# Crystal structure of μ-oxo-di-μ-sulfato-κ$^2$*O:O'*-bis[(2,2'-bipyridine-κ$^2$*N,N'*)-bis(dimethylsulfoxide-κ*O*)-diiron(III)]monohydrate, $C_{24}H_{30}Fe_2N_4O_{12}S_4$

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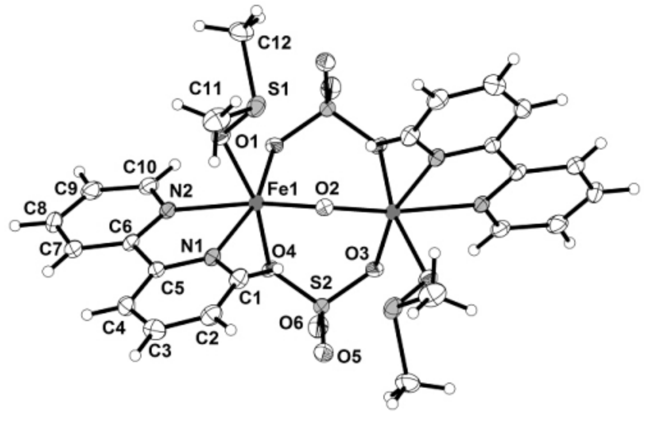

## Abstract

$C_{24}H_{30}Fe_2N_4O_{12}S_4$, monoclinic, $C2/c$ (no. 15), $a = 20.64(1)$ Å, $b = 8.762(4)$ Å, $c = 19.98(1)$ Å, $\beta = 120.31(3)°$, $V = 3119.0$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0437$, $wR_{ref}(F^2) = 0.1146$, $T = 100$ K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | green prisms, size 0.14×0.24×0.31 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 12.66 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 54° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 24893, 3393 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2553 |
| $N(param)_{refined}$: | 215 |
| Programs: | SHELX [23], SAINT [24], DIAMOND [25], WinGX [26] |

## Source of material

$FeSO_4{\cdot}7H_2O$ (0.173 g, 0.62 mmol) was dissolved in methanol, to which was added solid 2,2'-bipyridine (0.049 g, 0.31 mmol) followed by triethylamine base (0.11 mL, 0.78 mmol). The resulting blood red solution was stirred at room temperature for 5 h. The solution was filtered and the solvent was evaporated under *vacuo* to obtain a red solid. Crystallization from a methanol-dimethyl sulfoxide mixture (3:1) afforded green coloured crystals of the title compound after 15 days. Yield: 0.36 g, 72 % (based on Fe).

## Experimental details

All the hydrogen atoms except the H of water were included in idealized position and a riding model was used. The aromatic H atoms were positioned geometrically and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}$(parent) with a C–H distance of 0.93 Å. The methyl H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with $U_{iso}(H) = 1.5U_{eq}(C)$ and at a distance of 0.96 Å. The H atom of the water molecule was added from a difference Fourier map.

