Crystal structure of an aluminum spirocyclic hybrid complex, $C_{29}H_{41}N_2AlO_3B_2(C_{12}H_7O)_2$, $C_{53}H_{55}AlB_2N_2O_5$

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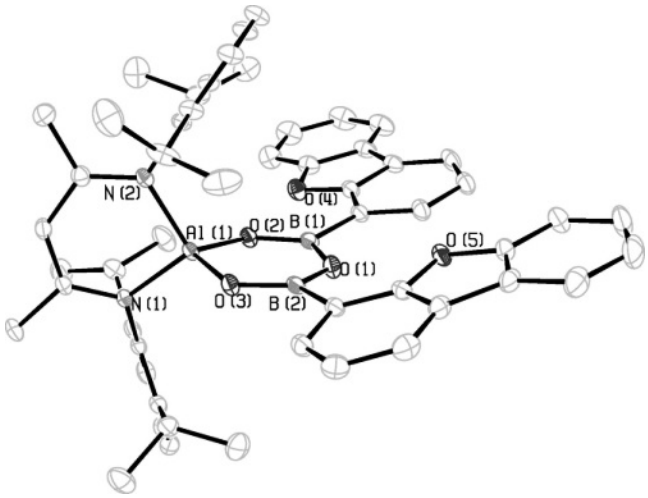

Abstract

$C_{53}H_{55}AlB_2N_2O_5$, triclinic, $P\bar{1}$ (no. 2), a = 11.663(4) Å, b = 13.476(5) Å, c = 15.988(7) Å, α = 89.70(2)°, β = 83.21(2)°, γ = 67.01(1)°, V = 2294.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0659, $wR_{ref}(F^2)$ = 0.1611, T = 153 K.

Table 1. Data collection and handling.

Crystal:	colourless plates, size 0.10×0.36×0.51 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.95 cm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ and ω
$2\theta_{max}$:	54.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22047, 1021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6384
$N(param)_{refined}$:	578
Programs:	SADABS [6], SHELX [7]

Source of material

A solution of $LAlH_2$ (0.45g , 1mmol) in toluene (10ml) was added dropwise to a solution of dibenzofuran-4-boric acid (0.44 g, 2 mmol) in toluene (10mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirring was continued overnight. After removal of all volatiles, the solid was extracted with *n*-hexane and colourless crystals were obtained at -27°C. Total yield, 0.55g (64.8%).

