

Bis[tris(2,2'-bipyridine)iron(II)] tetraaqua-sodium(I) dodeca- tungstoferrate(III) dihydrate

Ming-Xue Li, Peng-Tao Ma and Jing-Ping Wang*

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475001, People's Republic of China
Correspondence e-mail: jpwang@henu.edu.cn

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The title compound, bis[tris(2,2'-bipyridine)iron(II)] tetraaqua-tetra- μ_4 -oxo-pentacosa- μ_2 -oxo-undecaoxoiron(III)sodium(I)-dodecatungsten(VI) dihydrate, $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{NaFeW}_{12}\text{O}_{40}(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, consists of a dodecatungstoferrate(III) framework grafted on to an $[\text{Na}(\text{H}_2\text{O})_4]^+$ cation, two complex $[\text{Fe}(\text{2,2'}\text{-bipy})_3]^{2+}$ cations (2,2'-bipy is 2,2'-bipyridine) and two uncoordinated water molecules per formula unit.

Comment

Polyoxometallates (POMs) have been studied extensively in the field of solid-state materials due to their varied potential applications in magnetism, medicine and catalysis (Xu *et al.*, 2002; Judd *et al.*, 2001; Hill, 2004), as well as the variety of their structures (Hagman *et al.*, 1999). Of the various POM structures, the most interesting is the Keggin family, members of which act as versatile inorganic building blocks for constructing more abundant organic-inorganic hybrid materials. However, most of the work reported to date has been on Keggin-type polyoxotungstates with main group 3A atoms (B, Si, Ge, P, As) located in the central tetrahedral cavity of the Keggin cage (Zonnevijlle *et al.*, 1982), while studies of the analogues with transition metal ions acting as heteroatoms remain in their infancy. In particular, reports of Keggin-type polyanions with the transition metal Fe^{III} ion as the central atom are rather scarce (Gómez-García *et al.*, 1995; Weiner *et al.*, 2005). We report here the synthesis and structure of the title compound, (I), which contains the Keggin polyanion.

The structure of (I) comprises a polyanionic $[\text{Na}(\text{H}_2\text{O})_4\text{FeW}_{12}\text{O}_{40}]^{4-}$ framework, a pair of $[\text{Fe}(\text{2,2'}\text{-bipy})_3]^{2+}$ complex cations (2,2'-bipy is 2,2'-bipyridine) and two uncoordinated water molecules, one of which is disordered (O5W/O7W) (Fig. 1). As shown in Fig. 1, the $[\text{Na}(\text{H}_2\text{O})_4\text{FeW}_{12}\text{O}_{40}]^{4-}$ polyanion comprises the Keggin $[\text{Fe}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ skeleton, onto which a trigonal-bipyramidal $[\text{Na}(\text{H}_2\text{O})_4]^+$

