Crystal structure of hexakis(dimethylsulfoxide-κ*O*)iron(III)dodecatungstophosphate, $C_{12}H_{36}FeO_{46}PS_6W_{12}$

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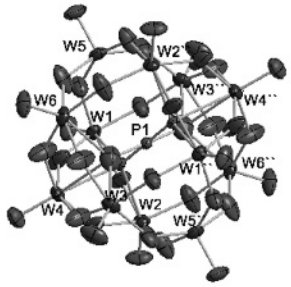

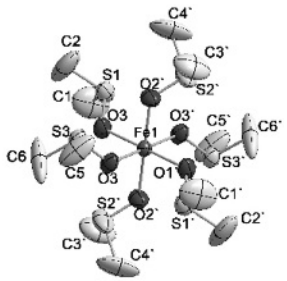

Abstract

$C_{12}H_{36}FeO_{46}PS_6W_{12}$, monoclinic, $P2_1/c$ (no. 14), a = 11.403(2) Å, b = 15.077(3) Å, c = 16.721(3) Å, β = 99.83(3)°, V = 2832.6 Å^3, Z = 2, $R_{gt(F)}$ = 0.0403, $wR_{ref(F^2)}$ = 0.0834, T = 298 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.10×0.11×0.13 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	248.50 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS 2, ω and φ
$2\theta_{max}$:	53.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24271, 6138
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4937
$N(param)_{refined}$:	368
Programs:	DIAMOND [10], SHELX [11]

Source of material

Phosphotungstic acid hydrat (0.5 g, 0.17 mmol) was dissolved in DMSO (20 ml) and a solution of ammonium ferric citrate (0.04 g, 0.17 mmol) in water (5 ml) was added. The solution was stirred over night and layered with diethylether. After several weeks a few crystals of the title compound had grown.

Experimental details

P1 is located on a inversion center, therefore the structure has a P center surrounded by a cube of eight oxygen atoms, affording a wrong formula of $PW_{12}O_{44}$, which was corrected to $PW_{12}O_{40}$.

Discussion

The coordination chemistry of iron(III) includes a wide variety of possible complexes where the regular octahedal arrangement is the preferred configuration [1]. A fairly large number of these crystal structures consist of iron(III) complexed to solvates [2]. Interestingly the combination of iron(III) complexes of oxygen containing solvents with polyoxotungstenate was not achieved yet, while four examples exist of Fe^{3+} complexes with *N*-containing ligands and polyoxotungstenate [3-6] have been reported. The iron-complex $[Fe(NH_4)(C_6H_8O_7)]$ cocrystallizes upon ligand exchange reaction with a Keggin tungstentate polyanion to form the title compound $[Fe(SOC_2H_6)_6][PW_{12}O_{40}]$, whose asymmetric unit consists of half a polyanion and half a complex. The polyanion shows a disorder in the centre, which is commonly observed for the Keggin-anion [7, 8]. The hexakis-(dimethylsulfoxide)iron(III) complex has six DMSO ligands coordinated to the iron(III) ion through their oxygen atoms in an octahedral geometry. The three crystallographic independent ligands have Fe–O distances of 2.009(10) Å (for Fe1–O1), 2.003(10) Å (for Fe1–O2) and 1.976(9) Å for Fe1–O3, which lies in the usual ranges for Fe-DMSO complexes (1.928 - 2.237 Å). The Fe–O–S bond angles are 123.0(6)° (for Fe1–O1–S1), 126.3(7)° for Fe1–O2–S2 and 126.3(6)° for Fe–O3–S3, which fit to to an average value of 125.7° [9]. In the packing, a layered arrangement with alternating rows of Keggin ions and Fe complexes is visible in *y*-direction. The distance between the polyanion rows is about 11.4 Å (measured from P1 to P1` of the neighboring anion).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	4*e*		0.7048	0.7082	0.1286	0.202
H(1B)	4*e*		0.8428	0.6982	0.1347	0.202
H(1C)	4*e*		0.7743	0.6384	0.1881	0.202
H(2A)	4*e*		0.8788	0.4760	0.0484	0.199
H(2B)	4*e*		0.8837	0.5009	0.1399	0.199
H(2C)	4*e*		0.9476	0.5610	0.0841	0.199
H(3A)	4*e*		0.5010	0.6119	0.2324	0.190
H(3B)	4*e*		0.4067	0.5736	0.2813	0.190
H(3C)	4*e*		0.3655	0.6330	0.2047	0.190
H(4A)	4*e*		0.2360	0.4119	0.1483	0.202
H(4B)	4*e*		0.2057	0.5134	0.1468	0.202
H(4C)	4*e*		0.2490	0.4654	0.2298	0.202
H(5A)	4*e*		0.5434	0.2105	–0.0338	0.168
H(5B)	4*e*		0.4882	0.2033	0.0456	0.168
H(5C)	4*e*		0.6176	0.1688	0.0447	0.168
H(6A)	4*e*		0.6705	0.3575	0.1823	0.264
H(6B)	4*e*		0.6944	0.2560	0.1726	0.264
H(6C)	4*e*		0.5648	0.2898	0.1745	0.264

