

# Synthesis, Spectroscopic Properties and Structural Characterization of Sodium Potassium Citrato Oxotungstate(VI) Dimer<sup>①</sup>

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**ABSTRACT** The sodium-potassium citrato oxotungstate(VI) dimer,  $\text{Na}_4\text{K}_2[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 11\text{H}_2\text{O}$  ( $\text{H}_4\text{cit} = \text{citric acid}$ ) was obtained by the reaction of sodium tungstate (VI) and excess potassium citrate monobasic ( $\text{KH}_3\text{cit}$ ) in neutral solution. The crystal data for the title compound: monoclinic,  $\text{C}_{12}\text{H}_{30}\text{K}_2\text{Na}_4\text{W}_2\text{O}_{30}$ ,  $M_r = 1192.21$ , space group  $P2_1/n$ ,  $a = 17.427(4)$ ,  $b = 10.022(2)$ ,  $c = 18.637(3)$  Å,  $\beta = 92.62(1)^\circ$ ,  $V = 3252(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.435$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 76.38$  cm<sup>-1</sup>,  $F(000) = 2288$ . The structure was refined to  $R = 0.0434$  for 6327 independent observed reflections with  $I > 3\sigma(I)$ . The complex anion contains a *quasi*-centrosymmetric ( $\text{O}_2\text{W}$ )<sub>2</sub> ( $\text{WO}_2$ ) core with a bent bridging oxo group [ $\text{W}-\text{O}_b-\text{W}$  175.0(4)<sup>°</sup>]. Each citrate as tridentate ligand coordinates to a tungsten atom through the alkoxy,  $\alpha$ -carboxyl, and one  $\beta$ -carboxyl group, while the other  $\beta$ -carboxyl group remains uncoordinated. Principal dimensions are:  $\text{W}-\text{O}_b$  1.883(6) Å, ( $\text{W}=\text{O}_t$ )<sub>av</sub> 1.715(6) Å,  $\text{W}-\text{O}$  (alkoxy) 1.959(6) Å,  $\text{W}-\text{O}$  ( $\alpha$ -carboxy) 2.176(6) Å and  $\text{W}-\text{O}$  ( $\beta$ -carboxy) 2.231(6) Å. The tungsten atom is located in a distorted octahedron environment.

**Keywords:** oxotungstate(VI), citrate, citric acid, citrate method, crystal structure

## 1 INTRODUCTION

The essential role of Mo in various fundamental biological conversions carried out by both microorganisms and higher life forms has been known for decades<sup>[1]</sup>. Recent studies on the nitrogenase enzyme has revealed its active site of  $\text{FeMo}\sigma\text{co}$  ( $\text{FeMo}\sigma\text{co}$  factor) as a cage like  $\text{MoFe}_7\text{S}_9$  homocitrate cluster, alternative polycarboxylic acids including citric, malic and citramalic by in vitro syntheses of the  $\text{FeMo}\sigma\text{co}$  displayed  $\text{N}_2$  reduction activity well above the background limits<sup>[2,3]</sup>. Tungsten (W) and molybdenum (Mo) are chemically analogous elements. Because of their great similarities in the properties, it was reasoned that insight into the catalytic role of Mo in var-

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ious enzymes might be provided by replacing Mo with W. In fact, for almost all of the known tungstoenzyme, there is an analogous molybdoenzyme that is present within the same organism or in a very closely related species, while of the vast array of life forms that utilize Mo, a very small subset are also able to use W<sup>[4]</sup>. This prompted us an investigation of the coordination chemistry of tungsten complex.

The solution coordination chemistry of tungsten(VI) with citric acid (H<sub>4</sub>cit, 3-carboxy-3-hydroxypentane-1,5-dioic acid) has been previously investigated<sup>[5,6]</sup>, and the solid complexes of Na<sub>6</sub>[W<sub>2</sub>O<sub>5</sub>(cit)<sub>2</sub>]·10H<sub>2</sub>O, K<sub>6</sub>[W<sub>2</sub>O<sub>5</sub>(cit)<sub>2</sub>]·5H<sub>2</sub>O and K<sub>6</sub>[W<sub>2</sub>O<sub>5</sub>(cit)<sub>2</sub>]·6H<sub>2</sub>O have been separated and their structures characterized as a centrosymmetric citrato oxotungstate(VI)<sup>[7-11]</sup>. More recently, we have reported the syntheses and characterization of monomeric citrato oxomolybdate(VI) raceme Δ/Λ-K<sub>4</sub>[MoO<sub>3</sub>(cit)]·2H<sub>2</sub>O from basic solution, and bidentate citrato oxomolybdate(VI) and oxotungstate(VI) racemes Δ/Λ-Na<sub>2</sub>[MO<sub>2</sub>(H<sub>2</sub>cit)<sub>2</sub>]·3H<sub>2</sub>O (M = Mo or W) from acidic solution, which may represent the early mobilized precursors in the biosynthesis of FeMo-co<sup>[12-13]</sup>. Here we further reported the synthesis and characterization of the title compound from neutral solution.

