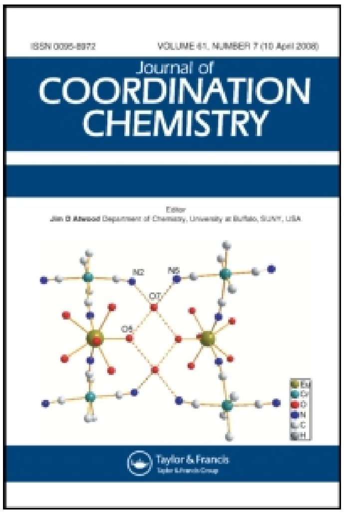

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SYNTHESIS AND STRUCTURE OF A NOVEL MONONUCLEAR TUNGSTEN (VI) CITRATO COMPLEX, $(NH_4)_3[Li(H_2O)_3WO_3(C_6H_4O_7)]$

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The first mononuclear tungsten–citrato complex, $(NH_4)_3[Li\ (H_2O)_3WO_3(C_6H_4O_7)]$ (**1**), has been prepared by the reaction of ammonium tetrathio tungstate and lithium citrate in CH_3OH-H_2O solution at pH 8.2. There are two crystallographically independent anions in the asymmetric crystallographic unit. The crystal structure of the title compound (triclinic, space group $P\bar{1}$, $a = 6.901(1)$, $b = 15.136(3)$, $c = 16.107(3)$ Å, $\alpha = 75.85(3)$, $\beta = 89.89(3)$, $\gamma = 89.97(3)$, $V = 1631.4(6)$ Å^3, $R = 0.068$, $R_w = 0.1674$ for 3878 reflections with $I > 2\sigma(I)$), reveals that in the compound a tungsten atom is coordinated to a fully deprotonated citrate as a tridentate ligand and three terminal oxygen atoms to form a distorted coordination octahedron.

Keywords: Synthesis; Crystal structure; Mononuclear complexes; Tungsten; Citric acid

INTRODUCTION

Citric acid is an important small molecule in many biochemical processes. For instance, citric acid or citrate regulates fundamentally physiological processes and are intermediates in carbohydrate metabolism [1,2]. The chemistry of citric acid and its complexes with metal ions has been investigated widely for a long time [3–6]. Numerous molybdenum citrato complexes have been prepared and their structures have been determined by

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X-ray crystallography, for example, $K_2[MoO(O_2)_2(C_6H_6O_7)]\cdot 1/2H_2O_2\cdot 3H_2O$ [7], $K_4[Mo_4O_{11}(Hcit)_2]\cdot 6H_2O$ [8], $K_6[Mo_2O_5(cit)_2]\cdot 5H_2O$ [9], $K_6[\{MoO_2(C_6H_4O_7)\}_2O]\cdot 2H_2O$ [10], $K_5(NH_4)[Mo_2O_2(\mu-s)_2(C_6H_4O_7)_2]\cdot CH_3OH\cdot 5H_2O$ [9b, 11] $K_{2.5}Na_2NH_4[Mo_2O_2S_2(cit)_2]\cdot 5H_2O$ [12], *etc.* However, syntheses and structures of only a few tungsten complexes with citrate such as $Na_6[\{WO_2(cit)\}_2O]\cdot 10H_2O$ [13] and $K_6[W_2O_5(cit)_2]\cdot 6H_2O$ [14] are reported. In this paper, we report the synthesis and structure of a novel mononuclear tungsten citrato complex $(NH_4)_3[Li(H_2O)_3WO_3(C_6H_4O_7)]$ (**1**).

EXPERIMENTAL

Materials and Physical Measurements

All solvents and chemicals were commercial analytical reagents and used without further purification. All reactions were carried out under an atmosphere of purified nitrogen. $(NH_4)_2WS_4$ was prepared as reported in the literature [15]. Elemental analyses (C, H, N) were performed using a Perkin–Elmer 240C instrument. W and Li were determined by use of a PE-ICP-1000 spectrophotometer.

