Inorganica Chimica Acta 391 (2012) 224–228

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Note

Hydrogen bonding-controlled assemblies of polymeric and octanuclear tungsten citrates

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ARTICLE INFO

Article history:
Received 2 November 2010
Received in revised form 1 March 2012
Accepted 18 April 2012
Available online 28 April 2012

Keywords:
Tungsten
Citric acid
NMR
Hydrogen bond
Crystal structure

ABSTRACT

Water-soluble polymeric tungsten citrate $(Him)_{10n}(NH_4)_{2n}[(WO_2)_2O(Hcit)_2]_{3n}\cdot 10nH_2O$ (**1**) and octanuclear tungsten citrate $(Him)_8(NH_4)_{13}\{[(WO_2)_2O(Hcit)(cit)H(cit)(Hcit)O(WO_2)_2][(WO_2)_2O(cit)_2]_2\}\cdot 14H_2O$ (**2**) (H_4cit = citric acid, im = imidazole), were obtained from aqueous solution. They were characterized by elemental analyses, NMR and IR spectra, thermogravimetric (TG) analyses and X-ray structural analyses. The basic units of the two complexes contain a dimeric tungsten citrate in different protonated forms, where tungsten atom is six-coordinated in an approximately octahedral geometry. Each citrate ligand uses its α-alkoxy, α-carboxy and one β-carboxy group to act as a tridentate ligand, while the other β-carboxy or carboxylic acid group is uncoordinated. The presences of the protonated/deprotonated terminal carboxylates and their participation in hydrogen-bonding interactions play an important role in the overall structures. In complex **1**, a hexanuclear tungsten citrate species $[(WO_2)_2O(Hcit)_2]_3^{12-}$ is linked by strong H-bonding between β-carboxylic acid group and terminal oxygen [2.587(6) Å], which extends into one-dimensional polymeric chain. In complex **2**, there exist two types of strong hydrogen bonds between β-carboxy and carboxylic acid groups [2.467(8), 2.516(6) Å], forming an octanuclear species $\{[(WO_2)_2O(Hcit)(cit)H(cit)(Hcit)O(WO_2)_2][(WO_2)_2O(cit)_2]_2\}^{21-}$. This is supported by the absence of IR band around 1700 cm^{-1} for protonated carboxylic acid. ^{13}C NMR spectra show the coordination of α-alkoxy and α-carboxy groups of citrate ligand in both complexes.

1. Introduction

Tungstates are a class of important inorganic materials owing to their potential applications in photoluminescence, optical fibers, scintillator materials, humidity sensors, catalysts, and so on [1,2]. Citric acid, an α-hydroxytricarboxylic acid, has been widely known for its abundance in physiological fluids and its chemical versatility toward transition metal ions. The citrate method as modified Pechini process was used for the synthesis of tungsten oxides [3–8]. Citrate was also used in electrodeposition of tungsten alloys [9,10]. The diverse coordination modes of citrate contribute largely to the formation of various structural types for transition metal citrates, such as mononuclear, dinuclear and polynuclear structural units [11–17].

The solution coordination chemistry of tungsten(VI) with citric acid has been previously investigated [18–25]. Cervilla et al. concluded that two dimeric complexes with a tungstate:citrate ratio of 2:2 exist in solution [22]. The structurally characterized dimeric tungsten citrate complexes [tungsten(VI) to citrate ratio of 2:2] reported hitherto are $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$, $K_6[W_2O_5(cit)_2]\cdot 5H_2O$, $Na_4K_2[W_2O_5(cit)_2]\cdot 11H_2O$, and $NaK_3[W_2O_5(Hcit)_2]\cdot 4H_2O$ [26–30]. In this paper, we reported the syntheses, spectroscopic properties and crystal structures of two new tungsten citrates $(Him)_{10n}(NH_4)_{2n}[(WO_2)_2O(Hcit)_2]_{3n}\cdot 10nH_2O$ (**1**) and $(Him)_8(NH_4)_{13}\{[(WO_2)_2O(Hcit)(cit)H(cit)(Hcit)O(WO_2)_2][(WO_2)_2O(cit)_2]_2\cdot 14H_2O$ (**2**) (H_4cit = citric acid, im = imidazole).