## Discussion

Several metal sulfates with varying dimensionality (1D, 2D and 3D) have been synthesized for their interesting physical properties and applications [1-9]. There are several examples of zero dimensional discrete metal sulfates [10-19]. Earlier Xu *et al.* synthesized a tetrameric Fe(III) cluster [4,4'-*bpy*H]$_2$-[$Fe_4O_2(SO_4)_6(H_2O)_4$]$\cdot 6H_2O$ using 4,4'-bipyridine (4,4'-*bpy*) as the directing ligand under hydrothermal conditions [19]. In 2006, Zhao *et.al.*, synthesized a Fe(III) sulfate dimer containing 1,10-phenanthroline as ligand [20]. Recently, Brechin *et.al.*, reported a couple of hexanuclear iron(III) cage compounds [21-22]. In all these instances, the Fe(III) source, $Fe_2(SO_4)_3{\cdot}9H_2O$ has been used. We found that the use of iron(II) source $FeSO_4{\cdot}7H_2O$ is sufficient to yield the molecular Fe(III) sulfate [$Fe_2$μ-O)(2,2'-*bpy*)-$(SO_4)_2((CH_3)_2SO)_2{\cdot}H_2O$] by aerial oxidation from Fe(II) to Fe(III). Thus the reaction of $FeSO_4{\cdot}7H_2O$, chelating 2,2'-bipyridine (2,2'-*bpy*), triethylamine base (2:1:2.5) and coordinating solvent such as dimethyl sulphoxide results in the formation of the title compound. The title compound is an iron(III) μ-oxo bridged dimer. The asymmetric unit contains one iron(III), a neutral 2,2'-*bpy* ligand, a dianionic sulfate ($SO_4^{2-}$) ligand and a DMSO solvent molecule. The μ-oxo ligand (O2) and the lattice water molecule (O7) lies on a crystallographic twofold axis. The iron atom is hexacoordinated with an octahedral geometry by 2N, and 4O atoms. The two nitrogen atoms are from the chelating 2,2'-*bpy* ligand. Among the 4O coordination, two are from the $SO_4^{2-}$ ligand and one each from the μ-O ligand and DMSO solvent molecule. The 2N of the 2,2'-*bpy* ligand, O2 of the μ-O and O3 of the $SO_4^{2-}$ ligand constitute the equatorial octahedral plane while the axial positions are occupied by the anionic O4 of the $SO_4^{2-}$ ligand and the neutral O1 of the DMSO molecule. All Fe–O distances are found to be different. The Fe–O distance obtained from the μ-O atom is very short (Fe1–O2 1.7955(16) Å) while the Fe–O distances from the neutral DMSO molecule (Fe1–O1 2.114(2) Å) and the anionic sulfate ligands (Fe1–O3 1.994(2) and Fe1–O4 2.026(2) Å) are longer. In other words, the axial Fe–O bonds are relatively longer than the equatorial Fe–O distances. It is interesting to note that the Fe–N distances are dissimilar (Fe1–N1 2.151(3) and Fe1–N2 2.195(3) Å). In the case of the $SO_4^{2-}$ ligands, the two neutral S=O distances are shorter (avg S–O 1.453(2) Å) than the two anionic S–O distances (avg. S–O 1.506(2) Å). The mean plane analysis of the title structure shows that the two individual monomeric Fe(2,2'-*bpy*) are planar with the maximum deviation is observed for C3 0.0524(19) and C10 0.0489(22)°. The dihedral angle between the two Fe(2,2'-*bpy*)

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plane is 65.690(12)°. It is also observed that the two supposedly straight angles that makes the equatorial plane are less than 180° (O2–Fe1–N2 168.77(9) and O3–Fe1–N1 163.96(10)°). The bite angle of the 2,2'-*bpy* ligand coordinated to Fe1 is 74.28(10)°.

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

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1) | 8*f* | 0.0982 | 1.0011 | 0.3208 | 0.026 |
| H(2) | 8*f* | 0.1963 | 1.1704 | 0.3921 | 0.029 |
| H(3) | 8*f* | 0.2785 | 1.1221 | 0.5239 | 0.029 |
| H(4) | 8*f* | 0.2561 | 0.9119 | 0.5828 | 0.025 |
| H(7) | 8*f* | 0.2258 | 0.7183 | 0.6291 | 0.027 |
| H(8) | 8*f* | 0.1894 | 0.4962 | 0.6672 | 0.030 |
| H(9) | 8*f* | 0.0905 | 0.3495 | 0.5736 | 0.031 |
| H(10) | 8*f* | 0.0303 | 0.4264 | 0.4447 | 0.025 |
| H(11A) | 8*f* | –0.0426 | 1.1178 | 0.4330 | 0.052 |
| H(11B) | 8*f* | –0.0776 | 1.2147 | 0.3545 | 0.052 |
| H(11C) | 8*f* | 0.0053 | 1.1460 | 0.3913 | 0.052 |
| H(12A) | 8*f* | –0.1899 | 0.8434 | 0.3115 | 0.048 |
| H(12B) | 8*f* | –0.1965 | 1.0250 | 0.3145 | 0.048 |
| H(12C) | 8*f* | –0.1477 | 0.9307 | 0.3929 | 0.048 |
| H(51) | 8*f* | 0.036(2) | 0.264(5) | 0.272(3) | 0.08(2) |