## 2 EXPERIMENTAL

### 2.1 Preparation of Na<sub>4</sub>K<sub>2</sub>[W<sub>2</sub>O<sub>5</sub>(cit)<sub>2</sub>]·11H<sub>2</sub>O

Sodium tungstate (10 mmol) was added to the solution of an excess amount of potassium citrate monobasic (KH<sub>3</sub>cit), and the mixture was left undisturbed for about 2 weeks at 25 °C. The compound Na<sub>4</sub>K<sub>2</sub>[W<sub>2</sub>O<sub>5</sub>(cit)<sub>2</sub>]·11H<sub>2</sub>O was isolated as colorless crystals (yield, 70%). Found: C, 11.7; H, 2.4. Calc. for C<sub>12</sub>H<sub>30</sub>N<sub>4</sub>K<sub>2</sub>W<sub>2</sub>O<sub>30</sub>: C, 12.1; H, 2.5%. IR (KBr): ν<sub>asym</sub>(C=O) 1633vs, 1578vs; ν<sub>sym</sub>(C=O) 1406s; ν(W=O) 920s, 888s; ν<sub>as</sub>(WO<sub>b</sub>W), 814s; <sup>1</sup>H NMR δ<sub>H</sub> (500 MHz, D<sub>2</sub>O), 2.681 (d, 4H, J 16.7 Hz, CH<sub>2</sub>), 2.548 (d, 4H, J 16.7 Hz, CH<sub>2</sub>); <sup>13</sup>C NMR δ<sub>C</sub>(D<sub>2</sub>O), 186.5 (CO<sub>2</sub>)<sub>α</sub>, 178.1 (CO<sub>2</sub>)<sub>β</sub>, 85.5 (≡C-O), 45.0 (=CH<sub>2</sub>).

### 2.2 Physical Measurements

Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 740 FT-IR spectrometer. Elemental analyses were performed using EA 1110 elemental analyzers. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian UNITY 500 NMR and 300 NMR spectrometer using DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as internal reference respectively.

### 2.3 X-ray Data Collection, Structure Solution and Refinement

A transparent colorless crystal with dimensions 0.15 mm × 0.25 mm × 0.25 mm was mounted on an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator MoKα radiation (λ = 1.5418 Å) for data collection. A total of 7840 independent reflections were collected in the range of 2° < 2θ < 56° by ω-2θ scan technique at room temperature, of which 6327 reflections with I > 3σ(I) were

considered to be observed and used in the structure analysis. Empirical absorption correction was made. The structure was solved by Patterson method. The coordinates of the other non-hydrogen atoms were determined by successive Fourier syntheses. Anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms of methylene groups were treated as riding on their attached atoms and not refined. Final  $R$  and  $R_w$  are 0.0434 and 0.0513 ( $w^{-1} = \{\sigma(F_0)^2\} + (0.01F_0)^2 + 1.0\}$ ).  $(\Delta/\sigma)_{\max} = 0.02$ ,  $S = 0.811$ ,  $(\Delta\rho)_{\max} = 2.645$  and  $(\Delta\rho)_{\min} = -0.152$  e  $\text{\AA}^{-3}$ . Computations were performed using the MoLEN software package on a 586/100 microcomputer. Table 1 lists the positional and thermal parameters, and Table 2 lists selected bond lengths and bond angles of the title compound.