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*		0.770(2)	0.667(1)	0.136(1)	0.16(1)	0.13(1)	0.11(1)	–0.07(1)	0.02(1)	–0.06(1)
C(2)	4*e*		0.880(1)	0.524(1)	0.086(1)	0.043(6)	0.14(1)	0.21(2)	–0.005(8)	–0.010(9)	0.04(1)
C(3)	4*e*		0.422(2)	0.589(1)	0.2282(8)	0.16(1)	0.16(1)	0.080(8)	–0.05(1)	0.058(8)	–0.052(9)
C(4)	4*e*		0.257(1)	0.468(1)	0.1737(9)	0.17(1)	0.13(1)	0.13(1)	–0.084(9)	0.106(8)	–0.039(9)
C(5)	4*e*		0.560(1)	0.2133(8)	0.024(1)	0.060(7)	0.053(6)	0.22(2)	–0.002(6)	0.014(9)	–0.056(9)
C(6)	4*e*		0.639(2)	0.303(1)	0.1572(8)	0.29(2)	0.18(1)	0.047(7)	0.19(1)	–0.014(9)	0.000(8)
O(1)	4*e*		0.6479(5)	0.5274(4)	0.0800(4)	0.047(3)	0.058(4)	0.055(4)	–0.016(3)	–0.006(3)	0.006(3)
O(2)	4*e*		0.3968(6)	0.5312(5)	0.0814(4)	0.064(3)	0.061(4)	0.054(4)	0.018(3)	0.023(3)	0.004(3)
O(3)	4*e*		0.5048(5)	0.3763(4)	0.0380(4)	0.043(3)	0.039(3)	0.074(4)	0.003(3)	0.006(3)	0.012(3)
O(4)	4*e*		0.6793(7)	0.0275(5)	0.9685(4)	0.118(5)	0.062(4)	0.053(4)	0.046(4)	0.041(3)	0.017(3)
O(5)	4*e*		0.5921(5)	–0.0657(5)	1.0900(5)	0.043(3)	0.058(4)	0.103(5)	–0.012(3)	0.040(3)	–0.014(4)
O(6)	4*e*		0.7696(7)	0.0603(5)	1.1192(6)	0.077(4)	0.035(4)	0.119(6)	–0.013(4)	–0.049(4)	0.014(4)
O(7)	4*e*		0.8289(7)	–0.1079(5)	1.1404(6)	0.084(5)	0.036(4)	0.122(7)	–0.008(4)	–0.055(5)	0.009(4)
O(8)	4*e*		0.9701(7)	0.0156(5)	1.2123(6)	0.069(4)	0.047(4)	0.129(7)	0.000(4)	–0.053(4)	0.005(4)
O(9)	4*e*		0.8876(7)	0.3355(5)	0.9601(5)	0.082(4)	0.039(4)	0.122(6)	0.017(3)	0.044(4)	0.021(4)
O(10)	4*e*		0.8684(6)	0.1778(5)	1.2385(4)	0.055(3)	0.097(5)	0.044(3)	0.008(4)	0.012(3)	–0.021(4)
O(11)	4*e*		1.0742(5)	0.1569(5)	1.1679(4)	0.043(3)	0.098(5)	0.056(4)	0.004(4)	0.012(3)	0.021(4)
O(12)	4*e*		0.7340(7)	–0.1405(5)	0.9890(4)	0.115(5)	0.066(4)	0.058(4)	0.034(4)	0.047(4)	0.013(3)
O(13)	4*e*	0.5	0.9377(7)	0.0725(6)	0.9410(5)	0.014(3)	0.032(5)	0.022(4)	0.011(4)	0.005(3)	0.004(4)
O(14)	4*e*		0.8743(5)	0.2018(5)	1.0744(4)	0.043(3)	0.095(5)	0.057(4)	0.005(3)	0.015(3)	0.028(4)
O(16)	4*e*		0.6044(6)	0.0902(6)	0.8120(4)	0.047(3)	0.122(7)	0.043(4)	0.025(4)	–0.001(3)	0.006(4)