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

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 8*f* | 0.03157(2) | 0.69989(5) | 0.34101(2) | 0.0155(2) | 0.0176(2) | 0.0137(2) | –0.0001(2) | 0.0080(2) | –0.0001(2) |
| S(1) | 8*f* | –0.08250(5) | 0.9587(1) | 0.32820(5) | 0.0289(5) | 0.0278(5) | 0.0211(4) | 0.0102(4) | 0.0151(4) | 0.0030(3) |
| S(2) | 8*f* | 0.11891(4) | 0.52363(9) | 0.26733(4) | 0.0156(4) | 0.0185(4) | 0.0148(4) | 0.0013(3) | 0.0084(3) | 0.0000(3) |
| O(1) | 8*f* | –0.0290(1) | 0.8332(2) | 0.3792(1) | 0.022(1) | 0.022(1) | 0.020(1) | 0.005(1) | 0.013(1) | 0.0031(9) |
| O(2) | 2*e* | 0 | 0.7946(3) | $\frac{1}{4}$ | 0.017(2) | 0.015(2) | 0.018(2) | 0 | 0.010(1) | 0 |
| O(3) | 8*f* | –0.0464(1) | 0.5378(2) | 0.3088(1) | 0.014(1) | 0.021(1) | 0.018(1) | –0.0016(9) | 0.009(1) | 0.0018(9) |
| O(4) | 8*f* | 0.1029(1) | 0.5541(2) | 0.3318(1) | 0.018(1) | 0.026(1) | 0.016(1) | 0.0048(9) | 0.012(1) | –0.0001(9) |
| O(5) | 8*f* | 0.1729(1) | 0.6346(3) | 0.2709(1) | 0.019(1) | 0.028(1) | 0.021(1) | –0.006(1) | 0.010(1) | –0.0019(9) |
| O(6) | 8*f* | 0.1450(1) | 0.3671(2) | 0.2747(1) | 0.029(1) | 0.019(1) | 0.023(1) | 0.008(1) | 0.014(1) | 0.0013(9) |
| N(1) | 8*f* | 0.1199(2) | 0.8609(3) | 0.4071(2) | 0.019(1) | 0.019(1) | 0.016(1) | 0.001(1) | 0.011(1) | –0.002(1) |
| N(2) | 8*f* | 0.0886(1) | 0.6156(3) | 0.4608(1) | 0.018(1) | 0.021(1) | 0.016(1) | 0.002(1) | 0.010(1) | 0.001(1) |
| C(1) | 8*f* | 0.1312(2) | 0.9829(4) | 0.3745(2) | 0.026(2) | 0.021(2) | 0.022(2) | –0.001(1) | 0.014(2) | –0.002(1) |
| C(2) | 8*f* | 0.1894(2) | 1.0838(4) | 0.4164(2) | 0.029(2) | 0.021(2) | 0.028(2) | –0.003(1) | 0.019(2) | –0.001(1) |
| C(3) | 8*f* | 0.2371(2) | 1.0562(4) | 0.4942(2) | 0.023(2) | 0.020(2) | 0.029(2) | –0.002(1) | 0.012(2) | –0.008(1) |
| C(4) | 8*f* | 0.2244(2) | 0.9314(4) | 0.5290(2) | 0.021(2) | 0.025(2) | 0.018(2) | 0.002(1) | 0.010(1) | –0.004(1) |
| C(5) | 8*f* | 0.1649(2) | 0.8368(4) | 0.4837(2) | 0.016(2) | 0.023(2) | 0.016(2) | 0.004(1) | 0.009(1) | –0.001(1) |
| C(6) | 8*f* | 0.1464(2) | 0.6992(4) | 0.5142(2) | 0.019(2) | 0.022(2) | 0.016(2) | 0.002(1) | 0.012(1) | –0.002(1) |
| C(7) | 8*f* | 0.1854(2) | 0.6577(4) | 0.5921(2) | 0.020(2) | 0.030(2) | 0.019(2) | 0.004(1) | 0.012(1) | –0.000(1) |
| C(8) | 8*f* | 0.1640(2) | 0.5265(4) | 0.6144(2) | 0.025(2) | 0.035(2) | 0.016(2) | 0.005(2) | 0.012(2) | 0.006(1) |
| C(9) | 8*f* | 0.1058(2) | 0.4402(4) | 0.5593(2) | 0.024(2) | 0.031(2) | 0.027(2) | 0.003(2) | 0.017(2) | 0.010(2) |
| C(10) | 8*f* | 0.0698(2) | 0.4874(4) | 0.4828(2) | 0.020(2) | 0.025(2) | 0.022(2) | 0.001(1) | 0.014(2) | 0.004(1) |
| C(11) | 8*f* | –0.0451(2) | 1.1283(4) | 0.3829(2) | 0.039(2) | 0.027(2) | 0.044(2) | 0.006(2) | 0.026(2) | 0.002(2) |
| C(12) | 8*f* | –0.1633(2) | 0.9370(4) | 0.3379(2) | 0.021(2) | 0.042(2) | 0.034(2) | 0.006(2) | 0.014(2) | –0.005(2) |
| O(7) | 2*e* | 0 | 0.2088(5) | $\frac{1}{4}$ | 0.043(3) | 0.025(2) | 0.059(3) | 0 | 0.028(2) | 0 |

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