A Keggin-type Arsenotungstate Anion-supported Transition Metal Complex: Hydrothermal Synthesis and Characterization of $[Fe(2,2'\text{-bipy})_3]_{1.5}[AsW^{VI}{}_{10}W^{V}{}_2O_{40}Fe(2,2'\text{-bipy})_2(H_2O)]\cdot 0.25H_2O$

Ming-Xue Li, Hong-Yu Niu, Wei Wang, and Jing-Ping Wang

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475001, China

Reprint requests to Prof. J.-P. Wang. E-mail: jpwang@henu.edu.cn

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A Keggin-type arsenotungstate anion-supported iron-bipyridine complex, $[Fe(2,2'\text{-bipy})_3]_{1.5}[AsW^{VI}{}_{10}W^{V}{}_2O_{40}Fe(2,2'\text{-bipy})_2(H_2O)]\cdot 0.25H_2O$, has been hydrothermally synthesized and characterized by IR and ESR spectra, TG-DTA analysis, and single crystal X-ray diffraction. Each structural unit of the title compound consists of one $[AsW^{VI}{}_{10}W^{V}{}_2O_{40}Fe(2,2'\text{-bipy})_2(H_2O)]^{3-}$ heteropolyanion, one and a half $[Fe(2,2'\text{-bipy})_3]^{2+}$ cations, and a quarter of an H_2O molecule. In the heteropolyanion the $[Fe(2,2'\text{-bipy})_2(H_2O)]^{2+}$ unit is covalently bonded to the reduced Keggin polyoxoanion $[AsW^{VI}{}_{10}W^{V}{}_2O_{40}]^{5-}$. The complex is monoclinic, space group $C2/c$ with $a = 46.8079(13)$, $b = 14.3990(4)$, $c = 26.1085(8)$ Å, $\beta = 90.00(5)^\circ$, $Z = 8$, $D_c = 3.10$ g/cm^3.

Key words: Keggin-type Anions, Arsenotungstate, Hydrothermal Synthesis

Introduction

Polyoxometalates have attracted general interest because of their diverse properties, with potential applications to catalysis, electrical conductivity, magnetism, photochemistry, biochemical analysis, medicinal chemistry, and materials science [1 – 3]. An important advancement of polyoxometalate chemistry is the design and synthesis of polyoxoanion-supported organic-inorganic hybrid complexes, owing to their extensive practical applications [4 – 6]. Keggin-type anions have mostly been used to support organic-inorganic complexes because the charge density of the Keggin-surface oxygen atoms can be increased either by reducing some of their metal centers or replacing higher-valent metal centers by lower-valent ones [7 – 8]. The structures of Keggin-type polyoxoanions that have been characterized were mainly those of phosphotungstate or phosphomolybdate anions-supported transition metal complexes including $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW^{VI}{}_{10}W^{V}{}_2O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$ [9], $[Co(1,10\text{-phen})_3]_{1.5}[PMo_{12}O_{40}Co(1,10\text{-phen})_2(H_2O)]\cdot 0.5H_2O$ [10], $\{PW_9V_3O_{40}[Ag(2,2'\text{-bipy})]_2[Ag_2(2,2'\text{-bipy})_3]_2\}$ [10] and others.

We here report the hydrothermal synthesis, structure and characterization of a Keggin arsenotungstate anion-supported transition metal complex $[Fe(2,2'\text{-bipy})_3]_{1.5}[AsW^{VI}{}_{10}W^{V}{}_2O_{40}Fe(2,2'\text{-bipy})_2(H_2O)]\cdot 0.25H_2O$.

Experimental Section

Materials and physical measurements

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H, N elemental analyses were performed on a Perkin-Elmer 2400-II elemental analyzer. The infrared spectrum was recorded on a Nicolet 170SXFT-IR spectrometer with KBr pellets in the range of 400 – 4000 cm^{-1}. The ESR spectrum was recorded with a Bruker ER-2000-DSRC10 spectrometer at the X-band. TG-DTA measurements were performed on an EXSTAR 6000 thermal analyzer in air with a heating rate of 10 °C min^{-1}.