Discussion

The chemistry of boroxines has been particularly fruitful and has been recently reported [1]. They play a vital role in a broad range of industrial applications [2]. In 2006, the group of Roesky reported a rare aluminum spirocyclic hybrid with an inorganic B_2O_3 and an organic C_3N_2 core [3]. Given the considerable current interest in aluminum heterometallic oxides [4], our group attempts to prepare aluminum substituted boroxines by the bulky β-diketimato ligand [5]. Herein, we synthesize the compound containing a Al-O-B moiety by the reaction of $LAlH_2$ (L = $HC[(CMe)(NAr)]_2$; Ar = 2,6-i$Pr_2C_6H_3$) with dibenzofuran-4-boric acid and investigate the influence of electronic and steric effects of the ligand. The compound ($LAlO_3B_2(C_{12}H_7O)_2$) is a rare species containing a spiro-centered aluminum atom, where the inorganic AlO_3B_2 ring is fused to the organic C_3N_2 part. The bond distances (Al1–O2 1.7357 Å, Al1–O3 1.7400 Å) are shorter than those of $LAl[(OBPh)_2O]$ [3], that should be attributed to the larger steric hinderance and electron donating effect of the dibenzofuran group. The O2–Al1–O3 angle (104.74°) for the title compound is more acute than that in $LAl(OH)_2$ [8] (115.38(8)°) due to a certain strain within the six-membered ring.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.7845	0.7294	1.0049	0.044
H(3)	2*i*	0.9043	0.8235	0.9539	0.048
H(4)	2*i*	0.8579	0.9238	0.8351	0.045
H(8)	2*i*	0.2249	0.9423	0.8517	0.036
H(12)	2*i*	0.2841	0.6610	0.4788	0.043
H(13)	2*i*	0.3390	0.4816	0.5095	0.046
H(14)	2*i*	0.4161	0.4187	0.6346	0.045
H(16)	2*i*	0.5101	0.7314	0.9215	0.045
H(17A)	2*i*	0.6911	0.5728	0.8831	0.067
H(17B)	2*i*	0.6044	0.5536	0.9615	0.067
H(17C)	2*i*	0.7289	0.5707	0.9763	0.067
H(18A)	2*i*	0.5989	0.7250	1.0813	0.066
H(18B)	2*i*	0.4756	0.7064	1.0655	0.066
H(18C)	2*i*	0.4806	0.8226	1.0531	0.066
H(19)	2*i*	0.6104	0.9481	0.7121	0.041
H(20A)	2*i*	0.8677	0.9225	0.6863	0.062
H(20B)	2*i*	0.7764	0.9475	0.6147	0.062
H(20C)	2*i*	0.8196	0.8333	0.6577	0.062
H(21A)	2*i*	0.5732	1.1030	0.7968	0.065
H(21B)	2*i*	0.6267	1.1154	0.7022	0.065
H(21C)	2*i*	0.7171	1.0866	0.7745	0.065
H(22A)	2*i*	0.4244	0.9536	0.9605	0.042
H(22B)	2*i*	0.3046	1.0353	0.9211	0.042
H(22C)	2*i*	0.4417	1.0307	0.8879	0.042
H(23A)	2*i*	0.1145	0.8665	0.7382	0.050
H(23B)	2*i*	0.1236	0.8204	0.8307	0.050
H(23C)	2*i*	0.1740	0.7391	0.7496	0.050
H(24)	2*i*	0.3165	0.8644	0.6049	0.055
H(25A)	2*i*	0.4574	0.7873	0.4799	0.074
H(25B)	2*i*	0.3533	0.9038	0.4655	0.074
H(25C)	2*i*	0.3403	0.7973	0.4324	0.074
H(26A)	2*i*	0.1297	0.8500	0.5095	0.083
H(26B)	2*i*	0.1351	0.9600	0.5420	0.083
H(26C)	2*i*	0.1044	0.8815	0.6083	0.083
H(27)	2*i*	0.5141	0.5544	0.7782	0.043
H(28A)	2*i*	0.4841	0.3575	0.7521	0.059
H(28B)	2*i*	0.5785	0.3755	0.8094	0.059

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Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(28C)	2*i*	0.6022	0.3799	0.7090	0.059
H(29A)	2*i*	0.3087	0.6215	0.8450	0.069
H(29B)	2*i*	0.3897	0.5140	0.8889	0.069
H(29C)	2*i*	0.2957	0.5105	0.8248	0.069
H(32)	2*i*	0.9082	0.4477	0.5184	0.041
H(33)	2*i*	1.0276	0.2652	0.4969	0.048
H(34)	2*i*	1.0439	0.1477	0.6067	0.050
H(37)	2*i*	1.0256	0.0583	0.7748	0.060
H(38)	2*i*	0.9748	0.0389	0.9178	0.068

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(39)	2*i*	0.8402	0.1856	1.0047	0.065
H(40)	2*i*	0.7589	0.3595	0.9513	0.057
H(44)	2*i*	0.6007	0.9298	0.4962	0.041
H(45)	2*i*	0.6140	0.9935	0.3622	0.048
H(46)	2*i*	0.7170	0.8744	0.2459	0.048
H(49)	2*i*	0.8740	0.6763	0.1371	0.064
H(50)	2*i*	1.0001	0.4982	0.0915	0.080
H(51)	2*i*	1.0432	0.3596	0.1856	0.080
H(52)	2*i*	0.9624	0.3939	0.3285	0.059