Synthesis of the Title Compound

Some 0.42 g (2 mmol) of citric acid was dissolved in 10 ml of water and 30 ml of CH_3OH; the pH of the solution was adjusted to 7.5 with LiOH. Then 0.4 g (1 mmol) of $(NH_4)_2WS_4$ was added to the solution, protected by purified nitrogen gas. After continuously stirring for 48 h, the mixture was filtered. The filtrate was yellow initially, but after keeping under nitrogen gas at room temperature for about a month, the solution had turned orange red, its pH was 8.2, and colourless prismatic crystals has formed. These were collected. Yield, 0.1 g (21% based on W). *Anal.* Calcd. for $C_6H_{22}LiN_3O_{13}W$ (%): C, 13.46; H, 4.11; N, 7.85; Li, 1.30; W, 34.38. Found: C, 13.16; H, 3.96; N, 6.98; Li, 1.60; W, 34.46.

Crystal Structure Determination

A colourless prismatic crystal with dimensions 0.46 × 0.38 × 0.26 mm was selected for structural analysis. Diffraction data were obtained on a Siemens P4 Four-Circle diffractometer using graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation, with the $\omega-2\theta$ scan technique. Unit cell parameters were determined from automatic centring of 25 reflections and refined by least-squares methods. Intensity data were corrected for Lorenz and polarization factors and absorption effects based on ψ-scans. A total of 4167 reflections were collected in the range $1.66° < \theta < 25.01°$, of which 3878 independent reflections with $I > 2\sigma(I)$ were used for structure solution and refinements. All calculation was carried out on a COMPAQ 486 computer with SHELXTL-PLUS program package. The locations of H atoms were obtained by theoretical models. The coordinates of the metal atoms were determined by direct methods and all the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms and isotropically for H atoms. The agreement factors converged to $R_1 = 0.069$, $R_w = 0.170$.

RESULTS AND DISCUSSION

Synthesis

The title compound was obtained by the reaction of $(NH_4)_2$ WS_4 and an excess of lithium citrate in water/methanol medium at pH 8.2. Our initial idea was to prepare tungsten–citrato complexes with a sulfido-bridge. Due to the lower stability of binuclear tungsten(V) citrato complexes with sulfur ligands than analogous molybdenum(V) species, the product was not the target compound but a mononuclear tungsten–citrato complex. Cervilla and co-workers investigated complex formation in aqueous solution between sodium tungstate and citric acid by using polarimetric, spectrophotometric and ^1H and ^{13}C NMR techniques [16]. They showed that at high pH (> 6) the complexes were monomers, dimers at low pH, and at pH 5.5 $Na_6[\{WO_2(cit)\}_2O] \cdot 10H_2O^{13}$ was obtained. During investigation of the reaction of tetrathiotungstate with citric acid (or citrate) in CH_3OH/H_2O solution, we found that the pH of the medium is one of the decisive factors affecting complex formation. In the range pH 6–7.5, dinuclear $[W_2O_5(cit)_2]^{6-}$ was obtained and its structure determined [14], while for pH 7.5–8.2 mononuclear $[WO_3(cit)]^{4-}$ was synthesized.

H_2S escaped in the course of obtaining complex **1**. Thus reaction (1) possibly applies during formation of **1**.

$$\begin{aligned} &Li^+ + WS_4^{2-} + C_6H_5O_7^{3-} + 6H_2O \\ &\quad \rightarrow [Li(H_2O)_3WO_3(C_6H_4O_7)]^{3-} + 3H_2S + SH^- \end{aligned} \tag{1}$$

Structure

Crystal data and data collection parameters are summarized in Table I. Atomic coordinates and thermal parameters, and selected interatomic distances and angles are listed in Tables II and III, respectively. Figure 1 shows the structure of the anion.

Crystals of compound **1** consist of discrete $[Li(H_2O)_3WO_3(C_6H_4O_7)]^{3-}$ anions and NH_4^+ cations. There are two crystallographically independent anions (A and B, Fig. 1) in the asymmetric unit. Both A and B anions have the same coordination geometry and comparable bondlengths and angles. We, here, only describe the structure of anion A.

