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The crystal structure of 1,1'-(((2 (dimethylamino) ethyl)azanediyl)bis(methylene)) bis(naphthalen-2-olato- $\kappa^4 N, N', O, O'$)-(pyridine-2,6-dicarboxylato- N, O, O')- titanium(IV) – dichloromethane (2/1), $C_{33}H_{29}N_3O_6Ti$

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Abstract

$C_{33}H_{29}N_3O_6Ti$, monoclinic, $C2/c$ (no. 15), $a = 27.4022(15)$ Å, $b = 14.0345(7)$ Å, $c = 17.0047(10)$ Å, $\beta = 116.009(3)^\circ$, $V = 5877.3(6)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0369$, $wR_{ref}(F^2) = 0.1125$, $T = 100(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.12 × 0.10 × 0.10 mm
Wavelength:	Ga K α radiation (1.34138 Å)
μ :	2.51 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	57.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	38312, 6027, 0.052
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5177
$N(param)_{refined}$:	418
Programs:	Bruker [1], SHELX [2]

CCDC no.: 2082174

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ONON ligand L_1 : (1,1'-(((2-(dimethyl-amino)ethyl)azanediyl)bis(methylene))bis(naphthalen-2-ol)) was prepared following the literature reported method by prolonging the reaction time from 2 to 6 h [3]. The corresponding Ti(IV) complex was synthesized according to lit. Under a nitrogen atmosphere, L_1 (1 mmol, 400 mg) was dissolved in anhydrous THF (15 mL), $Ti(O^iPr)_4$ (0.95 mmol, 0.28 mL) was then added to the solution. The reaction was heated to 50 °C and kept stirring for 2 h, Dipic (pyridine-2,6-dicarboxylic acid) (0.95 mmol, 158.8 mg) was added and the reaction was left stirring for another 10 h and monitored by TLC. When the reaction was complete, $[L_1Ti^{(IV)}(Dipic)]$ was separated by flash column chromatography ($CH_2Cl_2/CH_3OH = 30/1$) to obtain a red solid (0.80 mmol, 492.1 mg, 85%). Suitable crystals for X-ray diffraction measurements were obtained by slow diffusion of n -hexane to a dichloromethane solution of $[L_1Ti^{(IV)}(Dipic)]$ at room temperature.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C1	0.60189 (7)	0.50113 (13)	0.58013 (12)	0.0233 (4)
C2	0.58945 (7)	0.51514 (13)	0.64972 (12)	0.0216 (4)
C3	0.54729 (7)	0.46373 (14)	0.65755 (13)	0.0257 (4)
H3	0.539570	0.474178	0.706156	0.031*
C4	0.51786 (7)	0.39903 (14)	0.59457 (13)	0.0285 (4)
H4	0.489233	0.365464	0.599549	0.034*
C5	0.52879 (7)	0.38076 (14)	0.52254 (13)	0.0274 (4)
C6	0.57149 (7)	0.43256 (14)	0.51411 (13)	0.0255 (4)
C7	0.58010 (7)	0.41355 (15)	0.43924 (14)	0.0315 (5)
H7	0.607797	0.447275	0.431655	0.038*
C8	0.54954 (8)	0.34773 (16)	0.37731 (15)	0.0379 (5)
H8	0.555907	0.337312	0.327385	0.046*
C9	0.50878 (8)	0.29568 (16)	0.38777 (16)	0.0397 (6)
H9	0.488380	0.248968	0.345741	0.048*
C10	0.49865 (8)	0.31234 (14)	0.45804 (15)	0.0352 (5)
H10	0.470790	0.277395	0.464063	0.042*
C11	0.64373 (7)	0.56345 (14)	0.57011 (12)	0.0231 (4)
H11A	0.651376	0.536388	0.522901	0.028*
H11B	0.627497	0.627221	0.550497	0.028*
C12	0.72841 (7)	0.64323 (13)	0.62014 (11)	0.0203 (4)
H12A	0.707714	0.703407	0.600574	0.024*
H12B	0.731116	0.614728	0.568945	0.024*
C13	0.78488 (7)	0.66628 (12)	0.68869 (12)	0.0185 (4)
C14	0.79433 (7)	0.68331 (12)	0.77415 (12)	0.0185 (4)
C15	0.84694 (7)	0.70365 (13)	0.84046 (12)	0.0215 (4)
H15	0.852252	0.714900	0.898766	0.026*
C16	0.88981 (7)	0.70705 (14)	0.82051 (13)	0.0254 (4)
H16	0.925271	0.718108	0.865577	0.030*
C17	0.88219 (7)	0.69428 (13)	0.73334 (12)	0.0233 (4)
C18	0.82922 (7)	0.67450 (12)	0.66575 (12)	0.0186 (4)
C19	0.82341 (7)	0.66746 (13)	0.57918 (12)	0.0225 (4)
H19	0.788488	0.655293	0.533004	0.027*
C20	0.86674 (8)	0.67768 (14)	0.55999 (13)	0.0266 (4)
H20	0.861538	0.672721	0.501104	0.032*
C21	0.91865 (8)	0.69541 (16)	0.62681 (14)	0.0347 (5)
H21	0.948694	0.701718	0.613397	0.042*
C22	0.92602 (8)	0.70360 (16)	0.71120 (14)	0.0337 (5)
H22	0.961378	0.715836	0.756097	0.040*
C23	0.72777 (7)	0.48444 (13)	0.67352 (13)	0.0241 (4)
H23A	0.767214	0.497935	0.702948	0.029*
H23B	0.720080	0.448072	0.619458	0.029*
C24	0.71249 (7)	0.42561 (13)	0.73265 (13)	0.0262 (4)
H24A	0.674471	0.403672	0.700276	0.031*
H24B	0.736164	0.368694	0.752106	0.031*
C25	0.77619 (7)	0.48459 (14)	0.87507 (13)	0.0281 (4)
H25A	0.789033	0.419579	0.893957	0.042*
H25B	0.779958	0.522532	0.925811	0.042*
H25C	0.797847	0.513437	0.848288	0.042*
C26	0.68845 (8)	0.42931 (14)	0.85141 (14)	0.0306 (4)
H26A	0.649620	0.428229	0.811402	0.046*
H26B	0.693933	0.461093	0.905982	0.046*
H26C	0.702170	0.363861	0.864108	0.046*
C27	0.66641 (7)	0.77403 (13)	0.89390 (11)	0.0197 (4)
C28	0.65133 (8)	0.85380 (14)	0.92549 (13)	0.0274 (4)
H28	0.658098	0.857718	0.985179	0.033*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C29	0.62611 (9)	0.92803 (14)	0.86822 (14)	0.0316 (5)
H29	0.615201	0.983574	0.888247	0.038*
C30	0.61690 (8)	0.92068 (14)	0.78133 (13)	0.0266 (4)
H30	0.599543	0.970676	0.741017	0.032*
C31	0.63362 (7)	0.83877 (13)	0.75503 (12)	0.0195 (4)
C32	0.69347 (7)	0.68601 (13)	0.94366 (12)	0.0205 (4)
C33	0.62923 (7)	0.81744 (13)	0.66596 (12)	0.0216 (4)
N1	0.69711 (5)	0.57630 (10)	0.65008 (10)	0.0192 (3)
N2	0.71818 (6)	0.48192 (11)	0.81012 (10)	0.0225 (3)
N3	0.65750 (5)	0.76734 (10)	0.81067 (9)	0.0169 (3)
O1	0.61798 (5)	0.57717 (9)	0.71411 (8)	0.0217 (3)
O2	0.75358 (5)	0.68096 (9)	0.79766 (8)	0.0197 (3)
O3	0.69884 (5)	0.62172 (9)	0.89296 (8)	0.0218 (3)
O4	0.70781 (5)	0.67830 (10)	1.02224 (8)	0.0276 (3)
O5	0.65263 (5)	0.73842 (9)	0.66427 (8)	0.0236 (3)
O6	0.60584 (6)	0.87121 (10)	0.60429 (9)	0.0353 (4)
Ti1	0.68385 (2)	0.63935 (2)	0.76620 (2)	0.01642 (11)
C15 ^a	0.51005 (19)	0.0260 (3)	0.5073 (4)	0.0388 (11)
H15A ^a	0.494042	0.090634	0.497869	0.047*
H15B ^a	0.548342	0.030660	0.551686	0.047*
Cl1 ^a	0.47435 (7)	−0.04917 (14)	0.54657 (14)	0.0779 (5)
Cl2 ^a	0.50780 (5)	−0.01697 (13)	0.40881 (9)	0.0598 (4)