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(1)	2*i*	0.55293(6)	0.74695(6)	0.71372(4)	0.0297(4)	0.0195(4)	0.0212(4)	–0.0085(3)	–0.0021(3)	–0.0029(3)
O(1)	2*i*	0.7641(2)	0.6280(1)	0.5769(1)	0.0382(9)	0.0249(9)	0.0256(9)	–0.0078(8)	0.0021(7)	–0.0007(7)
O(2)	2*i*	0.6734(1)	0.6212(1)	0.7182(1)	0.0324(9)	0.0214(9)	0.0262(9)	–0.0076(7)	–0.0008(7)	–0.0014(7)
O(3)	2*i*	0.5899(1)	0.7948(1)	0.61728(9)	0.0352(9)	0.0225(9)	0.0230(8)	–0.0082(7)	0.0001(7)	–0.0016(7)
O(4)	2*i*	0.8039(2)	0.4035(1)	0.7895(1)	0.041(1)	0.023(1)	0.035(1)	–0.0070(8)	–0.0047(8)	0.0026(7)
O(5)	2*i*	0.8226(2)	0.5919(1)	0.3977(1)	0.043(1)	0.031(1)	0.0272(9)	–0.0163(8)	0.0028(8)	–0.0081(7)
N(1)	2*i*	0.5260(2)	0.8398(2)	0.8067(1)	0.026(1)	0.023(1)	0.021(1)	–0.0085(8)	–0.0017(8)	–0.0026(8)
N(2)	2*i*	0.3924(2)	0.7439(2)	0.7214(1)	0.031(1)	0.024(1)	0.022(1)	–0.0102(9)	–0.0031(8)	–0.0023(8)
B(1)	2*i*	0.7562(3)	0.5727(2)	0.6497(2)	0.031(1)	0.024(1)	0.028(1)	–0.013(1)	–0.004(1)	–0.001(1)
B(2)	2*i*	0.6822(3)	0.7305(2)	0.5595(2)	0.032(1)	0.021(1)	0.027(1)	–0.012(1)	–0.002(1)	–0.002(1)
C(1)	2*i*	0.6594(2)	0.7753(2)	0.9189(1)	0.041(1)	0.025(1)	0.019(1)	–0.010(1)	–0.002(1)	–0.0032(9)
C(2)	2*i*	0.7634(2)	0.7713(2)	0.9568(2)	0.043(2)	0.037(2)	0.025(1)	–0.007(1)	–0.009(1)	–0.004(1)
C(3)	2*i*	0.8353(2)	0.8264(2)	0.9264(2)	0.036(1)	0.045(2)	0.038(2)	–0.015(1)	–0.007(1)	–0.013(1)
C(4)	2*i*	0.8074(2)	0.8859(2)	0.8557(2)	0.033(1)	0.043(2)	0.038(2)	–0.018(1)	–0.000(1)	–0.009(1)
C(5)	2*i*	0.7066(2)	0.8919(2)	0.8138(2)	0.033(1)	0.024(1)	0.029(1)	–0.011(1)	–0.000(1)	–0.005(1)
C(6)	2*i*	0.6330(2)	0.8371(2)	0.8468(1)	0.028(1)	0.024(1)	0.020(1)	–0.009(1)	–0.0017(9)	–0.0049(9)
C(7)	2*i*	0.4098(2)	0.9026(2)	0.8431(1)	0.034(1)	0.021(1)	0.021(1)	–0.009(1)	0.000(1)	–0.0010(9)
C(8)	2*i*	0.3023(2)	0.8909(2)	0.8247(2)	0.028(1)	0.027(1)	0.030(1)	–0.006(1)	0.003(1)	–0.005(1)
C(9)	2*i*	0.2935(2)	0.8126(2)	0.7711(2)	0.032(1)	0.025(1)	0.030(1)	–0.009(1)	–0.003(1)	0.002(1)