In the coordination sphere, W is coordinated to three unshared oxygen atoms, O(4), O(5) and O(6), and these terminal oxygen groups adopt *fac* stereochemistry. The remaining coordination positions are occupied by a fully deprotonated citrate ion as a tridentate ligand. Specifically, coordination occurs *via* O(2) of the deprotonated hydroxyl group and O(3) of the α-carboxylate and O(1) of a β-carboxylate group, thus forming a five- and

TABLE I Crystal data and structure refinement details for the title compound

Crystal data	
Molecular formula	$C_6H_{22}LiN_3O_{13}W$
Formula weight	535.06
Colour	colorless
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters	
a (Å)	6.9010(14)
b (Å)	15.136(3)
c (Å)	16.107(3)
α (°)	75.85(3)
β (°)	89.89(3)
γ (°)	89.97(3)
Volume (Å^3)	1631.4(6)
Z	4
Density (calculated) (g cm^{-3})	2.178
Radiation	Graphite-monochromatized MoKα, $\lambda = 0.71073$ Å
Absorption coefficient (mm^{-1})	7.151
Data collection	
Limiting indices	$-1 \le h \le 8$, $-1 \le k \le 17$, $-18 \le l \le 19$
θ(°)	1.66 to 25.01
Total reflection collected	4167
Independent reflections	3878 ($R_{int} = 5.47\%$)
F(000)	1040
Structure determination and refinement	
Weighting scheme	$w = [\sigma^2\|Fo\|^2 + (0.1213P)^2]^{-1}$ where $P = (\|Fo\|^2 + 2\|Fc\|^2)/3$
GOF	1.025
R [$I > 2\sigma(I)$]	0.069
R_w	0.170

TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_3[Li\ (H_2O)_3WO_3(C_6H_4O_7)]$

Atoms	*x/a*	*y/b*	*z/c*	*U*
W1	7969.2(13)	−3208.4(5)	11749.8(5)	22(1)
W2	2973(13)	3209.2(5)	3251.4(5)	22(1)
Li1	1763(71)	−824(18)	6707(22)	32(9)
Li2	6747(84)	805(32)	8274(21)	32(8)
O1	8115(28)	−4385(10)	11082(11)	38(4)
O2	6391(21)	−2741(10)	10673(8)	21(3)
O3	10107(23)	−2696(11)	10725(9)	30(4)
O4	8172(21)	−2190(10)	12001(9)	33(3)
O5	9933(28)	−3826(13)	12330(9)	36(4)
O6	5963(25)	−3754(11)	12325(9)	27(3)
O7	7547(26)	−5214(10)	10165(10)	32(5)
O8	10563(23)	−2255(10)	9317(9)	29(4)
O9	5720(24)	−395(9)	8665(10)	31(4)
O10	7946(28)	−828(11)	9687(11)	44(6)
O11	3123(26)	4369(9)	3918(11)	36(4)
O12	5061(21)	2705(10)	4282(8)	24(3)
O13	1475(22)	2757(9)	4327(8)	21(3)
O14	1002(30)	3743(13)	2676(10)	44(5)
O15	4923(25)	3839(12)	2687(9)	39(5)
O16	3035(28)	2162(10)	2976(11)	45(5)
O17	2602(23)	5213(9)	4842(9)	28(4)
O18	5517(26)	2235(11)	5699(10)	34(5)
O19	722(23)	408(9)	6345(9)	32(4)
O20	2979(27)	795(11)	5273(12)	43(5)
N1	−2922(30)	4575(12)	8473(12)	34(5)
N2	1865(28)	−293(13)	9161(11)	32(4)
N3	2182(28)	6556(11)	8291(11)	30(5)
N4	3067(31)	−293(12)	4208(11)	30(5)
N5	2948(27)	6527(10)	3313(10)	26(4)
N6	8022(35)	4553(13)	3485(13)	42(7)
C1	7644(31)	−4478(13)	10382(12)	22(4)
C2	7155(34)	−3641(12)	9654(11)	21(4)
C3	7317(35)	−2712(13)	9874(12)	21(5)
C4	6301(34)	−1994(15)	9185(13)	24(5)
C5	6702(30)	−994(15)	9198(11)	18(4)
C6	9426(32)	−2516(12)	9965(12)	19(5)
C7	2668(38)	4455(13)	4643(11)	24(4)
C8	4474(33)	2513(13)	5030(10)	18(4)
C9	2051(36)	3645(12)	5335(13)	27(5)
C10	2273(33)	2718(13)	5091(11)	18(4)
C11	1301(31)	1977(11)	5824(12)	17(4)
C12	1765(34)	982(13)	5779(14)	26(5)
OW1	6650(25)	1644(10)	9070(10)	37(5)
OW2	1685(26)	−1641(10)	5925(10)	45(5)
OW3	−98(26)	−1340(12)	7626(10)	42(6)
OW4	4463(24)	−850(11)	7147(10)	38(5)
OW5	9390(24)	865(10)	7865(11)	39(5)
OW6	4853(31)	1354(13)	7384(13)	55(6)