2. Experimental

2.1. Materials and general methods

The pH value was measured with the potentiometric method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 200 FT-IR spectrometer. Elemental analyses were performed using Vario EL III elemental analyzer. NMR spectra were recorded on a Bruker Avance II spectrometer (400 MHz) using sodium-2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal reference. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1 instrument under flowing N_2 with a heating rate of 10 °C/min^{-1}.

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http://dx.doi.org/10.1016/j.ica.2012.04.025

2.2. Preparation of $(Him)_{10n}(NH_4)_{2n}[(WO_2)_2O(Hcit)_2]_{3n}\cdot 10nH_2O$ (**1**)

Citric acid (0.63 g, 3.0 mmol) and imidazole (0.20 g, 3.0 mmol) were added to a stirred solution of ammonium tungstate $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ (0.80 g, 0.50 mmol) in water (25 mL). The pH of the solution was adjusted to 3.8 with dilute ammonium hydroxide. The mixture was heated in a water bath at 70 °C for 8 days. The mixture was cooled to room temperature and left standing for several weeks. Colorless crystals obtained are suitable for X-ray diffraction. The product **1** was isolated by filtration and dried in air. Yield: 0.42 g (25%). IR (KBr, cm^{-1}): ν = 1726(s), 1620(vs), 1400(s), 1223(m), 1186(m), 1086(m), 920(s), 855(s), 745(s), 681(m), 633(m), 598(s), 559(m), 537(m); *Anal.* Calc. for $C_{66}H_{108}N_{22}O_{67}W_6$: C, 23.42; H, 3.22; N, 9.10. Found: C, 23.84; H, 3.12; N, 9.05%. ^{1}H NMR (400 MHz, D_2O, 25 °C, DSS): δ = 8.77 (s, 10H; CH=N, im), 7.50 (s, 20H; CH=CH, im), 2.75 (q_{AB}, J = 17 Hz, 24H; CH_2); ^{13}C NMR (100 MHz, D_2O, 25 °C, DSS): δ = 187.9, 178.3, 136.4, 121.7, 86.7, 45.9 ppm.

2.3. Preparation of $(Him)_8(NH_4)_{13}\{[(WO_2)_2O(Hcit)(cit)H(cit)(Hcit)O(WO_2)_2][(WO_2)_2O(cit)_2]_2\cdot 14H_2O$ (**2**)

The synthesis of **2** was similar to that of **1**, except that the pH of the reaction mixture was 5.5. Colorless crystals were obtained. Yield: 0.44 g (27 %). IR (KBr, cm^{-1}): ν = 1591(vs), 1564(vs), 1405(vs), 1305(m), 1083(m), 952(m), 918(s), 872(vs), 794(s), 691(m), 632(m), 609(m), 559(m); *Anal.* Calc. for $C_{72}H_{155}N_{29}O_{90}W_8$: C, 19.94; H, 3.60; N, 9.36. Found: C, 19.51; H, 3.67; N, 9.01%. ^{1}H NMR (400 MHz, D_2O, 25 °C, DSS): δ = 8.78 (s, 8H; CH=N, im), 7.50 (s, 16H; CH=CH, im), 2.68 (q_{AB}, J = 17 Hz, 32H; CH_2); ^{13}C NMR (100 MHz, D_2O, 25 °C, DSS): δ = 188.6, 179.9, 136.4, 121.6, 87.6, 47.0 ppm.

2.4. X-ray crystallography

Data collections of **1** and **2** were performed on an Oxford Gemini S Ultra system with Mo Kα radiation (λ = 0.71073 Å) at 296 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by WinGX package [31] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms using SHELXL-97 [32]. Hydrogen atoms, except the disordered water and ammonium molecules (O1w–O5w, N11 of **1**) and the uncoordinated β-carboxy groups of **1** (O7, O17, O27), were included and located from difference Fourier map but not refined anistropically. Crystal data collections and refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in the Supporting information (see Tables S1 and S2).

2.5. Solution NMR

The samples for solution NMR studies were prepared by dissolving the crystalline complexes in D_2O, at concentrations in the range 0.05–0.10 M. NMR spectra were recorded on a Bruker Avance II spectrometer. In order to obtain a clear picture, ^{13}C NMR spectra of the two complexes were recorded at about 10 h. Chemical shifts are reported in ppm relative to an internal reference of DSS.