C(10)	2*i*	0.3747(2)	0.6699(2)	0.6627(1)	0.032(1)	0.025(1)	0.028(1)	–0.015(1)	–0.004(1)	–0.001(1)
C(11)	2*i*	0.3282(2)	0.7095(2)	0.5866(2)	0.040(1)	0.030(1)	0.031(1)	–0.019(1)	–0.011(1)	0.005(1)
C(12)	2*i*	0.3157(2)	0.6366(2)	0.5305(2)	0.046(2)	0.037(2)	0.033(1)	–0.024(1)	–0.011(1)	0.003(1)
C(13)	2*i*	0.3483(2)	0.5299(2)	0.5487(2)	0.051(2)	0.031(2)	0.040(2)	–0.022(1)	–0.009(1)	–0.005(1)
C(14)	2*i*	0.3943(2)	0.4926(2)	0.6231(2)	0.048(2)	0.026(1)	0.046(2)	–0.021(1)	–0.011(1)	0.003(1)
C(15)	2*i*	0.4097(2)	0.5607(2)	0.6820(2)	0.032(1)	0.028(1)	0.031(1)	–0.016(1)	–0.005(1)	0.004(1)
C(16)	2*i*	0.5829(3)	0.7133(2)	0.9544(2)	0.054(2)	0.035(2)	0.029(1)	–0.021(1)	–0.007(1)	0.007(1)
C(17)	2*i*	0.6586(3)	0.5917(2)	0.9428(2)	0.092(2)	0.036(2)	0.038(2)	–0.027(2)	0.005(2)	0.000(1)
C(18)	2*i*	0.5297(3)	0.7446(3)	1.0469(2)	0.074(2)	0.043(2)	0.043(2)	–0.023(2)	0.015(2)	–0.000(1)
C(19)	2*i*	0.6826(2)	0.9563(2)	0.7349(2)	0.041(2)	0.033(2)	0.030(1)	–0.017(1)	–0.002(1)	0.002(1)
C(20)	2*i*	0.7968(3)	0.9108(3)	0.6673(2)	0.056(2)	0.063(2)	0.036(2)	–0.026(2)	0.006(1)	0.003(1)
C(21)	2*i*	0.6467(3)	1.0760(2)	0.7538(2)	0.083(2)	0.035(2)	0.045(2)	–0.026(2)	–0.004(2)	0.005(1)
C(22)	2*i*	0.3937(2)	0.9880(2)	0.9089(2)	0.040(1)	0.027(1)	0.032(1)	–0.008(1)	–0.002(1)	–0.011(1)
C(23)	2*i*	0.1651(2)	0.8094(2)	0.7726(2)	0.034(1)	0.048(2)	0.043(2)	–0.017(1)	–0.003(1)	–0.006(1)
C(24)	2*i*	0.2936(3)	0.8250(2)	0.5611(2)	0.071(2)	0.031(2)	0.048(2)	–0.029(2)	–0.033(2)	0.012(1)
C(25)	2*i*	0.3677(3)	0.8287(3)	0.4773(2)	0.067(2)	0.064(2)	0.072(2)	–0.041(2)	–0.030(2)	0.036(2)
C(26)	2*i*	0.1530(3)	0.8845(3)	0.5547(2)	0.074(2)	0.037(2)	0.077(3)	–0.001(2)	–0.016(2)	0.006(2)
C(27)	2*i*	0.4587(2)	0.5174(2)	0.7645(2)	0.044(2)	0.035(2)	0.036(2)	–0.021(1)	–0.011(1)	0.011(1)
C(28)	2*i*	0.5379(3)	0.3969(2)	0.7582(2)	0.049(2)	0.048(2)	0.052(2)	–0.020(2)	–0.013(1)	0.020(2)
C(29)	2*i*	0.3539(3)	0.5431(3)	0.8373(2)	0.069(2)	0.053(2)	0.043(2)	–0.016(2)	–0.004(2)	0.018(2)
