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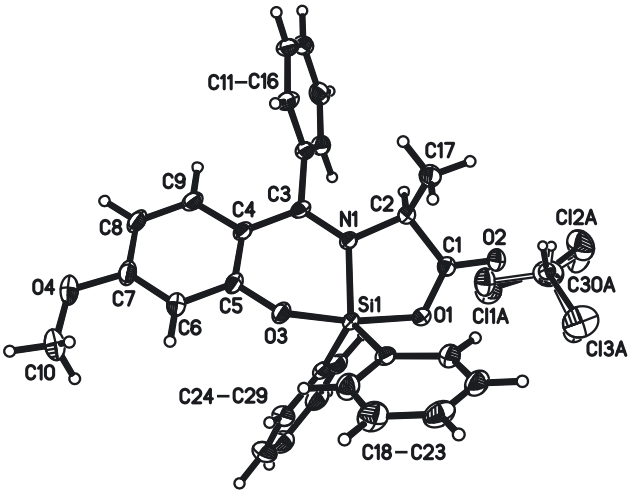
The crystal structure of [*N*-{[2-(oxy)-4-methoxyphenyl](phenyl)methylidene} alaninato]-diphenyl-silicon(IV) – chloroform (1/1), $C_{29}H_{25}NO_4Si{\cdot}CHCl_3$



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Abstract

$C_{29}H_{25}NO_4Si{\cdot}CHCl_3$, monoclinic, $P2_1/c$ (no. 14), a = 17.1316(8) Å, b = 10.1173(3) Å, c = 18.2252(8) Å, β = 117.195(3)°, V = 2809.7(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0431, $wR_{ref}(F^2)$ = 0.1050, T = 153 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.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.33 × 0.25 × 0.13 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.41 mm^{-1}
Diffractometer, scan mode:	STOE IPDS 2,
θ_{max}, completeness:	27.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	43,582, 6398, 0.060
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5352
$N(param)_{refined}$:	391
Programs:	X-RED [1], SHELX [2, 3], ORTEP-3 [4]

1 Source of materials

The *O,N,O*′-ligand was prepared from 2-hydroxy-4-methoxy benzophenone and *L*-alanine according to a literature procedure [5].

