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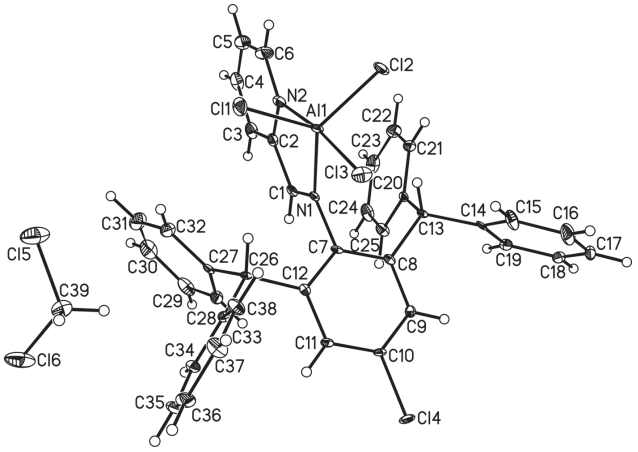
Crystal structure of trichloro-(4-chloro-2,6-bis(diphenylmethyl)-*N*-((pyridin-2-yl)methylene)aniline)-aluminum dichloromethane solvate, $C_{39}H_{31}AlCl_6N_2$



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Abstract

$C_{39}H_{31}AlCl_6N_2$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 10.09080(1)$ Å, $b = 18.5381(2)$ Å, $c = 19.7643(2)$ Å, $V = 3697.19(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0516$, $wR_{ref}(F^2) = 0.1430$, $T = 150(10)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Ligand 4-chloro-2,6-bis(diphenylmethyl)-*N*-((pyridin-2-yl) methylene) aniline was prepared by following a literature procedure [4]. The synthesis of the title compound was performed under a dinitrogen atmosphere using standard Schlenk technique. A solution of the ligand (0.55 g, 1.00 mmol) in dichloromethane was added to a Schlenk flask charged with

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.30 × 0.20 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	4.71 mm^{-1}
Diffractometer, scan mode:	XtaLAB AFC12 (RINC), φ and ω
θ_{max}, completeness:	74.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14544, 6845, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6566
$N(param)_{refined}$:	433
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.17020(13)	0.36332(8)	0.62171(6)	0.0280(3)
Cl2	−0.01810(11)	0.30960(8)	0.77917(6)	0.0253(3)
Cl3	0.22321(12)	0.21652(7)	0.71205(7)	0.0261(3)
Cl4	0.75359(11)	0.14713(7)	0.86396(6)	0.0211(3)
Al1	0.16585(12)	0.33089(8)	0.72677(6)	0.0132(3)
N1	0.3314(3)	0.3509(2)	0.78094(18)	0.0104(7)
N2	0.1428(4)	0.4412(2)	0.7522(2)	0.0190(9)
C1	0.3473(4)	0.4157(2)	0.8021(2)	0.0128(9)
H1	0.4230	0.4287	0.8260	0.015*
C2	0.2445(5)	0.4684(2)	0.7879(2)	0.0160(9)
C3	0.2479(6)	0.5396(3)	0.8103(3)	0.0239(11)
H3	0.3196	0.5573	0.8348	0.029*
C4	0.1405(6)	0.5832(3)	0.7948(3)	0.0305(13)
H4	0.1390	0.6310	0.8091	0.037*
C5	0.0370(6)	0.5558(3)	0.7584(3)	0.0350(14)
H5	−0.0355	0.5846	0.7476	0.042*
C6	0.0419(6)	0.4834(3)	0.7378(3)	0.0314(13)
H6	−0.0286	0.4647	0.7131	0.038*
C7	0.4334(4)	0.2996(2)	0.8000(2)	0.0100(8)
C8	0.4194(4)	0.2629(2)	0.8616(2)	0.0112(8)
C9	0.5206(4)	0.2164(2)	0.8813(2)	0.0125(9)
H9	0.5152	0.1921	0.9224	0.015*
C10	0.6284(4)	0.2065(3)	0.8397(2)	0.0123(9)
C11	0.6400(4)	0.2410(2)	0.7775(2)	0.0126(8)
H11	0.7131	0.2325	0.7500	0.015*
C12	0.5411(4)	0.2884(2)	0.7567(2)	0.0109(8)
C13	0.2911(4)	0.2713(2)	0.9023(2)	0.0106(8)
H13	0.2186	0.2686	0.8694	0.013*
C14	0.2708(4)	0.2082(2)	0.9508(2)	0.0131(9)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C15	0.2245(6)	0.1431(3)	0.9254(3)	0.0272(12)
H15	0.2016	0.1395	0.8800	0.033*
C16	0.2121(6)	0.0829(3)	0.9672(3)	0.0351(14)
H16	0.1820	0.0394	0.9496	0.042*
C17	0.2447(5)	0.0881(3)	1.0350(3)	0.0270(12)
H17	0.2360	0.0482	1.0631	0.032*
C18	0.2901(5)	0.1527(3)	1.0609(3)	0.0251(11)
H18	0.3110	0.1565	1.1066	0.030*
C19	0.3047(5)	0.2124(3)	1.0186(2)	0.0185(10)
H19	0.3376	0.2554	1.0360	0.022*
C20	0.2777(4)	0.3445(2)	0.9371(2)	0.0121(8)
C21	0.1509(5)	0.3730(3)	0.9457(2)	0.0188(10)
H21	0.0777	0.3471	0.9306	0.023*
C22	0.1325(5)	0.4395(3)	0.9765(3)	0.0260(12)
H22	0.0474	0.4577	0.9821	0.031*
C23	0.2403(7)	0.4786(3)	0.9989(3)	0.0307(13)
H23	0.2282	0.5235	1.0188	0.037*
C24	0.3668(6)	0.4504(3)	0.9915(3)	0.0262(12)
H24	0.4396	0.4764	1.0069	0.031*
C25	0.3851(5)	0.3832(3)	0.9609(2)	0.0203(10)
H25	0.4701	0.3644	0.9565	0.024*
C26	0.5474(4)	0.3280(2)	0.6890(2)	0.0108(9)
H26	0.4576	0.3261	0.6701	0.013*
C27	0.5795(4)	0.4078(3)	0.6982(2)	0.0126(8)
C28	0.6584(5)	0.4330(3)	0.7504(2)	0.0181(10)
H28	0.6997	0.4007	0.7795	0.022*
C29	0.6761(6)	0.5073(3)	0.7593(3)	0.0281(12)
H29	0.7287	0.5241	0.7946	0.034*
C30	0.6161(6)	0.5555(3)	0.7162(3)	0.0341(14)
H30	0.6267	0.6048	0.7230	0.041*
C31	0.5404(6)	0.5307(3)	0.6630(3)	0.0347(14)
H31	0.5021	0.5633	0.6331	0.042*
C32	0.5214(5)	0.4572(3)	0.6542(3)	0.0226(11)
H32	0.4694	0.4407	0.6185	0.027*
C33	0.6359(4)	0.2886(3)	0.6386(2)	0.0125(9)
C34	0.7712(4)	0.3042(3)	0.6314(2)	0.0168(9)
H34	0.8088	0.3417	0.6561	0.020*
C35	0.8492(5)	0.2641(3)	0.5877(3)	0.0235(11)
H35	0.9391	0.2743	0.5839	0.028*
C36	0.7947(5)	0.2089(3)	0.5496(3)	0.0267(12)
H36	0.8471	0.1824	0.5200	0.032*
C37	0.6608(6)	0.1938(3)	0.5561(3)	0.0273(12)
H37	0.6231	0.1571	0.5304	0.033*
C38	0.5827(5)	0.2326(3)	0.6005(3)	0.0216(11)
H38	0.4934	0.2212	0.6050	0.026*
Cl5	0.57493(16)	0.41374(10)	0.42924(11)	0.0511(5)
Cl6	0.85614(15)	0.40166(10)	0.45475(11)	0.0514(5)
C39	0.7035(6)	0.3561(3)	0.4550(3)	0.0316(13)
H39A	0.7081	0.3150	0.4246	0.038*
H39B	0.6852	0.3382	0.5002	0.038*

