



Pamoic acid in forming metallo-organic framework: Synthesis, characterization and first crystal structure of a dimeric Ti(IV) complex

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ARTICLE INFO

Article history:

Received 9 May 2009

Accepted 28 July 2009

Available online 6 August 2009

Keywords:

4,4'-Methylene-bis(3-hydroxy-2-naphthalene carboxylic acid)
Dimeric Ti(IV) complex
Octahedral Ti(IV) center
Helical structure

ABSTRACT

Two novel dinuclear Ti(IV) complexes of the ligand, 4,4'-methylene-bis(3-hydroxy-2-naphthalene carboxylic acid) (H_4L) or pamoic acid having compositions, $[(HL)_2Ti_2(\mu-O)(DMF)_2] \cdot (DMF)_6$ (**1**) and $[(L)_2Ti_2(\mu-O)(DMF)_2] \cdot (DMF)_4(4,4'-Bipy-2H)(H_2O)$, (**2**) have been synthesized and characterized by analytical and spectral methods and the structure has been established by single crystal XRD. Unlike the reported polymeric structures observed in case of H_4L or pamoic acid, the anti-conformation of H_4L changes to syn - orientation to avoid poly-metallic complex formation, as noticed in **1** and **2**. The dimeric Ti(IV) units stack in the lattice to form helical columns and the space between the adjacent columns is being filled by the solvent molecules in **1** and solvent plus the protonated 4,4'-bipy in the lattice of **2** and thus the neighbor columns are connected through weak interactions.

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1. Introduction

Pamoic acid {4,4'-methylene-bis(3-hydroxy-2-naphthalene carboxylic acid)}, H_4L is having flexible molecular backbone bridged by methylene group wherein in it can easily form polymeric complexes owing to the *anti-like* orientation of the binding groups present on both the naphthyl moieties [1]. A series of metal ion complexes of pamoic acid have been reported for Mn(II), Cu(II), Zn(II) and Cd(II) wherein the complexes were crystallized using pyridyl rich co-ligands, viz., 2,2'-bipyridyl, 4,4'-bipyridyl and 1,10-phenanthroline to result in 1-D, 2-D or 3-D co-ordination networks [2–13]. To our knowledge, monomeric and dimeric complexes involving directly the pamoic acid were not reported in the literature, though it would be of great interest and importance to the development of the co-ordination chemistry of such molecular systems. Therefore, the present paper deals with the dinuclear Ti(IV) complexes of pamoic acid and the structural influence of a co-ligand, 4,4'-bipyridyl on this complex.

2. Experimental

2.1. General

All the solvents were purified and dried before use by standard procedures. FTIR spectra were recorded on an Impact 400 Nicolet machine in KBr matrix. C, H and N analysis were performed on a Carlo Erba 1106 elemental analyzer. The 1H and ^{13}C NMR spectra

were recorded on a Varian 400S spectrometer in DMSO- d_6 . UV-Vis spectra were obtained on a Shimadzu UV-260 or UV-2101PC spectrophotometer. The fluorescence emission spectra were recorded on a Perkin Elmer LS 55 spectrofluorimeter.

2.2. 4,4'-Methylene-bis(3-hydroxy-2-naphthalene carboxylic acid), H_4L

H_4L has been synthesized in a single step as reported in the literature [14]. 3-Hydroxy-2-naphthoic acid (5 g, 26 mmol) and formaldehyde (25 mL) were refluxed together with the required quantities of glacial acetic acid (40 mL) and sulfuric acid catalyst. After 2 h, the product was cooled, filtered under vacuum, and washed several times with cold water, then with ethyl alcohol to remove any traces of unreacted 3-hydroxy-2-naphthoic acid, and finally with water. It was dried at 100 °C to constant weight. Yield: 80%. M.p. 280–290 °C. *Anal.* Calc. for $C_{23}H_{16}O_6$ (388): C, 71.13; H, 4.15. Found: C, 71.82; H, 4.36%. Selected IR (KBr, cm^{-1}): 3281(s), 3054(s), 1658(s), 1601(s), 1502(s), 1455(w), 1431(w), 1295(s). 1H NMR (DMSO- d_6 , δ ppm): 12.18 (s, 2H, COOH), 8.49 (s, 2H, naph-H), 8.13 (d, 2H, naph-H, J = 8.98 Hz), 7.89 (d, 2H, naph-H, J = 7.94 Hz), 7.38 (m, 2H, naph-H), 7.24 (m, 2H, naph-H), 4.79 (s, 2H, Ar-CH₂-Ar). ^{13}C NMR (CDCl₃, δ ppm): 20.08 (Ar-CH₂-Ar), 114.12, 120.74, 123.44, 126.83, 128.94, 130.23, 131.62, 136.322, 153.54, 172.73. (Nap-C). ESI MS: m/z (%), 411 (100, $[M + Na]^+$). Absorption spectral data for H_4L in MeOH in terms of λ_{max}/nm ($\epsilon/lit\ mol^{-1}\ cm^{-1}$): 249 (33 900), 278 (13 940), 289 (17 100), 299 (12 900), 375 (10 300). Fluorescence (λ_{ex} = 370 nm, DMSO/methanol): 520 nm. Single crystals of H_4L were obtained from a solution made for measuring NMR spectra in DMSO- d_6 in a 5 mm tube.