U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

six-membered ring, respectively, and completing the distorted octahedral coordination geometry of W^{VI}. The bond lengths of three tungsten–terminal oxygen bonds, W(1)—O(5) (1.78(2)Å), W(1)—O(6) (1.754(12)Å)

TABLE III Selected bondlengths (Å) and angles (°) for $(NH_4)_3[Li(H_2O)_3WO_3(C_6H_4O_7)]$

W(1)—O(4)	1.721(14)	W(1)—O(6)	1.755(13)
W(1)—O(5)	1.79(2)	W(1)—O(2)	2.026(14)
W(1)—O(3)	2.20(2)	W(1)—O(1)	2.30(2)
W(2)—O(14)	1.73(2)	W(2)—O(16)	1.75(2)
W(2)—O(15)	1.765(13)	W(2)—O(13)	1.991(12)
W(2)—O(12)	2.19(2)	W(2)—O(11)	2.28(2)
Li(1)—O(19)	1.94(4)	Li(1)—Ow3	1.95(4)
Li(1)—Ow2	1.98(4)	Li(1)—Ow4	2.00(4)
Li(2)—O(9)	1.91(3)	Li(2)—Ow5	1.94(5)
Li(2)—Ow6	1.97(5)	Li(2)—Ow1	2.00(4)
O(1)—C(1)	1.23(2)	O(2)—C(3)	1.42(2)
O(3)—C(6)	1.27(2)	O(7)—C(1)	1.24(2)
O(8)—C(6)	1.29(2)	O(9)—C(5)	1.28(3)
O(10)—C(5)	1.24(2)	O(11)—C(7)	1.24(2)
O(12)—C(8)	1.24(2)	O(13)—C(10)	1.34(2)
O(17)—C(7)	1.27(2)	O(18)—C(8)	1.27(2)
O(19)—C(12)	1.31(2)	O(20)—C(12)	1.25(3)
C(1)—C(2)	1.53(3)	C(2)—C(3)	1.55(2)
C(3)—C(6)	1.50(3)	C(3)—C(4)	1.52(3)
C(4)—C(5)	1.54(2)	C(7)—C(9)	1.50(2)
C(8)—C(10)	1.55(3)	C(9)—C(10)	1.56(3)
C(10)—C(11)	1.56(2)	C(11)—C(12)	1.55(3)
O(4)—W(1)—O(6)	105.0(7)	O(4)—W(1)—O(5)	102.2(7)
O(6)—W(1)—O(5)	101.9(7)	O(4)—W(1)—O(2)	96.1(6)
O(6)—W(1)—O(2)	92.8(6)	O(5)—W(1)—O(2)	152.5(7)
O(4)—W(1)—O(3)	88.2(6)	O(6)—W(1)—O(3)	162.7(6)
O(5)—W(1)—O(3)	85.6(6)	O(2)—W(1)—O(3)	74.5(5)
O(4)—W(1)—O(1)	165.5(6)	O(6)—W(1)—O(1)	88.0(6)
O(5)—W(1)—O(1)	80.8(7)	O(2)—W(1)—O(1)	76.6(6)