3. Results and discussion

3.1. Syntheses

The syntheses of **1** and **2** were carried out in aqueous solutions. The synthetic conditions for **1** and **2** are similar except for the different pH values. When a pH value between 3.2 and 4.0 was maintained, the solutions containing W(VI) ions, citric acid, and imidazole with a molar ratio of 1:1:1 deposited **1**. In contrast, control of pH value between 5.0 and 6.0 yielded **2**. The reaction shows that the pH value plays a key role in the formation of **1** and **2**. It is noted that imidazole is not coordinated to W(VI) ion, only acting as cations with a protonated form.

3.2. Structure descriptions

In the crystal structure of **1**, the basic structure of dimeric unit $[(WO_2)_2O(Hcit)_2]^{4-}$ (Fig. S1) is similar to that of the anion in $K_3Na[(WO_2)_2O(Hcit)_2]\cdot 4H_2O$ [30]. Each W(VI) ion is six-coordinated with approximately octahedral geometry, which is surrounded by three oxygen atoms from α-hydroxy, α-carboxy and β-carboxy groups of citrate, two terminal oxo groups in a *cis*-configuration and one bridging oxo group. Two W(VI) ions are connected by the bridging oxo group to form a dimeric unit $[(WO_2)_2O(Hcit)_2]^{4-}$. Furthermore, the other β-carboxy group of each citrate is uncoordinated and protonated, and participates in hydrogen-bonding interactions. It is noted that, in these discrete dimeric units all of the bound citrates in each central metal ion possess the same deprotonation state. Each β-carboxylic acid group of the bound citrates in central metal ions W3 and W3a is linked to the coordinated terminal oxo group of an adjacent dimeric unit $[(WO_2)_2O(Hcit)_2]^{4-}$ by strong hydrogen bonds [O27···O8 and O27a···O8a 2.587(6) Å], forming an assembly of a hexanuclear species $[(WO_2)_2O(Hcit)_2]_3^{12-}$ (Fig. 1). The hexanuclear species are further connected through hydrogen-bonding interactions [O7···O25 2.660(6) Å and O17···O29 2.758(6) Å] to form 1D polymeric chain (Fig. 1). In the case of tungsten citrate complex $K_3Na[(WO_2)_2O(Hcit)_2]\cdot 4H_2O$ [30] reported previously, the free β-carboxylic acid groups in the dinuclear complex form strong hydrogen bonds with coordinated β-carboxy groups [O7···O5 2.530(7) Å, O16···O15 2.586(8) Å], which is different from that of hydrogen bonds in **1**. The W–O distances in **1** vary systematically according to its bond type. W=O is in the range 1.712(4)–1.748(4) Å, indicating that they are double bonds. The W–O distances in W–O–W bridges range from 1.894(2) to 1.904(3) Å. The W–O (α-alkoxy) distances vary

Table 1
Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{66}H_{108}N_{22}O_{67}W_6$	$C_{72}H_{155}N_{29}O_{90}W_8$
Formula weight	3384.84	4338.05
Crystal color		colorless
Crystal size (mm)	0.35 × 0.10 × 0.08	0.38 × 0.25 × 0.20
Crystal system	monoclinic	triclinic
Cell constants		
a (Å)	30.1474(7)	13.6607(3)
b (Å)	17.7030(5)	13.8904(4)
c (Å)	19.9701(3)	20.0333(6)
α (°)		106.524(2)
β (°)	92.278(2)	97.523(2)
γ (°)		110.994(2)
V (Å^3)	10649.6(4)	3285.3(2)
Space group	$C\,2/c$	$P\,\bar{1}$
Formula units/unit cell	4	1
D_{calc} (g cm^{-3})	2.111	2.193
F(000)	6552	2102
Reflections collected/unique/R_{int}	34060/10413/0.0459	32101/12678/0.0287
Data/restraints/parameters	10413/0/726	12678/92/1030
θ range (°)	2.33–26.00	2.20–26.00
Goodness-of-fit (GOF) on F^2	0.950	1.080
R_1, wR_2 [$I > 2\sigma(I)$]	0.0290, 0.0576	0.0274, 0.0633
R_1, wR_2(all data)	0.0526, 0.0638	0.0451, 0.0709
Largest difference in peak and hole (e Å^{-3})	1.962, −0.942	1.814, −0.969