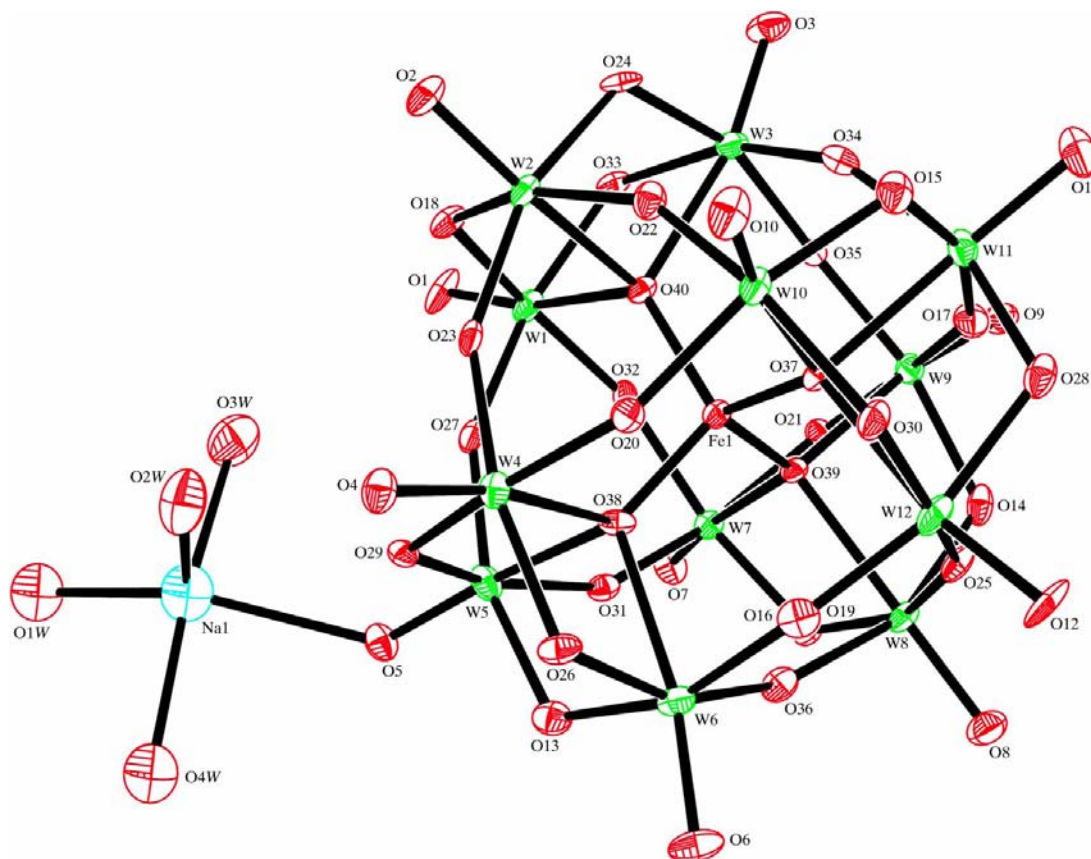
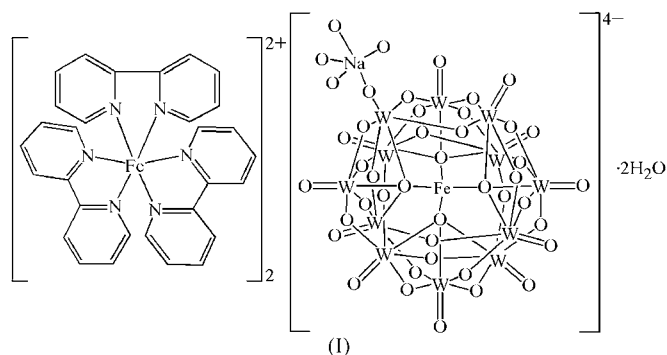


Figure 1

The structural components of the $[\text{Na}(\text{H}_2\text{O})_4\text{FeW}_{12}\text{O}_{40}]^{4-}$ polyanion, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

cation is grafted *via* a bridging O atom. The Keggin [$\text{Fe}^{\text{III}}\text{W}_{12}\text{O}_{40}$] $^{5-}$ moiety is constructed from an FeO_4 tetrahedron surrounded by 12 WO_6 octahedra, present in four corner-sharing W_3O_{13} groups, as found in other Keggin anions (Pope, 1983). In each WO_6 octahedron, the W—O bond lengths and O—W—O angles are in the ranges 1.690 (8)–2.231 (7) Å and 72.3 (3)–104.1 (3)°, respectively, which indicates substantial distortion from a regular octahedron.



According to the different coordination modes in the Keggin framework, the O atoms can be classified into three groups, namely terminal O_t atoms [W—O = 1.690 (8)–1.718 (8) Å], μ_2 -bridging O atoms [W—O = 1.867 (8)–1.988 (8) Å] and μ_4 -bridging O atoms [W—O = 2.213 (7)–2.231 (7) Å]. For the FeO_4 tetrahedron, the Fe—O distances range from 1.811 (7) to 1.822 (8) Å, with an average of 1.814 (7) Å, while the O—Fe—O angles vary from 108.8 (3) to 110.5 (4)° (Table 1).

It is noteworthy that the asymmetric unit of (I) contains two complex $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$ cations, which is confirmed by bond-valence-sum calculations (Brese & O'Keeffe, 1991). These calculations show that the values for the calculated oxidation states of atoms Fe1, Fe2 and Fe3 are 3.222, 2.240 and 2.180, respectively, which is consistent with the formula of the title compound. In the course of the reaction, the 2,2'-bipyridine acts as an effective agent to reduce Fe^{III} to Fe^{II} , and then the reduced Fe^{II} is coordinated by additional 2,2'-bipyridine residues to form the complex $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$ cations, which self-assemble with $[\text{Fe}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ during crystal formation