^aOccupancy: 0.5.

Experimental details

H atoms bonded to C atoms were positioned geometrically with C–H = 0.95 Å (aromatic), 0.99 Å (methylene) and 0.98 Å (methyl) and refined in a riding mode [$U_{iso}(H) = 1.2U_{eq}C$ (aromatic and methylene)], $1.5U_{eq}C$ (methyl).

Comment

Various ONNO ligands stabilizing Ti(IV) complexes containing different substituents have been synthesized and tested for antitumor activities in recent years [4]. The use of pyridine-2,6-dicarboxylate as a second chelator gives a novel heptacoordinated Ti(IV) complex with enhanced aqueous stability and cytotoxicity [5, 6], which is considered as a new generation of anti-tumor Ti complexes [7]. The isotopic titanium complex $[45Ti]([Salan]Ti^{(IV)}(Dipic))$ could be synthesized based on this ligand system and studied as PET probes [8, 9]. ONNO Ti(IV) complexes are structurally close to ONON Ti(IV) complexes, which exhibit much higher space flexibility because of the amino side arm [10]. However, only one report is related to the ONON Ti(IV) complex due to the difficult synthesis of ligands [10], no reports are found on the ONON Ti(IV) complexes containing a naphthalene moiety.

As shown in the Figure, the central Ti cation is seven-coordinated by three nitrogen atoms and four oxygen atoms, forming a distorted pentagonal bipyramidal geometry. The bond lengths of four Ti–O and three Ti–N bonds are ranging from 1.8390(12) to 2.0902(13) Å and from 2.1906(14) to 2.3891(15) Å, respectively, which is in accordance with the literature [7]. Surprisingly, the Mannich reaction of naphthalen-2-ol gave a rearranged ONON ligand L_1 , thus giving the titled ONON–Ti(IV) compound. The CH_2Cl_2 is disordered by an inversion center.

In the crystal packing, the molecules are linked together by some weak intermolecular interactions such as $\pi \cdots \pi$ and $C-H \cdots \pi$. For instance, the centroid-to-centroid distance between two inversion-related C1–C6 aromatic rings is only 3.596(1) Å, indicating a $\pi \cdots \pi$ interaction.

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