In a representative experiment 1.2 g (4.0 mmol) 2-{(*E*)-[(2-hydroxy-4-methoxyphenyl)(phenyl)methylidene]amino} propanoic acid were placed in a Schlenk flask under argon and solved in 40 mL dry THF. To this solution were added 0.9 g (8.9 mmol) triethylamine and cooled to 0 °C. 1.0 g (4.0 mmol) $SiCl_2Ph_2$ were diluted with 20 mL THF and added via a dropping funnel to the solution. The mixture was stirred for 14 h at room temperature. The white precipitate of triethylammonium chloride was separated by filtration. The filtrate was reduced in a vacuum and the pale yellow residue was solved in 20 mL chloroform. The resulting suspension was filtered again. 2 mL *n*-hexane were added to the filtrate and the solution was stored for 5 months at 8 °C. Pale yellow crystals suitable for crystal structure analysis were obtained. Yield: 1.7 g (71 %). **M.pt:** 383 K.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.08 (d, $^3J_{HH}$ = 8 Hz, 3H, CH_3 at C17), 3.72 (s, 3H, CH_3 at C10), 4.21 (d, $^3J_{HH}$ = 8 Hz, 1H, CH at C2), 6.16–7.99 (m, 18 H, Ph). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ = 19.8 (C17), 55.9 (C10), 59.4 (C2), 102.9, 110.1, 112.9, 125.9, 127.5, 129.1, 129.3, 130.5, 136.7, 137.3, 138.0, 139.8 (12 × aromatic C), 167.0, 168.8, 172.6 (C3, C5, C7), 178.1 (C1). **^{29}Si NMR** ($CDCl_3$, 80 MHz) δ = −99.2 ppm.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Si1	0.26915 (3)	0.07087 (5)	0.46704 (3)	0.01644 (11)
O1	0.34140 (8)	0.01134 (12)	0.42679 (7)	0.0202 (3)
O2	0.44570 (9)	−0.13470 (13)	0.44274 (8)	0.0254 (3)
O3	0.20677 (8)	0.10764 (13)	0.51919 (7)	0.0218 (3)
N1	0.35954 (9)	0.00980 (14)	0.56762 (8)	0.0169 (3)
C1	0.40348 (11)	−0.07246 (17)	0.46952 (10)	0.0183 (3)
C2	0.41860 (11)	−0.08735 (17)	0.55767 (10)	0.0177 (3)
H2	0.480941	−0.064901	0.596238	0.021*
C3	0.37773 (11)	0.05492 (17)	0.64205 (10)	0.0182 (3)
C4	0.32019 (12)	0.14396 (17)	0.65510 (10)	0.0198 (3)
C5	0.23540 (12)	0.16870 (18)	0.59194 (10)	0.0200 (3)
C6	0.17745 (13)	0.25088 (19)	0.60467 (11)	0.0246 (4)
H6	0.120055	0.266101	0.561505	0.029*
C7	0.20451 (14)	0.31029 (19)	0.68113 (12)	0.0268 (4)
C8	0.28921 (14)	0.2877 (2)	0.74534 (11)	0.0281 (4)
H8	0.307453	0.329186	0.797372	0.034*
C9	0.34492 (13)	0.20606 (19)	0.73260 (11)	0.0245 (4)
H9	0.401753	0.190143	0.776548	0.029*
O4	0.15459 (11)	0.39373 (16)	0.69988 (10)	0.0385 (4)
C10	0.06749 (15)	0.4210 (3)	0.63776 (15)	0.0413 (5)
H10A	0.069884	0.463766	0.590578	0.062*
H10B	0.038326	0.479879	0.660293	0.062*
H10C	0.034510	0.338147	0.619797	0.062*
C11	0.45960 (12)	0.01428 (17)	0.71633 (10)	0.0203 (3)
C12	0.45315 (13)	−0.06245 (19)	0.77695 (11)	0.0251 (4)
H12	0.397428	−0.093282	0.768954	0.030*
C13	0.52796 (13)	−0.09383 (19)	0.84893 (11)	0.0272 (4)
H13	0.523491	−0.147539	0.889607	0.033*
C14	0.60902 (13)	−0.04697 (19)	0.86150 (11)	0.0278 (4)
H14	0.660042	−0.066731	0.911299	0.033*
C15	0.61554 (13)	0.02883 (19)	0.80125 (12)	0.0268 (4)
H15	0.671346	0.060156	0.809800	0.032*
C16	0.54132 (12)	0.05959 (18)	0.72838 (11)	0.0227 (4)
H16	0.546353	0.111109	0.687167	0.027*
C17	0.39917 (14)	−0.22784 (18)	0.57414 (12)	0.0269 (4)
H17A	0.409753	−0.235395	0.631560	0.040*
H17B	0.437518	−0.289499	0.564308	0.040*
H17C	0.337724	−0.249169	0.537172	0.040*
C18	0.17441 (12)	−0.03388 (17)	0.39072 (10)	0.0198 (3)
C19	0.08810 (13)	−0.0086 (2)	0.37608 (12)	0.0291 (4)
H19	0.077630	0.061093	0.405398	0.035*
C20	0.01717 (14)	−0.0820 (2)	0.32011 (14)	0.0379 (5)
H20	−0.040591	−0.061095	0.311094	0.045*
C21	0.03068 (14)	−0.1853 (2)	0.27762 (13)	0.0347 (5)
H21	−0.017305	−0.237300	0.240471	0.042*
C22	0.11488 (15)	−0.2119 (2)	0.28986 (12)	0.0316 (4)
H22	0.124744	−0.282441	0.260693	0.038*
C23	0.18530 (13)	−0.13633 (19)	0.34450 (11)	0.0262 (4)
H23	0.242364	−0.154679	0.350656	0.031*
C24	0.27989 (12)	0.24721 (18)	0.44063 (10)	0.0201 (3)
C25	0.20765 (13)	0.3326 (2)	0.41217 (12)	0.0285 (4)
H25	0.153673	0.301245	0.408421	0.034*
C26	0.21290 (16)	0.4616 (2)	0.38933 (13)	0.0369 (5)
H26	0.162367	0.516593	0.368516	0.044*
C27	0.29141 (16)	0.5104 (2)	0.39676 (13)	0.0365 (5)
H27	0.295200	0.599261	0.381757	0.044*
C28	0.36459 (15)	0.4295 (2)	0.42613 (12)	0.0311 (4)
H28	0.419021	0.463349	0.432383	0.037*
C29	0.35852 (12)	0.29867 (18)	0.44653 (11)	0.0228 (4)
H29	0.408647	0.243149	0.464808	0.027*
C30A[a]	0.8465 (6)	0.1894 (11)	0.4388 (6)	0.019 (3)
H30A[a]	0.832235	0.125688	0.472825	0.023*
Cl1A[a]	0.8367 (7)	0.3505 (11)	0.4689 (10)	0.060 (3)
Cl2A[a]	0.9530 (5)	0.1579 (8)	0.4538 (6)	0.0628 (13)
Cl3A[a]	0.7749 (5)	0.1634 (10)	0.3362 (5)	0.0638 (18)
C30B[b]	0.8507 (6)	0.1954 (11)	0.4353 (6)	0.059 (4)
H30B[b]	0.843096	0.118517	0.465864	0.071*
Cl1B[b]	0.8384 (4)	0.3416 (5)	0.4818 (5)	0.0441 (8)
Cl2B[b]	0.9551 (3)	0.1860 (12)	0.4424 (5)	0.0827 (16)
Cl3B[b]	0.7710 (2)	0.1843 (6)	0.3329 (2)	0.0541 (9)

[a]Occupancy: 0.38 (3), [b]occupancy: 0.62 (3).