Synthesis

The title compound was prepared from a mixture of $Na_2WO_4\cdot 2H_2O$ (2.80 g, 8.50 mmol), $Na_3AsO_4\cdot 12H_2O$ (0.43 g, 1.00 mmol), $FeSO_4\cdot 7H_2O$ (0.42 g, 1.50 mmol), 2,2′-bipy (0.15 g, 1.00 mmol) and H_2O (25 mL, 1389 mmol) heated in a Teflon-lined steel autoclave inside a programmable electric furnace at 175 °C for 8 d with a starting pH value of 6.3 adjusted with 2 M hydrochloric acid. After cooling the mixture to 35 °C for 72 h, black green crystals were iso-

Table 1. Crystallographic data and numbers pertinent to the structure refinement for the title compound.

Formula	$C_{65}H_{54.5}AsFe_{2.5}N_{13}O_{41.25}W_{12}$
M_r	4098.31
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	46.8079(13)
b, Å	14.3990(4)
c, Å	26.1085(8)
β, deg	90.00(5)
Volume, Å^3	17596.8(9)
Z	8
D_{calcd}, g · cm^{-3}	3.10
Absorption coefficient, mm^{-1}	16.5
Max./min. transmission	0.32/0.19
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15103/157/1218
GoF (F^2)	0.883
$R(F)/wR(F^2)$ [$I > 2\sigma(I)$]	0.0484/0.1053
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	2.74/−2.34

lated from the blue solid powders and washed with water. Yield: 42 % based on W. Anal. for $C_{65}H_{54.5}AsFe_{2.5}O_{41.25}N_{13}W_{12}$: calcd. C 18.98, H 1.58, N 4.43; found C 19.12, H 1.52, N 4.50.

X-Ray diffraction

A single crystal with dimensions $0.15 \times 0.11 \times 0.09$ mm^3 was selected for intensity data collection at 293(2) K on a Bruker Apex-2 CCD diffractometer using MoK_α radiation (λ = 0.71073 Å) in the range $1.67 < \theta < 25.00°$. A total of 61118 reflections was measured in the range $-55 \le h \le 55$, $-17 \le k \le 16$, $-25 \le l \le 31$, 15103 of which were independent (R_{int} = 0.1101) and 8786 above the $2\sigma(I)$ limit. All the independent reflections were used in the refinement. The intensities were corrected for Lorentz and polarization effects and empirically for absorption. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques based on F^2 using the program SHELXL-97 [11]. All non-hydrogen atoms were refined anisotropically. Although the metrical symmetry of the unit cell (β = 90.00(5)°) pointed to an orthorhombic symmetry, this was not confirmed by the reflection intensities. Checks with the program PLATON [12] on the refined coordinate set confirmed the absence of additional crystallographic symmetry. Due to the large number of heavy atoms in the cell, 157 restraints had to be applied in the refinement. This was frequently necessary in related structures [9, 10]. Crystallographic data and structure refinement of the title compound are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 657142 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Selected bond lengths (Å) and angles (deg) for the title compound.