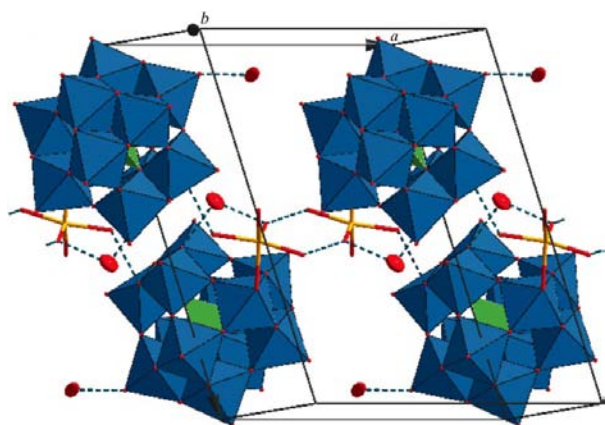


Figure 2

A packing diagram of one unit cell, showing the hydrogen bonds as dashed lines.

and separate out from the hydrothermal solution. A similar experimental phenomenon has been observed previously (Yang *et al.*, 2002).

There are multiple O...O contacts suitable for O—H...O hydrogen bonding, with O...O distances in the range 2.80 (2)–3.07 (2) Å (Table 2). These interactions link the water molecules and the anionic cages into infinite one-dimensional chains that run parallel to the *a* axis (Fig. 2). In addition, the complex $[\text{Fe}(2,2'\text{-bipy})_3]^{2+}$ cations fill the space between the polyanions and thereby contribute to the robustness of the crystal structure.

Experimental

A mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (4 mmol), 2,2'-bipyridine (2 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) was fully dissolved in water (20 ml) by stirring at room temperature (molar ratio of 4:2:1:1111). The mixture was adjusted to pH 3.4 with HCl solution (1:1). The solution was then sealed in a 30 ml Teflon-lined autoclave and heated to 458 K for 4 d. The autoclave was then cooled to room temperature over a period of 2 d at a rate of 10 K h $^{-1}$, and black block-shaped crystals of (I) were obtained. IR (KBr disk, ν , cm $^{-1}$): 1625, 1603, 1466, 1443, 1314, 1292, 1218, 1156, 953, 868, 783, 759, 723, 559, 446.

Crystal data

$[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{NaFeW}_{12}\text{O}_{40} \cdot (\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$
 $M_r = 4081.78$
 Triclinic, $P\bar{1}$
 $a = 13.7572$ (10) Å
 $b = 17.8992$ (13) Å
 $c = 18.8730$ (14) Å
 $\alpha = 88.043$ (1)°
 $\beta = 72.829$ (1)°

$\gamma = 75.128$ (1)°
 $V = 4287.1$ (5) Å 3
 $Z = 2$
 $D_x = 3.161$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 16.62$ mm $^{-1}$
 $T = 293$ (2) K
 Block, black
 0.11 × 0.11 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.262$, $T_{\max} = 0.316$
 (expected range = 0.186–0.224)

22240 measured reflections
 14845 independent reflections
 10640 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.095$
 $S = 0.98$
 14845 reflections
 1216 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.89$ e Å $^{-3}$
 $\Delta\rho_{\min} = -1.87$ e Å $^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe1—O37	1.811 (7)	Fe1—O38	1.812 (7)
Fe1—O39	1.811 (7)	Fe1—O40	1.822 (8)
O37—Fe1—O39	109.0 (4)	O37—Fe1—O40	109.3 (3)
O37—Fe1—O38	109.7 (3)	O39—Fe1—O40	109.5 (4)
O39—Fe1—O38	108.8 (3)	O38—Fe1—O40	110.5 (4)

In the unrestrained refinement, the C8—C9 and C9—C10 bond distances were not normal, the ratios of the maximum and minimum

Table 2

Hydrogen-bond geometry (Å).

O2W...O6W	2.80 (2)	O6W...O18	2.923 (14)
O2W...O4W ⁱ	2.753 (15)	O7W...O9	3.07 (2)
O3W...O33 ⁱⁱ	2.972 (17)		

Symmetry codes: (i) $-x + 2, -y + 2, -z$; (ii) $-x + 1, -y + 2, -z$.

atomic displacement parameters for atoms C2, C12, C23 and C48 were larger than 5, and the U_{eq} values of atoms O1W and O4W were larger than 0.1 Å². Therefore, the C8—C9 and C9—C10 bond distances were restrained to 1.35 (1) Å, pseudo-isotropic restraints were applied to atoms C2, C12, C23 and C48, and the atomic displacement ellipsoids of atoms W5, Na1, O5, O1W and O4W were restrained to be similar. H atoms bound to C atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms associated with the water molecules could not be located reliably and were omitted from the model. One water molecule appears to be disordered across two sites (O5W/O7W); these atoms were assigned fixed site-occupation factors of 0.5.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3017). Services for accessing these data are described at the back of the journal.

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