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2.3. Dinuclear Ti(IV) complex **1**

H₄L (0.388 g, 1.0 mmol) was dissolved in 10 mL N,N-dimethylformamide (DMF). To this clear solution *cis*-bis(acetylacetonato)dichloro-titanium(IV), *cis*-[Ti(acac)₂Cl₂], (0.316 g, 1 mmol) dissolved in 20 mL DMF was slowly added. The color of the solution changed from yellow to orange. The solution was filtered and kept in refrigerator. After 10–15 days the orange colored crystals start separating from the solution. Yield, 57%. M.p: >300 °C (decomp.). *Anal.* Calc. for C₇₀H₈₂N₈O₂₁Ti₂: C, 57.30; H, 5.63; N, 7.64. Found: C, 56.80; H, 5.81; N, 7.53%. Selected IR (KBr, cm⁻¹): 3437(s), 3414(s), 1654(s), 1598(s), 1495(w), 1361(s). ¹H NMR (DMSO-d₆, δ ppm): 8.52 (d, 2H, naph-H), 8.40 (d, 2H, naph-H), 8.14 (d, 2H, naph-H), 7.77 (d, 2H, naph-H), 7.62 (t, 2H, naph-H), 7.52 (d, 2H, naph-H), 7.34 (t, 2H, naph-H), 7.49 (d, 2H, naph-H), 7.01 (t, 2H, naph-H), 6.99 (t, 2H, naph-H), 5.02, 4.79 (s, 4H, Ar-CH₂-Ar). ¹³C NMR (CDCl₃, δ ppm): 22.169 (Ar-CH₂-Ar), 119.63, 120.55, 121.067, 122.91, 123.28, 124.082, 126.61, 127.40, 128.86, 129.76, 130.78, 131.27, 134.93, 135.52, 159.53, 170.00, 170.93 (Nap-C), 34.47, 35.87, 160.43, 162.77 (DMF-C). Absorption spectral data for **1** in MeOH in terms of λ_{max}/nm (ε/lit mol⁻¹ cm⁻¹): 247 (49 690), 263 (44 040), 294 (30 510), 377 (17 800). Single crystals of **1** were obtained from slow evaporation of DMF solution at room temperature.

2.4. Dinuclear Ti(IV) complex **2**

H₄L, 4,4'-methylene-bis(3-hydroxy-2-naphthalene carboxylic acid) (0.388 g, 1.0 mmol) was dissolved in 10 mL DMF. To this clear solution *cis*-bis(acetylacetonato)dichloro-titanium(IV), *cis*-[Ti(acac)₂Cl₂], (0.316 g, 1 mmol) dissolved in 10 mL DMF was slowly added and the color of the solution changed from yellow to orange. After 1 h of stirring, 4,4'-bipyridine (0.156 g, 1.0 mmol) was added to the reaction mixture and the resulting solution was stirred for 6 h. The solution was then filtered and kept at room temperature. After 10–15 days the orange colored crystals start were obtained from the solution. Yield, 52%. M.p: >300 °C. *Anal.* Calc. for

