site allow the fixation of several cations with different modes of coordination and offer the possibility to functionalize the transition metals by substitution of the water ligands.

## Notes and references

† *Experimental procedure*: The crystal **1** used for the X-ray diffraction experiment was obtained as follows: 7.2 g of  $K_{10}A-\alpha-[SiW_9O_{34}]\cdot 13H_2O$  are added to 100 mL of  $H_2O$ . To solubilize the powder, 1 M HCl (5 mL) was added (the pH was about 5.7). After two days, colorless crystals of  $K_{16}\alpha-[Si_2W_{18}O_{66}]\cdot 25H_2O$  (**1**) suitable for X-ray diffraction were obtained. Yield: 40%. Found: W, 58.9; K, 10.0%. Calcd for  $K_{16}\alpha-[Si_2W_{18}O_{66}]\cdot 25H_2O$ : W, 60.2; K, 11.4%.

‡ *Crystal data*:  $K_{16}O_{86}Si_2W_{18}$ ,  $M = 5367.08$ , triclinic,  $a = 12.4908(2)$ ,  $b = 15.5014(1)$ ,  $c = 25.5553(1)$  Å,  $\alpha = 94.983(1)$ ,  $\beta = 94.987(1)$ ,  $\gamma = 111.012(1)^\circ$ ,  $V = 4564.42(8)$  Å<sup>3</sup>,  $T = 296$  K, space group  $P\bar{1}$  (2),  $Z = 2$ ,  $\mu = 23.444$  mm<sup>-1</sup>, 30505 reflections measured, 21634 unique ( $R_{int} = 0.0982$ ) which were used in all calculations. The final  $wR$  ( $F^2$ ) was 0.1207 (all data) and  $R = 0.0747$  for 14886 reflections with  $F^2 > 2\sigma(F^2)$ . CCDC 213848. See <http://www.rsc.org/suppdata/cc/b3/b307276b/> for crystallographic data in .cif or other electronic format.

§ *Crystal data*:  $Co_2K_{12}O_{90}Si_2W_{18}$ ,  $M = 5392.54$ , triclinic,  $a = 15.0033(1)$ ,  $b = 18.2970(3)$ ,  $c = 18.4060(2)$  Å,  $\alpha = 66.570(1)$ ,  $\beta = 78.802(1)$ ,  $\gamma = 87.053(1)^\circ$ ,  $V = 4545.98(9)$  Å<sup>3</sup>,  $T = 296$  K, space group  $P\bar{1}$  (2),  $Z = 2$ ,  $\mu = 23.712$  mm<sup>-1</sup>, 31855 reflections measured, 22472 unique ( $R_{int} = 0.0482$ ) which were used in all calculations. The final  $wR$  ( $F^2$ ) was 0.1049 (all data) and  $R = 0.0494$  for 12676 reflections with  $F^2 > 2\sigma(F^2)$ . CCDC 213849. See <http://www.rsc.org/suppdata/cc/b3/b307276b/> for crystallographic data in .cif or other electronic format.

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