IR (KBr, cm^{-1}) 429.8 (m), 445.3 (w), 491.0 (s), 520.1 (s), 531.5(s), 575.8 (w), 618.9 (m), 627.8 (m), 665.1 (m), 701.7 (s), 742.9 (s), 755.9 (s), 811.0 (s), 837.5 (m), 870.2 (m), 914.9 (m), 962.4 (m), 978.3 (m), 999.3 (m), 1028.8 (m), 1073.9 (m), 1094.0 (m), 1109.5 (m), 1130.8 (s), 1173.9 (m), 1219.8 (s), 1249.2 (m), 1278.7 (vs), 1328.0 (s), 1370.9 (s), 1382.9 (s), 1428.8 (m), 1457.1 (m), 1486.9 (s), 1509.9 (vs), 1566.6 (vs), 1609.8 (vs), 1714.2 (vs), 2845.2 (w), 2932.3 (w), 3004.6 (m), 3046.3 (m), 3392.6 (w).

2 Experimental details

The carbon-bound H atoms were geometrically placed (C–H = 0.95–1.0 Å) and refined as riding atoms with U_{iso}(H) = 1.2–1.5 U_{eq}(C). The disordered chloroform molecule was refined with a split atom model. Site occupation factors for parts A and B were refined to 0.38/0.62, respectively. Restraints were applied in order to keep both parts of the disordered chloroform to sensible values regarding bond lengths and anisotropic displacement parameters.

3 Comment

Tridentate *O,N,O*-chelate ligands based on Schiff bases are used frequently for the generation of pentacoordinated silicon complexes [6]. We wanted to explore the ability of the Schiff base 2-{(*E*)-[(2-hydroxy-4-methoxyphenyl)(phenyl) methylidene]amino}propanoic acid to be a tridentate ligand in pentacoordinate silicon complexes. This ligand has not been used so far for the generation of any coordination compound. Related silicon complexes contain Schiff base

ligands derived from salicyl aldehyde [7], acetophenone [8] or naphthyl aldehyde [9].

The asymmetric unit of the title structure contains one molecule [*N*-{[2-(oxy)-4-methoxyphenyl](phenyl)methylidene}alaninato]-diphenyl-silicon(IV) and one chloroform molecule. The molecular structure is shown in the figure (50 % displacement ellipsoids) with a silicon complex and a disordered chloroform in the asymmetric unit. The centrosymmetric space group $P2_1/c$ indicates that both enantiomers of the amino acid derivative are present in the crystal under investigation. The batch product shows no rotation of polarized light ($[\alpha]^{20}_D$ = 0°). L-alanine has been used for the synthesis of the Schiff-base ligand. Racemization of the ligand system must have occured during complex formation. This was already observed in other cases [7, 10].

The silicon complex features a pentacoordinated silicon atom, coordinated by carboxyl–O1, phenoxy–O3, imine–N1 and two carbon atoms from phenyl groups (C18 and C24). The coordination geometry of the pentacoordinate silicon atom was analysed with the parameter τ. This is defined as $\tau = (\beta - \alpha)/60°$ with β as largest and α as the second largest angle at the central atom [11]. If τ = 0 it is a perfect square pyramid, while τ = 1 indicates a perfect trigonal bipyramid. Largest angle at the silicon atom is O1–Si1–O3 with 170.17(6)° and second largest N1–Si1–C18 with 125.15(7)°. This gives a parameter τ = 0.75, which corresponds to a distorted trigonal bipyramid. The apical positions are occupied by O1 and O3 of the tridentate ligand, while the atoms N1, C18, and C24 represent the atoms in the trigonal plane.

The bond Si–O1 [1.806(2) Å] is longer than the bond Si1–O3 [1.764(2) Å]. This can be explained with the carboxyl type oxygen atom O1 and the electronegative character of the phenyl bound O3. The bond lengths Si1–N1 and Si–C are similar as in comparable pentacoordinate silicon complexes [8, 9, 12, 13].

Two closely related complexes with the [*N*-{[2-(oxy)-4-methoxyphenyl](phenyl)methylidene}glycinato] ligand have been reported [14, 15]. This Schiff-base ligand lacks the methyl group at C2 with a glycinato instead of alaninato group.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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