C₆₉H₇₃N₇O₂₀Ti₂: C, 58.52; H, 5.20; N, 6.92. Found: C, 58.31; H, 5.19; N, 6.19%. Selected IR (KBr, cm⁻¹): 3435(s), 3043 (s), 1621 (s), 1593(s), 1572(w), 1552(w), 1451(w), 1421(s). ¹H NMR (DMSO-d₆, δ ppm): 8.79 (d, 4H, 4,4'-BiPy-H), 8.52 (d, 2H, naph-H), 8.40 (d, 2H, naph-H), 8.14 (d, 2H, naph-H), 7.89 (d, 4H, 4,4'-BiPy-H), 7.77 (d, 2H, naph-H), 7.62 (t, 2H, naph-H), 7.52 (d, 2H, naph-H), 7.46 (d, 2H, naph-H), 7.34 (t, 2H, naph-H), 7.01 (t, 2H, naph-H), 6.99 (t, 2H, naph-H), 5.02, 4.79 (s, 4H, Ar-CH₂-Ar). ¹³C NMR (CDCl₃, δ ppm): 22.92 (Ar-CH₂-Ar), 119.63, 120.55, 121.07, 122.91, 123.28, 124.08, 126.61, 127.40, 128.86, 129.76, 130.78, 131.27, 134.93, 135.52, 158.83, 159.53, 170.00, 170.93 (Nap-C and 4,4'-bipyridine-C), 34.47, 35.87, 160.43, 162.77 (DMF-C). Absorption spectral data for **2** in MeOH in terms of λ_{max}/nm (ε/lit mol⁻¹ cm⁻¹): 251(49 540), 264 (46 480), 278 (44 900), 375 (21 690). Single crystals of **2** were obtained by slow evaporation of DMF solution at room temperature.

2.5. Crystallography

Single crystal X-ray diffraction data were collected for H₄L, **1** and **2** on an OXFORD DIFFRACTION XCALIBUR-S CCD system by ω-2θ scan mode and the absorption corrections were applied by using multi-scan method. Preliminary data corresponding to the data collection and refinement are given in Table 1. The structure was solved by direct methods SHELXS97 and refined by full-matrix least squares against F² using SHELXL97 software [15]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

3. Results and discussions

3.1. Structure of H₄L

The ligand, H₄L has been synthesized starting from 3-hydroxy-2-naphthoic acid in a single step as reported in the literature [14]

Table 1
Crystal data and structure determination data for H₄L, **1** and **2**.

	H ₄ L	1	2
CCDC deposit number	711046	710613	710614
Molecular formula	C ₂₃ H ₁₆ O ₆ H ₄ L	C ₇₀ H ₈₂ N ₈ O ₂₁ Ti ₂ [(HL) ₂ Ti ₂ (μ-O) (DMF) ₂] (DMF) ₆	C ₆₉ H ₇₃ N ₇ O ₂₀ Ti ₂ (L) ₂ Ti ₂ (μO)(DMF) ₂ (DMF) ₄ (4,4'-bipy-2H)(H ₂ O)
MW	388.36	1467.24	1416.14
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$
Z	4	2	2
a (Å)	19.7083(7)	15.4330(16)	15.4892(6)
b (Å)	4.7561(2)	15.820(2)	16.5524(6)
c (Å)	19.0796(7)	17.028(2)	16.8884(7)
α (°)	90	109.524(13)	103.298(3)
β (°)	109.022(4)	107.073(10)	105.685(4)
γ (°)	90	101.910(10)	116.435(4)
V (Å ³)	1690.76(11)	3525.3(8)	3410.6(2)
ρ _{calc} (g cm ⁻³)	1.526	1.382	1.379
Absorption coefficient (mm ⁻¹)	0.111	0.307	0.314
T (K)	120(2) K	150(2)	150(2) K
λ (Å)	0.71073	0.71073	0.71073
F (0 0 0)	808	1540	1480
Goodness of fit (GOF) (F ²)	1.075	1.096	0.936
Reflections collected/unique	5630/1485 [R _{int} = 0.0247]	33676/12301 [R _{int} = 0.0396]	26698/11891 [R _{int} = 0.0534]
Data/restraints/parameter	1485/0/140	12301/0/954	11891/0/915
R ₁ , wR ₂ [I > 2σ(I)]	0.0315, 0.0780	0.0829, 0.2265	0.0532, 0.1217
R ₁ , wR ₂ (all data)	0.0490, 0.0841	0.1054, 0.2381	0.1043, 0.1354
GOF	1.075	1.096	0.936
Largest difference in peak/hole (e Å ⁻³)	0.126 and -0.186	2.268 and -0.638	1.344 and -0.372

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