Fe(1)–O(1W)	2.125(10)	Fe(1)–O(12)	2.109(11)
Fe(1)–N(1)	2.103(17)	Fe(1)–N(1′)	2.120(14)
Fe(1)–N(2)	2.067(15)	Fe(1)–N(2′)	2.109(17)
Fe(2)–N(3)	2.068(13)	Fe(2)–N(3′)	2.060(13)
Fe(2)–N(4)	2.062(14)	Fe(2)–N(4′)	2.086(13)
Fe(2)–N(5)	2.078(13)	Fe(2)–N(5′)	2.086(14)
Fe(3)–N(6)	2.089(14)	Fe(3)–N(6′)	2.089(12)
Fe(3)–N(7)	2.060(14)		
As(1)–O(37)	1.667(9)	As(1)–O(38)	1.664(9)
As(1)–O(39)	1.679(10)	As(1)–O(40)	1.662(9)
W(5)–O(5)	1.708(9)	W(6)–O(6)	1.688(11)
W(3)–O(24)	1.888(10)	W(11)–O(13)	1.958(10)
W(4)–O(37)	2.387(9)	W(12)–O(39)	2.331(10)
O(40)–As(1)–O(38)	109.8(5)	O(40)–As(1)–O(37)	107.7(5)
O(38)–As(1)–O(37)	109.8(4)	O(40)–As(1)–O(39)	110.8(4)
O(38)–As(1)–O(39)	108.9(5)	O(37)–As(1)–O(39)	109.8(4)

Results and Discussion

Structure description

The asymmetric unit of the crystals contains one heteropolyanion $[AsW^{VI}{}_{10}W^{V}{}_2O_{40}Fe(2,2'\text{-bipy})_2(H_2O)]^{3-}$, one and a half $[Fe(2,2'\text{-bipy})_3]^{2+}$ cations, and a quarter of an H_2O molecule. As shown in Fig. 1, the anion consists of a reduced Keggin hereropolyanion $[AsW^{VI}{}_{10}W^{V}{}_2O_{40}]^{5-}$ and a bonded cation $[Fe(2,2'\text{-bipy})_2(H_2O)]^{2+}$. As in other Keggin structures, the reduced polyanion is viewed as a shell of twelve WO_6 octahedra encapsulating an AsO_4 moiety, which is present at the center and responsible for the local tetrahedral geometry. Each oxygen atom of the AsO_4 group is covalently bonded to three different tungsten centers of the shell with As–O distances in the range 1.662 – 1.680 Å and O–As–O angles between 107.7° and 110.8° (Table 2). The twelve WO_6 octahedra in the polyoxoanion have an essentially similar, distorted octahedral environment defined by one terminal oxo-group with shorter W–O_t bond lengths (1.689 – 1.708 Å), four doubly bridging oxo-groups with intermediate W–$O_{b,c}$ bond lengths (1.888 – 1.958 Å), and one μ_4-oxygen atom, also bonded to an arsenic atom, with longer W–O_a distances (2.331 – 2.387 Å).

In comparison with discrete Keggin structural units, the $[AsW^{VI}{}_{10}W^{V}{}_2O_{40}]^{5-}$ group acts as a ligand towards the Fe^{2+} ion *via* the O(12) atom, which links Fe(1) and W(12). W(12) is also bonded to the μ_4-oxygen O(39) in the Keggin unit. The effect of the coordinated cation $[Fe(2,2'\text{-bipy})_2(H_2O)]^{2+}$ results in an As–O(39) distance of 1.679 Å,

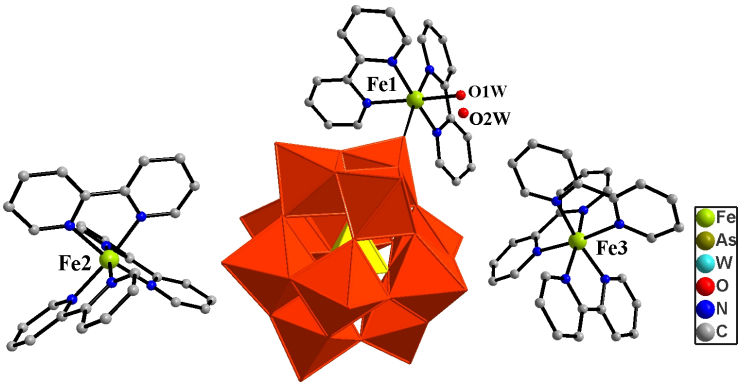

Fig. 1. The molecular structure of the title compound. The occupancy of Fe3 and O2W is 0.5 and 0.25, respectively.