anhydrous $AlCl_3$ (0.13 g, 1.00 mmol) and a stir bar. The mixture was stirred at ambient temperature for 24 hours. The solution was concentrated under vacuum and hexane was added to induce precipitation of the yellow product. Crystals of the title compound were obtained by recrystallization from a hexane/CH_2Cl_2 solution.

Experimental details

Coordinates of all hydrogen atoms were refined with constraints. H-U_{iso} values were set to 1.2U_{eq} of the parent atoms. The absolute structure was established by refinement of the Flack parameter [0.006(13) from 2463 selected quotients] using Parsons' method [5]. The classical refinement of the Flack parameter gave a similar result [−0.002(14)] [3].

Comment

Iminopyridine represents one important type of redox-active ligands, and their complexes have drawn increasing attentions in the last decade [6]. Specifically, incorporation of such ligands onto main group metal centers [e.g. Al(III)] has been shown to be an effective way for developing new homogeneous catalysts for various transformations [7–9]. To the best of our knowledge, only one example of structurally characterized iminopyridine aluminum trihalide complex has been reported [9]. This contribution is part of our ongoing investigation on the synthesis, characterization and reactivity of earth-abundant-metal complexes supported by redox-active ligands [10, 11].

The asymmetric unit of the title structure contains one Al(III) center coordinated with one α-iminopyridine ligand, as well as one CH_2Cl_2 solvent molecule. The aluminum center is five-coordinate in a distorted trigonal bipyramidal geometry, with the pyridine N atom (N2) and one chlorine atom (Cl3) occupying the axial positions, and the imine N atom (N1) and the other two chlorine atoms (Cl1 and Cl2) occupying the equatorial positions. The bond lengths and angles within the structure are in the expected ranges. For instance, the Al—N bond distances [2.018(4) and 2.119(5) Å] are comparable to those of the previously reported iminopyridine $AlCl_3$ compound [2.041(3) and 2.100(3) Å] [9]. Furthermore, the bond lengths of the iminopyridine N—C—C—N backbone confirm that the ligand exists as a neutral bidentate ligand. The five-membered ring formed by the ligand and aluminum is almost perfectly planar, with an acute bite angle of 77.76(16)°. The two bulky $CHPh_2$ substituents on the N-aryl ring are oriented with the benzhydryl protons directing towards the metal center, in order to minimize intramolecular steric repulsions.

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