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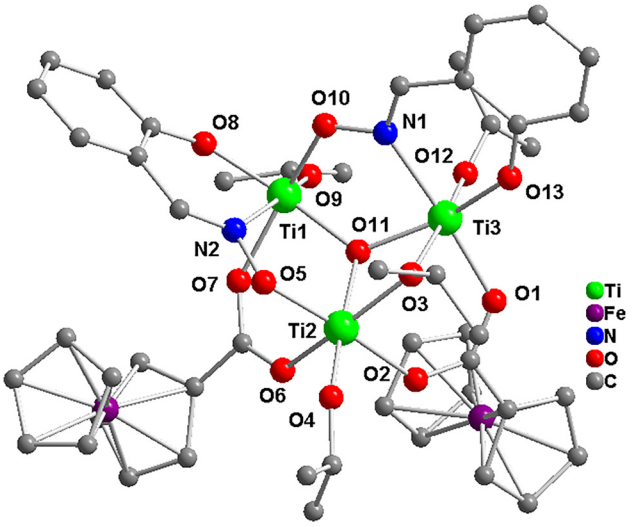
Crystal structure of bis(μ_2-ferrocenylcarboxylato-O,O′)-(μ_3-oxido-κ^3O:O:O)-bis(μ_2-salicyladoximato-κ^2N,O,O′)-(μ_2-isopropoxo)-tris(isopropoxy-κ^1O trititanium(IV)), $C_{48}H_{55}N_2O_{13}Fe_2Ti_3$



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Abstract

$C_{48}H_{55}N_2O_{13}Fe_2Ti_3$, monoclinic, $P2_1/n$, a = 19.1705(9) Å, b = 13.8600(4) Å, c = 20.7161(8) Å, β = 112.445(5)°, V = 5087.4(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0751, w$R_{ref}(F^2)$ = 0.1798, T = 293(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Dark-red block
Size:	0.26 × 0.25 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.07 mm^{-1}
Diffractometer, scan mode:	Bruker Apex2, φ and ω scans
θ_{max}, completeness:	28.3°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49831, 12606, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8,030
$N(param)_{refined}$:	620
Programs:	Bruker,[1] Shelx,[2] Diamond[3]

1 Source of material

All reagents and solvents employed in this work were commercially available and used without further purification.

In the first step, a mixture of salicylaldoxime (H_2Saox) (1 mmol, 0.137 g) and ferrocenecarboxylic acid ($FcCO_2H$) (0.87 mmol, 0.201 g) were placed in a Teflon-lined stainless vessel (15 mL). Secondly, isopropanol (2 mL) and acetonitrile (6 mL) as solvents were added. The above mixture was stirred for 5 min and then Ti(O^{i}Pr)$_4$ (1.63 mmol, 0.5 mL) was added. The resulting mixture was finally sealed and heated at 353 K for 96 h under autogenous pressure. After cooling to room temperature at a rate of 5 K·h^{-1}, red and block crystals were obtained and washed with acetonitrile. The yield was 0.151 g (31 %, based on $FcCO_2H$). Elemental analysis calcd. (found) for the title compound (%): C, 51.33 (51.28); H, 4.94 (4.89); N, 2.49 (2.54). IR (KBr, pellet, cm^{-1}): 2970 (m), 2920 (w), 2864 (w), 1694 (m), 1542 (m), 1478 (s), 1391 (s), 1295 (s), 1199 (m), 1128 (s), 1006 (s), 915 (m), 844 (m), 753 (w), 683 (s) and 627 (s).

2 Experimental details

All the non-H atoms were refined anisotropically. H atoms were subsequently treated as riding atoms with distances

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C–H = 0.98 (CH_3), 0.99 (CH) and 0.95 (ArH) Å. The H atom isotropic displacement parameters were fixed; U_{iso}(H) = 1.2 U_{eq}(C) for aromatic atoms, U_{iso}(H) = 1.2 U_{eq}(C) for saturated CH atoms, U_{iso}(H) = 1.5 U_{eq}(C) for CH_3 atoms, allowing them to ride on the parent atom.

3 Discussion

Crystalline titanium oxo clusters with accurate structures have drawn much interest in recent years.[4–6] Titanium oxo clusters not only can provide structure and reactivity model for further study on the photocatalytic mechanism of titanium dioxide nanoparticles[7] but also have important potential applications in photocatalysis, such as photocatalytic CO_2 reduction,[8] degradation[9] and hydrogen production.[10] Utilization multidentate and dye-functional as ligands are of great importance for titanium oxo clusters to increase hydrolytic stability and broaden light absorption, which is crucial for photocatalysis applications.[11] Both ferrocenecarboxylic acid and salicylaldoxime belong to multidentate and dye-functional ligands, and have proven to be effective ligands for construction of titanium oxo clusters with wide-ranged light absorption.[12,13] Simultaneously application of ferrocenecarboxylic acid and salicylaldoxime as ligands for titanium oxo clusters construction is appealing but has not been reported. In this work, a Ti_3 core-based titanium oxo cluster protected by the above two ligands has been successfully synthesized and structurally analyzed.

The title titanium oxo cluster formulates as $[Ti_3(\mu_3O)(O_2CFc)_2(Saox)_2(OiPr)_4]$, crystallizes in the monoclinic system and $P2_1/n$ space group. There are three Ti(IV) ions, one μ_3O atom, two ferrocenecarboxylates, two salicylaldoxime and four isopropoxide groups in the molecular structure (the figure). The two salicylaldoxime groups adopt μ_2-η^1:η^1:η^1 coordination mode which are different from that of μ_3-η^1:η^1:η^2 in the literature.[14–16] The three Ti(IV) ions are all six-coordinated, among which two Ti(IV) ions present octahedral TiO_5N coordination environments and one Ti(IV) ion shows TiO_6 mode. The μ_3O atom connects the three Ti(IV) ions together forming Ti_3O core with a nearly flat mode. The bond lengths of Ti–O range from 1.765 to 2.127 Å. The band lengths of Ti(1)–N(1) and Ti(2)–N(2) are 2.153 and 2.236 Å, respectively. Both the bonds of Ti–O and the bonds of Ti–N are consistent with the literature.[14,17,18] No classical intermolecular and intramolecular hydrogen bonds are found in the structure. However, the weak intermolecular interactions of C(22)–H(22)···O(13) with length 3.089(8) Å could be found in the adjacent moleculars. In summary, this work will not only enrich the types of titanium oxide clusters, but also provide a facile synthetic route to crystalline titanium oxide clusters using mixed dye-functional ligands.

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