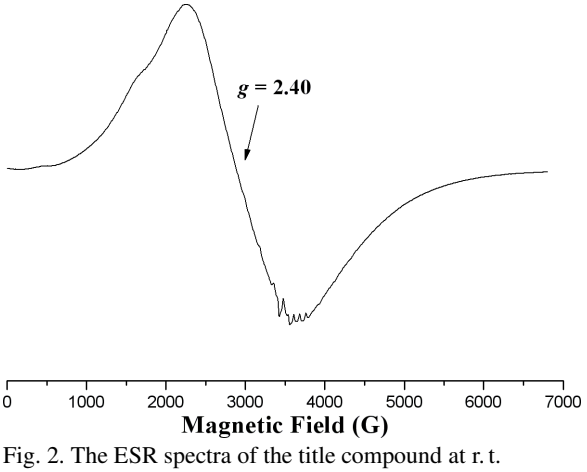

Fig. 2. The ESR spectra of the title compound at r. t.

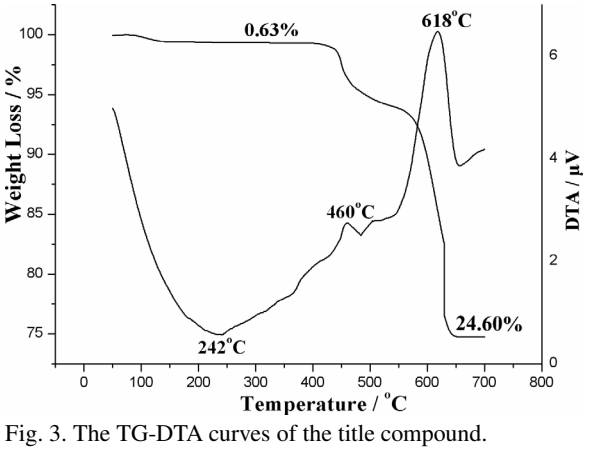

Fig. 3. The TG-DTA curves of the title compound.

longer than the other three distances (1.666, 1.665, 1.662 Å).

In the cation $[Fe(2,2'\text{-bipy})_3]^{2+}$ of the title complex, Fe is coordinated by three 2,2′-bipy molecules, with Fe–N bond lengths in the range of 2.059(13)–2.086(13) Å. There are two W^V centers in the Keggin unit, and the assignment of the iron oxidation state is consistent with the electric charge and confirmed by bond valence sum calculations. Using an empirical bond valence calculation, $S = \exp[-(R-1.898)/0.315]$ (S = bond valence, R = bond length) [13], leads to S values for W(1) – W(12) of 5.796, 5.921, 5.711, 5.835, 5.837, 5.931, 5.944, 5.815, 5.873, 5.909, 5.832, and 5.754, respectively. The average value for the calculated oxidation state of W is 5.846 (expected value 5.833 for $W^{VI}{}_{10}W^{V}{}_{2}$), consistent with the formula of the title complex. However, the BVS values do not clearly identify the reduced W(V) sites. This is due to the possible delocalization of the *d* electrons of the reduced tungsten centers over the polyanion framework involving all W atoms as found in heteropolyblues [14 – 17].

IR spectra

The IR spectra of the title compound cations exhibit a series of characteristic bands from the 2,2′-bipyridine molecules at 1100 – 1600 cm^{-1}. Besides the bands of the complex cations, the anion has four characteristic peaks at 907, 973, 866, and 791 cm^{-1} attributed to $\nu(As–O_a)$, $\nu(W–O_d)$, $\nu(W–O_b)$, and $\nu(W–O_c)$, respectively. Comparing the IR spectrum with that of $(TBA)_3[AsW_{12}O_{40}]$ (983, 912, 873, 793 cm^{-1}) [18], the bands have slight blue shifts. The results indicate that the $[AsW_{12}O_{40}]^{3-}$ anion is affected only weakly by the coordinated $[Fe(2,2'\text{-bipy})_2(H_2O)]^{2+}$ cation.