O(3)—W(1)—O(1)	77.8(6)		
O(14)—W(2)—O(16)	102.5(8)	O(14)—W(2)—O(15)	101.7(8)
O(16)—W(2)—O(15)	105.1(9)	O(14)—W(2)—O(13)	94.4(7)
O(16)—W(2)—O(13)	95.0(7)	O(15)—W(2)—O(13)	150.6(6)
O(14)—W(2)—O(12)	162.5(7)	O(16)—W(2)—O(12)	90.4(7)
O(15)—W(2)—O(12)	86.2(6)	O(13)—W(2)—O(12)	72.3(5)
O(14)—W(2)—O(11)	88.6(7)	O(16)—W(2)—O(11)	166.3(7)
O(15)—W(2)—O(11)	80.1(7)	O(13)—W(2)—O(11)	75.8(5)
O(12)—W(2)—O(11)	77.3(6)		
O(19)—Li(1)—Ow3	100(2)	O(9)—Li(2)—Ow5	114(2)
O(19)—Li(1)—Ow2	120(2)	O(9)—Li(2)—Ow6	101(2)
O(19)—Li(1)—Ow4	112(2)	O(9)—Li(2)—Ow1	119(2)
C(1)—O(1)—W(1)	134(2)	C(8)—O(12)—W(2)	119(2)
C(6)—O(3)—W(1)	115.4(13)	C(7)—O(11)—W(2)	134.7(11)
C(3)—O(2)—W(1)	117.1(14)	C(10)—O(13)—W(2)	121.1(11)
O(1)—C(1)—O(7)	125(2)	O(1)—C(1)—C(2)	121(2)
O(7)—C(1)—C(2)	114(2)	C(1)—C(2)—C(3)	115(2)
O(2)—C(3)—C(6)	108.5(14)	O(2)—C(3)—C(4)	108(2)
C(6)—C(3)—C(4)	113.2(14)	O(2)—C(3)—C(2)	110.3(13)
C(6)—C(3)—C(2)	108(2)	C(4)—C(3)—C(2)	108.2(14)
C(3)—C(4)—C(5)	116(2)	O(10)—C(5)—O(9)	125(2)
O(10)—C(5)—C(4)	119(2)	O(9)—C(5)—C(4)	116(2)
O(3)—C(6)—O(8)	121(2)	O(3)—C(6)—C(3)	116(2)
O(8)—C(6)—C(3)	123(2)	O(11)—C(7)—O(17)	124(2)
O(11)—C(7)—C(9)	121(2)	O(17)—C(7)—C(9)	115(2)
O(12)—C(8)—O(18)	126(2)	O(12)—C(8)—C(10)	112(2)
O(18)—C(8)—C(10)	122(2)	C(7)—C(9)—C(10)	114(2)

TABLE III (Continued)

O(13)—C(10)—C(8)	108(2)	O(13)—C(10)—C(9)	111(2)
C(8)—C(10)—C(9)	109(2)	O(13)—C(10)—C(11)	111.9(13)
C(8)—C(10)—C(11)	111(2)	C(9)—C(10)—C(11)	107(2)
C(12)—C(11)—C(10)	113(2)	O(20)—C(12)—C(19)	127(2)
O(20)—C(12)—C(11)	123(2)	O(19)—C(12)—C(11)	110(2)