**Table 1. Atomic Coordinates and Thermal Parameters(  $\text{\AA}^2$ )**

| Atom  | <i>x</i>   | <i>y</i>    | <i>z</i>   | <i>B<sub>eq</sub></i> | Atom   | <i>x</i>  | <i>y</i>   | <i>z</i>  | <i>B<sub>eq</sub></i> |
|-------|------------|-------------|------------|-----------------------|--------|-----------|------------|-----------|-----------------------|
| W(1)  | 0.55145(2) | 0.15219(3)  | 0.26732(2) | 0.984(5)              | O(18)  | 0.3582(4) | -0.1226(6) | 0.2232(4) | 2.0(1)                |
| W(2)  | 0.45079(2) | -0.17744(3) | 0.24171(2) | 1.050(5)              | O(19)  | 0.4471(4) | -0.2181(7) | 0.3327(3) | 1.9(1)                |
| K(1)  | 0.2921(2)  | 0.9223(3)   | 0.8433(1)  | 3.66(5)               | O(w1)  | 0.1347(4) | 0.6747(7)  | 0.8810(4) | 2.5(1)                |
| K(2)  | 0.7835(2)  | 0.6116(4)   | 0.8411(2)  | 5.34(7)               | O(w2)  | 0.1726(5) | 0.1723(8)  | 0.5902(4) | 2.8(1)                |
| Na(1) | 0.2451(2)  | 0.4977(4)   | 0.3411(2)  | 2.16(7)               | O(w3)  | 0.8568(4) | 0.3514(7)  | 0.6301(4) | 2.5(1)                |
| Na(2) | 0.0142(3)  | 0.5949(4)   | 0.9270(2)  | 2.52(8)               | O(w4)  | 0.7690(5) | 0.8952(8)  | 0.7287(4) | 3.1(2)                |
| Na(3) | 0.7416(2)  | 0.9750(4)   | 0.3460(2)  | 2.27(7)               | O(w5)  | 0.7859(5) | 0.6235(8)  | 0.5547(4) | 3.2(2)                |
| Na(4) | 0.4067(3)  | 0.9881(5)   | 0.0454(2)  | 3.10(9)               | O(w6)  | 0.8282(5) | 0.8424(9)  | 0.9039(4) | 3.4(2)                |
| O(1)  | 0.5653(4)  | 0.3308(6)   | 0.3086(3)  | 1.6(1)                | O(w7)  | 0.7682(5) | 0.8661(8)  | 0.2340(4) | 2.9(2)                |
| O(2)  | 0.5250(4)  | 0.1306(6)   | 0.3797(3)  | 1.9(1)                | O(w8)  | 0.4767(5) | 0.8875(9)  | 0.9528(4) | 3.3(2)                |
| O(3)  | 0.4292(4)  | 0.2189(6)   | 0.2648(3)  | 1.8(1)                | O(w9)  | 0.7763(6) | 0.5972(9)  | 0.0495(4) | 4.1(2)                |
| O(4)  | 0.3252(4)  | 0.3303(8)   | 0.2884(5)  | 3.0(2)                | O(w10) | 0.6084(7) | 0.998(1)   | 0.5348(6) | 6.8(3)                |
| O(5)  | 0.6818(4)  | 0.5761(8)   | 0.4383(4)  | 2.7(1)                | O(w11) | 0.1605(6) | 0.614(1)   | 0.5511(6) | 5.1(2)                |
| O(6)  | 0.6705(5)  | 0.3569(8)   | 0.4467(4)  | 3.4(2)                | C(1)   | 0.5229(5) | 0.3662(8)  | 0.3680(4) | 1.4(1)                |
| O(7)  | 0.4982(6)  | 0.2457(8)   | 0.4778(4)  | 4.2(2)                | C(2)   | 0.5170(6) | 0.239(1)   | 0.4154(5) | 2.2(2)                |
| O(8)  | 0.6423(4)  | 0.0924(6)   | 0.2863(3)  | 1.7(1)                | C(3)   | 0.4398(5) | 0.4075(9)  | 0.3446(5) | 1.8(2)                |
| O(9)  | 0.5600(4)  | 0.2086(7)   | 0.1796(3)  | 1.8(1)                | C(4)   | 0.3957(5) | 0.3109(9)  | 0.2973(5) | 1.9(2)                |
| O(10) | 0.5002(4)  | -0.0112(6)  | 0.2502(4)  | 1.9(1)                | C(5)   | 0.5601(5) | 0.4857(9)  | 0.4068(5) | 1.9(2)                |
| O(11) | 0.4365(4)  | -0.3619(6)  | 0.2071(3)  | 1.8(1)                | C(6)   | 0.6438(6) | 0.4698(9)  | 0.4316(5) | 2.0(2)                |
| O(12) | 0.4748(4)  | -0.1713(6)  | 0.1279(3)  | 1.7(1)                | C(11)  | 0.4813(5) | -0.4042(9) | 0.1505(4) | 1.5(1)                |
| O(13) | 0.5732(4)  | -0.2430(6)  | 0.2440(4)  | 1.8(1)                | C(12)  | 0.4936(6) | -0.2850(9) | 0.1004(5) | 1.9(2)                |
| O(14) | 0.6785(4)  | -0.3591(8)  | 0.2258(5)  | 3.1(2)                | C(13)  | 0.5622(5) | -0.4480(9) | 0.1780(5) | 1.8(2)                |
| O(15) | 0.3239(4)  | -0.6000(8)  | 0.0676(4)  | 3.0(2)                | C(14)  | 0.6073(5) | -0.3413(9) | 0.2179(5) | 1.7(2)                |
| O(16) | 0.3469(5)  | -0.3833(8)  | 0.0561(4)  | 3.3(2)                | C(15)  | 0.4447(6) | -0.524(1)  | 0.1113(5) | 2.2(2)                |
| O(17) | 0.5237(5)  | -0.3012(9)  | 0.0436(4)  | 3.5(2)                | C(16)  | 0.3654(6) | -0.497(1)  | 0.0770(5) | 2.0(2)                |