ESR spectra

The ESR spectrum of the title compound measured at r. t. is shown in Fig. 2. Only a very broad signal is observed with g = 2.40 which is attributed to

Fe^{2+} [19]. The absence of signals for W(V) proved that the two unpaired electrons of the Keggin unit are delocalized [9]. Similar results were found at 110 K.

Thermal properties

The TG curve of the title compound shows a two stage weight loss (Fig. 3), giving a total loss of 25.03 % (calcd. 25.22 %). The first weight loss of 0.63 % (calcd. 0.55 %) is slow in the range of 25 – 400 °C, corresponding to the release of 1.25 water molecules. There is a strong and broad endothermal peak at 242 °C in the DTA curve. The second weight loss of 24.60 % (calcd. 24.67 %), from 400 to 655 °C, is attributed to the removal of 6.5 bipyridine molecules. In the corresponding DTA, two exothermal peaks that appear at 460 and 618 °C result from the combustion of the organic molecules and the decomposition of the title polyoxoanion.

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[1] C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev*. **1995**, *143*, 407 – 455.
[2] C. L. Hill, *Chem. Rev*. **1998**, *98*, 1 – 390.
[3] M. I. Kan, E. Yohannes, R. J. Doesdens, *Inorg. Chem*. **2003**, *42*, 3125 – 3129.
[4] P. J. Hagraman, D. Hagraman, J. Zubieta, *Angew. Chem*. **1999**, *111*, 2798 – 2848; *Angew. Chem. Int. Ed*. **1999**, *38*, 2638 – 2684.
[5] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, **1983**.
[6] H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem*. **2000**, *112*, 1841 – 1844; *Angew. Chem. Int. Ed*. **2000**, *39*, 1771 – 1774.
[7] A. Müller, W. Plass, E. Krickemeyer, S. Dillinger, H. Bögge, A. Armatage, A. Prousst, C. Beugholt, U. Bergmann, *Angew. Chem*. **1994**, *106*, 897 – 899; *Angew. Chem. Int. Ed*. **1994**, *33*, 849 – 851.
[8] P. Gouzerh, A. Proust, *Chem. Rev*. **1998**, *98*, 77 – 111.
[9] Y. Xu, J. Q. Xu, K. L. Zhang, Y. Zhang, X. Z. You, *Chem. Commun*. **2000**, 153 – 154.
[10] G. Y. Luan, Y. G. Li, S. T. Wang, E. B. Wang, Z. B. Han, C. W. Hu, N. H. Hu, H. Q. Jia, *Dalton Trans*. **2003**, 233 – 235.
[11] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
[12] A. L. Spek, PLATON, A. Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2000**. See also: A. L. Spek, *J. Appl. Cryst*. **2003**, *36*, 7 – 13.
[13] I. D. Brown, *Stucture and Bonding in Crystals*, Vol. II, Eds.: M. O'Keefe, A. Navrotsky, Academic Press, New York, **1981**, pp. 1 – 30.
[14] M. I. Khan, S. Cevik, R. Hayashi, *J. Chem. Soc.*, *Dalton Trans*. **1999**, 1651 – 1654.
[15] M. T. Pope, A. Müller, *Angew. Chem*. **1991**, *103*, 56 – 70; *Angew. Chem. Int. Ed*. **1991**, *30*, 34 – 48.
[16] N. Casan-Pastor, L. C. W. Baker, *J. Am. Chem. Soc*. **1992**, *114*, 10384 – 10394.
[17] M. I. Khan, S. Cevik, R. J. Doedens, Q. Chen, S. Li, C. J. O'Connor, *Inorg. Chim. Acta* **1998**, *277*, 69 – 75.
[18] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem*. **1983**, *22*, 207 – 216.
[19] Z. F. Li, S. W. Wang, W. S. Song, H. N. Deng, Y. Q. Wang, Y. X. Wang, *Chin. J. Org. Chem*. **2003**, *23*, 588 – 594.