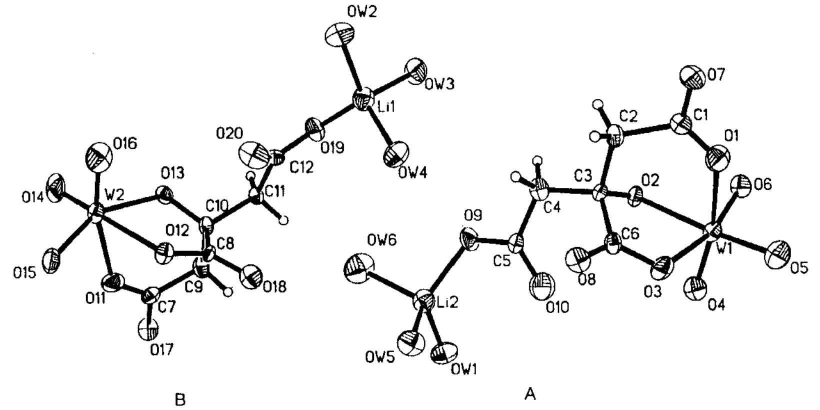

FIGURE 1 Perspective view of $[Li(H_2O)_3\,WO_3(C_6H_4O_7)]^{3-}$ (the anion of the title compound) showing the atom-labeling scheme.

and W(1)—O(4) (1.69(2)Å) being *trans* to O(2) (hydroxyl), O(3) (α-carboxyl) and O(1) (β-carboxyl), respectively, are different and this is probably due to different *trans* effects of carboxyl and hydroxyl groups. As observed for other complexes with O-donor ligands, single-bond W — O_{ligand} distances vary widely in **1** (from 1.99–2.30 Å) and this may be ascribed to the different donor nature and chelate effects of the coordinated oxygen atoms of the citrate ligand [13].

Three water molecules and the β-carboxyl group of a citrate ligand are coordinated to a lithium atom forming a distorted tetrahedron with Li(2)–O(9) bondlengths of 1.91(4) Å and Li(2)–Ow bondlengths of 1.93–2.02 Å.

An extensive network of hydrogen bonding (< 3.00 Å) in the lattice involves terminal oxygen, α-carboxyl oxygen, β-carboxyl oxygen atoms, coordinated water and NH_4^+ cations. The O···O distances range from 2.753 to 2.992 Å and N···O distances from 2.653 to 2.844 Å.

It is interesting to compare carbon–oxygen bondlengths of non-coordinated carboxyl groups and metal–oxygen bond lengths for some transition metal complexes with citrate ligands. From the comparison, the following preliminary conclusions may be drawn. The lengths of C — O and C=O bonds of non-coordinated carboxyl groups are similar (differences in

0.01 – 0.05 Å), displaying "average effects", when the carboxyl groups are deprotonated [9 – 11, 14, 17 – 19]. The two bond possess are obviously different (0.10 – 0.12 Å) when non-coordinated carboxyl groups are protonated [8, 20 – 22]. In molybdenum or tungsten citrato complexes the bondlength relation of different M — O single bonds is $M — O_{hydroxy} < M — O_{\alpha\text{-carboxy}} < M — O_{\beta\text{-carboxy}}$ [8 – 14, 17, 20], but no such pattern occurs in other transition metal complexes with citrate ligand [18, 19, 21, 22, 24]. $V — O_{hydroxy}$ bondlength of 2.206(2) Å in $Na_4[VO(C_6H_6O_7)]_2 \cdot 6H_2O$ [18], $V — O_{\alpha\text{-carboxy}}$ of 2.303(5) Å in $(Hneo)_3[(VO)_2(C_6H_4O_7)(C_6H_5O_7)] \cdot 4H_2O$ [21] and $V — O_{\beta\text{-carboxy}}$ of 2.561(1) Å in $K_2[VO(O_2)(C_6H_6O_7)]_2 \cdot 2H_2O$ [20] are much longer than corresponding bonds in other complexes. The reason for this may be that the abovementioned M—O bonds are all *trans* to a terminal oxygen atom possessing stronger *trans* effect. A citrate may adopt different coordination modes in different transition metal complexes. For example, in dinuclear complexes of molybdenum or tungsten each citrate ligand usually coordinates to only one transition metal atom [8 – 15], but each citrate coordinates two metal atoms in dinuclear complexes of other transition metals [18, 20, 21, 23 – 25].

Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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