$$B_{eq} = (4/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

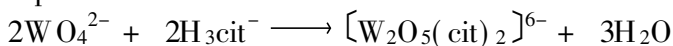
### 3 RESULTS AND DISCUSSION

The pH of the medium is the principle variable controlling complex formation and interconversion equilibria in solution<sup>[5-6]</sup>. At high pH (> 6), the monomeric complexes  $[\text{WO}_2(\text{OH})_2(\text{cit})]^{4-}$  or  $[\text{WO}_2(\text{cit})_2]^{6-}$  are formed, at lower pH two different dinuclear complexes with a  $[\text{W}_2\text{O}_3(\text{OH})_4(\text{cit})_2]^{6-}$  and  $[\text{W}_2\text{O}_3(\text{OH})_3(\text{Hcit})_2]^{3-}$  are the major species. However, in this experiment, only dimeric citrato oxotungstate (VI) are separated as solid state in high yield between pH 5.0 to 7.5. This species is stable in the different pH range, which implies only the deprotonated

**Table 2. Selected Bond Lengths (Å) and Bond Angles (°)**

| Bond       | Dist.    | Angle           | (°)      | Angle            | (°)      |
|------------|----------|-----------------|----------|------------------|----------|
| W(1)–O(1)  | 1.959(6) | O(1)–W(1)–O(2)  | 75.0(2)  | O(11)–W(2)–O(12) | 74.6(2)  |
| W(1)–O(2)  | 2.176(6) | O(1)–W(1)–O(3)  | 80.5(2)  | O(11)–W(2)–O(13) | 80.6(3)  |
| W(1)–O(3)  | 2.231(6) | O(1)–W(1)–O(8)  | 98.2(3)  | O(11)–W(2)–O(18) | 97.5(3)  |
| W(1)–O(8)  | 1.715(6) | O(1)–W(1)–O(9)  | 93.3(3)  | O(11)–W(2)–O(19) | 95.1(3)  |
| W(1)–O(9)  | 1.743(7) | O(1)–W(1)–O(10) | 155.4(3) | O(11)–W(2)–O(10) | 155.5(3) |
| W(1)–O(10) | 1.886(6) | O(2)–W(1)–O(3)  | 78.9(2)  | O(12)–W(2)–O(13) | 78.5(2)  |
| W(2)–O(11) | 1.970(7) | O(2)–W(1)–O(8)  | 90.1(3)  | O(12)–W(2)–O(18) | 90.9(3)  |
| W(2)–O(12) | 2.182(6) | O(2)–W(1)–O(9)  | 165.1(3) | O(12)–W(2)–O(19) | 165.2(3) |
| W(2)–O(13) | 2.230(6) | O(2)–W(1)–O(10) | 87.5(3)  | O(12)–W(2)–O(10) | 87.1(3)  |
| W(2)–O(18) | 1.724(6) | O(3)–W(1)–O(8)  | 168.8(3) | O(13)–W(2)–O(18) | 169.4(3) |
| W(2)–O(19) | 1.749(6) | O(3)–W(1)–O(9)  | 90.3(3)  | O(13)–W(2)–O(19) | 89.4(3)  |
| W(2)–O(10) | 1.879(6) | O(3)–W(1)–O(10) | 79.2(3)  | O(13)–W(2)–O(10) | 79.9(3)  |
|            |          | O(8)–W(1)–O(9)  | 100.9(4) | O(18)–W(2)–O(19) | 101.1(3) |
|            |          | O(8)–W(1)–O(10) | 99.0(3)  | O(18)–W(2)–O(10) | 99.0(3)  |
|            |          | O(9)–W(1)–O(10) | 100.6(3) | O(19)–W(2)–O(10) | 99.3(3)  |
|            |          | W(1)–O(10)–W(2) | 175.0(4) |                  |          |

dimeric citrato oxotungstate(VI) exists in solution between pH 5.0 to 7.5, or the equilibria will forward the other species to the deprotonated species in the solid formation. The reaction processes as follows:



