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Synthesis and crystal structure of 4,4'-di(4-pyridyl)-6,6'-di(*tert*-butyl)-2,2'-[propylenedioxybis(nitrilomethylidyne)]diphenol, C₃₅H₄₀N₄O₄

Table 1: Data collection and handling.

Crystal:	White block
Size:	0.12 × 0.12 × 0.11 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	0.65 mm ⁻¹
Diffraction, scan mode:	Brucker, φ and ω
$\theta_{\max}$, completeness:	66.6°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18294, 2709, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2482
$N(\text{param})_{\text{refined}}$:	199
Programs:	Brucker [1], SHELX [2], Diamond [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.39892(4)	0.4416(2)	0.53835(7)	0.0453(3)
C2	0.38236(4)	0.3907(2)	0.60505(7)	0.0457(3)
C3	0.34892(4)	0.5263(2)	0.62737(7)	0.0482(3)
H3	0.3377	0.4919	0.6709	0.058*
C4	0.33210(4)	0.7107(2)	0.58607(7)	0.0456(3)
C5	0.29794(4)	0.8609(2)	0.61092(7)	0.0465(3)
C6	0.29737(5)	0.8954(3)	0.68718(8)	0.0575(4)
H6	0.3186	0.8225	0.7243	0.069*
C7	0.26520(6)	1.0379(3)	0.70718(9)	0.0653(4)
H7	0.2657	1.0578	0.7585	0.078*
C8	0.23380(5)	1.1140(2)	0.58538(9)	0.0603(4)
H8	0.2117	1.1870	0.5496	0.072*
C9	0.26479(5)	0.9764(2)	0.55970(8)	0.0529(3)
H9	0.2635	0.9606	0.5080	0.064*
C10	0.34871(4)	0.7538(2)	0.51960(7)	0.0465(3)
H10	0.3371	0.8766	0.4912	0.056*
C11	0.38145(4)	0.6243(2)	0.49367(7)	0.0449(3)
C12	0.39878(5)	0.6822(2)	0.42044(8)	0.0524(3)
C13	0.37181(7)	0.8771(3)	0.38017(10)	0.0750(5)
H13A	0.3393	0.8392	0.3658	0.113*
H13B	0.3839	0.9131	0.3358	0.113*
H13C	0.3752	1.0017	0.4136	0.113*
C14	0.39199(6)	0.4863(3)	0.36524(8)	0.0666(4)
H14A	0.4119	0.3672	0.3865	0.100*
H14B	0.3998	0.5304	0.3181	0.100*
H14C	0.3600	0.4390	0.3568	0.100*
C15	0.45065(6)	0.7452(3)	0.43996(11)	0.0749(5)
H15A	0.4545	0.8723	0.4722	0.112*
H15B	0.4616	0.7780	0.3943	0.112*
H15C	0.4683	0.6247	0.4656	0.112*
C16	0.39993(5)	0.2041(2)	0.65300(7)	0.0506(3)
H16	0.3863	0.1724	0.6943	0.061*
C17	0.48253(5)	−0.2113(2)	0.68031(8)	0.0539(3)
H17A	0.5072	−0.1170	0.6695	0.065*
H17B	0.4721	−0.3065	0.6371	0.065*

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Abstract

C₃₅H₄₀N₄O₄, monoclinic, C2/c (no. 15), $a = 29.1768(5)$ Å, $b = 6.0734(1)$ Å, $c = 18.0123(3)$ Å, $\beta = 101.2260(10)^\circ$, $Z = 4$, $V = 3130.75(9)$ Å³, $R_{\text{gt}}(F) = 0.0422$, $wR_{\text{ref}}(F^2) = 0.1185$, $T = 273(2)$ K.

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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

All solvents and other reagents were of analytical grade. The starting material 1,3-bis(aminooxy)propane can be prepared according to similar methods reported earlier [4]. The title compound was synthesized according to a previously reported similar method [5, 6]. An ethanol solution (10 mL) of 1,3-bis(aminooxy)propane (106.13 mg, 1.0 mmol) was added

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C18	0.5000	−0.3467(3)	0.7500	0.0522(4)
H18A ^a	0.4749	−0.4410	0.7593	0.063 [*]
H18B ^a	0.5251	−0.4410	0.7407	0.063 [*]
N1	0.43319(4)	0.08274(19)	0.64063(6)	0.0533(3)
N2	0.23342(5)	1.1494(2)	0.65847(8)	0.0659(4)
O1	0.43238(3)	0.31595(17)	0.51712(6)	0.0596(3)
H1	0.4411	0.2220	0.5495	0.089 [*]
O2	0.44436(3)	−0.08124(17)	0.69532(6)	0.0620(3)

^aOccupancy: 0.5.

to an ethanol solution (15 mL) of 3-*tert*-butyl-5-(4-pyridinyl) salicylaldehyde (510.62 mg, 2.0 mmol). The mixed solution was heated under refluxing for about 6 h, then, a white crystalline solid was precipitated when the solution was cooled to room temperature. Yield: 62.6%. Elemental analysis—Anal. Calcd. for C₃₅H₄₀N₄O₄: C, 66.45%; H, 7.34%; N, 12.24%. Found: C, 66.53%; H, 7.26%; N, 12.17%. A certain amount of the title compound obtained above was heated and dissolved in an ethanol solution. The solution was filtered, and the filtrate was left undisturbed for about one week to form clear white block-like crystals suitable for X-ray crystallographic analysis.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

Salamo-type ligands are an important class of multidentate chelating ligands containing a N₂O₂ coordination cavity [7], which can coordinate with alkaline earth metal ions, transition metal ions and rare earth metal ions to yield structurally interesting metal complexes [8]. In recent years, there has been a great interest in the study of metal complexes of these ligands by virtue of their luminescent [9], ion recognitions [10] and catalytic [11] properties, as well as their use as building blocks for supramolecular structures [12, 13].

This work reports the synthesis and crystal structure of the title compound. X-ray crystallographic data reveals that the title compound crystallizes in the monoclinic space group C2/c. All bond lengths are in normal ranges. Interestingly, the entire molecule is symmetrical about C18, with the 2-fold rotation axis passing through this atom. In addition, there are three pairs of significant intramolecular hydrogen bonding interactions (O1—H1···N1, C14—H14A···O1 and C15—H15A···O1) in the structure of the title ligand

C14—H14C···N2 interactions link successive molecules along the [1 0 1] direction.

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