O(17)	4*e*		1.0802(5)	0.2345(5)	1.0298(4)	0.054(3)	0.093(5)	0.059(4)	0.012(4)	0.026(3)	0.030(4)
O(18)	4*e*		1.2832(7)	0.2436(6)	1.1491(5)	0.092(5)	0.101(6)	0.076(5)	–0.063(4)	0.008(4)	–0.023(5)
O(19)	4*e*		1.2582(7)	0.0608(5)	1.1501(4)	0.116(5)	0.083(5)	0.049(3)	0.035(4)	0.046(3)	0.016(4)
O(20)	4*e*	0.5	0.9298(7)	–0.0028(6)	1.0730(5)	0.023(4)	0.027(5)	0.014(4)	0.001(4)	–0.001(3)	–0.003(4)
O(21)	4*e*		0.7793(6)	0.1713(6)	0.9211(4)	0.079(3)	0.096(4)	0.061(3)	–0.021(3)	0.039(2)	–0.022(3)
O(22)	4*e*		0.9857(6)	0.2027(6)	0.8786(4)	0.066(3)	0.106(5)	0.073(4)	–0.037(4)	0.047(3)	–0.047(4)
O(23)	4*e*		1.0120(6)	0.1531(6)	0.7203(4)	0.079(3)	0.096(4)	0.061(3)	–0.021(3)	0.039(2)	–0.022(3)
O(26)	4*e*	0.5	1.1250(7)	0.0282(6)	1.0302(5)	0.022(4)	0.023(4)	0.018(4)	–0.002(4)	–0.007(3)	0.002(4)
O(27)	4*e*		0.8465(6)	0.0805(6)	0.8048(5)	0.066(4)	0.126(6)	0.084(4)	–0.039(4)	0.049(3)	–0.059(4)
O(29)	4*e*	0.5	1.0092(7)	0.0885(6)	1.0403(5)	0.024(4)	0.021(4)	0.018(4)	–0.006(4)	0.001(3)	–0.002(3)
S(1)	4*e*		0.7477(2)	0.5877(2)	0.0598(2)	0.053(1)	0.077(2)	0.055(1)	–0.018(1)	–0.005(1)	0.008(1)
S(2)	4*e*		0.4067(3)	0.4935(3)	0.1663(2)	0.111(2)	0.103(2)	0.047(1)	0.038(2)	0.029(1)	0.004(2)
S(3)	4*e*		0.6154(2)	0.3155(2)	0.0539(2)	0.044(1)	0.041(1)	0.059(1)	0.001(1)	0.005(1)	0.000(1)
Fe(1)	2*d*		$\frac{1}{2}$	$\frac{1}{2}$	0	0.0332(7)	0.0313(7)	0.0314(7)	–0.0002(6)	0.0026(6)	–0.0015(6)
W(1)	4*e*		0.91280(3)	0.12188(2)	1.16195(2)	0.0389(1)	0.0332(2)	0.0324(1)	0.0016(1)	0.0069(1)	–0.0102(1)
W(2)	4*e*		0.72240(2)	–0.04510(2)	1.06105(2)	0.0246(1)	0.0426(2)	0.0453(2)	–0.0034(1)	0.0107(1)	0.0023(2)
W(3)	4*e*		0.92208(3)	0.22845(2)	0.97336(2)	0.0512(2)	0.0266(2)	0.0508(2)	0.0053(1)	0.0237(1)	0.0019(1)
W(4)	4*e*		1.00749(3)	0.10581(3)	0.81028(2)	0.0492(2)	0.0478(2)	0.0300(2)	–0.0045(2)	0.0070(1)	0.0107(1)
W(5)	4*e*		1.19142(3)	0.16705(2)	1.10214(2)	0.0363(1)	0.0431(2)	0.0430(2)	–0.0139(1)	0.0098(1)	–0.0179(1)
W(6)	4*e*		0.73071(3)	0.06136(3)	0.87229(2)	0.0267(1)	0.0747(3)	0.0327(2)	0.0106(2)	–0.0013(1)	0.0014(2)
P(1)	2*a*		1	0	1	0.024(1)	0.028(1)	0.023(1)	–0.002(1)	0.0039(9)	0.000(1)

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