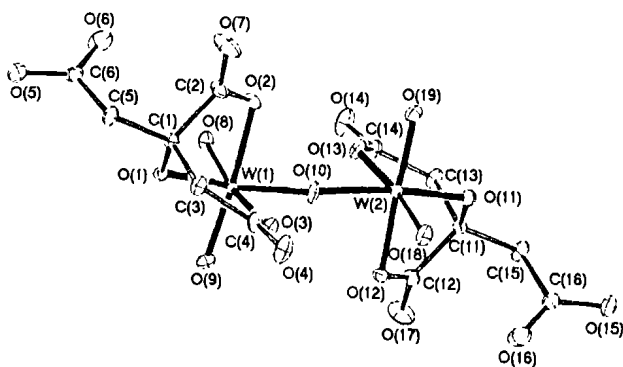
The IR spectrum of the complex  $\text{Na}_4\text{K}_2[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 11\text{H}_2\text{O}$  is similar to those of  $\text{Na}_6[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 10\text{H}_2\text{O}$  and  $\text{K}_6[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 6\text{H}_2\text{O}$ . The strong band at  $814\text{cm}^{-1}$  is assigned to the asymmetric W–O–W stretch in agreement with the previous studies<sup>[8–10]</sup>. The W=O bonds give rise to three strong bands centered around  $900\text{cm}^{-1}$ , and the two strong band at  $1633$  and  $1578\text{cm}^{-1}$  can be assigned to the free and the bonded deprotonated carboxylate respectively.

The 500MHz  $^1\text{H}$  NMR spectrum of the well formed crystals isolated shows only a sharp AB quartet with  $\delta_{\text{A}} = 2.681$ ,  $\delta_{\text{B}} = 2.548$  and  $J_{\text{AB}} = 16.73\text{Hz}$  for methylene protons of the coordinated citrate ligand, implying that less strongly bonded  $\beta$ -carboxylate dissociates when the solid complex is redissolved in  $\text{D}_2\text{O}$ . Whereas the large low-field shift of some  $^{13}\text{C}$  resonance compared with uncoordinated citrate anion shows the chelation of the citrate anions.

The structure of sodium potassium citrato oxotungstate(VI)  $\text{Na}_4\text{K}_2[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 11\text{H}_2\text{O}$  with labeled is presented in Fig. 1. It can be found that the citrato oxotungstate(VI) anion is *quasi*-centrosymmetric. The W–O<sub>b</sub>–W is slightly bend with an angle of  $175.0(4)^\circ$ . Each tungsten atom is coordinated by two unshared oxygens and bridging oxo groups, which adopt *fac* stereochemistry. The remaining positions are occupied by a fully deprotonated citrate acting as a tridentate ligand with alkoxy,  $\alpha$  carboxy and one of the two  $\beta$  carboxyl groups, while the other  $\beta$  carboxyl group remains uncoordinated. The coordinated carboxyl groups form five and six membered chelate rings respectively, completing the distorted octahedral coordination

of W(VI).

In single oxo bridged dinuclear molybdenum(VI) complexes the Mo–O–Mo angle ranges from strictly  $180^\circ$  in  $K_4[(MoO_2)_2O(Hcit)_2] \cdot 4H_2O$  to  $144.7^\circ$  in  $Na_4K_2[(MoO_2)_2O(cit)_2] \cdot 5H_2O$ ,  $137.1^\circ$  in  $K_6[(MoO_2)_2O(cit)_2] \cdot 2H_2O$  and  $K_6[(MoO_2)_2O(cit)_2] \cdot 5H_2O$ <sup>[12,15~17]</sup>. In comparison we found that the W system has somewhat different trend with the W–O–W angle ranging from  $180^\circ$  in  $Na_6[W_2O_5(cit)_2] \cdot 10H_2O$  and  $K_6[W_2O_5(cit)_2] \cdot 6H_2O$  to  $175.0^\circ$  in the title complex. This may be concluded that the citrato oxotungstate(VI) anions with only one kind of cation are symmetrical since they exist in symmetrical cation atmosphere. However, the title complex has two different cations with different radius, this may has some effects on the structure of the anion. The reason why the anion  $[W_2O_5(cit)_2]^{6-}$  is less susceptible to such an effect than  $[Mo_2O_5(cit)_2]^{6-}$  may be lanthanide contraction. W has a radius similar to that of Mo, but it has more nuclear charge, so the bond strength between W–O is stronger than that of Mo–O, which has a more rigid and directional property.



**Fig 1** Perspective view of the anion structure of  $Na_4K_2[W_2O_5(cit)_2] \cdot 11H_2O$ , showing the 50% thermal ellipsoids

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