C(30)	2*i*	0.8582(2)	0.3758(2)	0.7061(2)	0.028(1)	0.027(1)	0.035(1)	–0.010(1)	–0.006(1)	–0.004(1)
C(31)	2*i*	0.8433(2)	0.4493(2)	0.6426(2)	0.027(1)	0.023(1)	0.034(1)	–0.008(1)	–0.004(1)	–0.005(1)
C(32)	2*i*	0.9117(2)	0.4022(2)	0.5645(2)	0.030(1)	0.031(1)	0.038(2)	–0.006(1)	–0.005(1)	–0.007(1)
C(33)	2*i*	0.9843(2)	0.2925(2)	0.5513(2)	0.036(1)	0.033(2)	0.044(2)	–0.006(1)	–0.005(1)	–0.012(1)
C(34)	2*i*	0.9945(2)	0.2227(2)	0.6161(2)	0.034(1)	0.025(1)	0.055(2)	0.001(1)	–0.011(1)	–0.013(1)
C(35)	2*i*	0.9307(2)	0.2649(2)	0.6955(2)	0.030(1)	0.023(1)	0.049(2)	–0.007(1)	–0.014(1)	–0.001(1)
C(36)	2*i*	0.9224(2)	0.2209(2)	0.7772(2)	0.038(1)	0.025(1)	0.051(2)	–0.011(1)	–0.019(1)	0.004(1)
C(37)	2*i*	0.9717(3)	0.1191(2)	0.8100(2)	0.056(2)	0.026(2)	0.069(2)	–0.010(1)	–0.027(2)	0.008(1)
C(38)	2*i*	0.9409(3)	0.1081(3)	0.8948(2)	0.072(2)	0.035(2)	0.066(2)	–0.017(2)	–0.034(2)	0.021(2)
C(39)	2*i*	0.8613(3)	0.1959(3)	0.9470(2)	0.067(2)	0.045(2)	0.052(2)	–0.020(2)	–0.022(2)	0.019(2)
C(40)	2*i*	0.8122(3)	0.2986(2)	0.9159(2)	0.056(2)	0.040(2)	0.044(2)	–0.016(2)	–0.009(1)	0.010(1)
C(41)	2*i*	0.8444(2)	0.3083(2)	0.8313(2)	0.038(1)	0.027(1)	0.046(2)	–0.012(1)	–0.015(1)	0.008(1)
C(42)	2*i*	0.7599(2)	0.7033(2)	0.3959(2)	0.034(1)	0.025(1)	0.030(1)	–0.014(1)	–0.002(1)	–0.001(1)
C(43)	2*i*	0.6988(2)	0.7697(2)	0.4674(1)	0.034(1)	0.025(1)	0.027(1)	–0.014(1)	–0.001(1)	–0.002(1)
C(44)	2*i*	0.6445(2)	0.8794(2)	0.4505(2)	0.040(1)	0.028(1)	0.034(1)	–0.014(1)	–0.001(1)	–0.001(1)
C(45)	2*i*	0.6516(3)	0.9182(2)	0.3699(2)	0.048(2)	0.034(2)	0.042(2)	–0.019(1)	–0.009(1)	0.012(1)

Table 3. continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(46)	2*i*	0.7128(2)	0.8480(2)	0.3009(2)	0.046(2)	0.053(2)	0.027(1)	–0.025(2)	–0.009(1)	0.012(1)
C(47)	2*i*	0.7682(2)	0.7380(2)	0.3138(2)	0.036(1)	0.045(2)	0.022(1)	–0.020(1)	–0.004(1)	0.002(1)
C(48)	2*i*	0.8430(2)	0.6422(2)	0.2611(2)	0.036(1)	0.058(2)	0.024(1)	–0.026(1)	0.001(1)	–0.006(1)
C(49)	2*i*	0.8917(3)	0.6201(3)	0.1758(2)	0.049(2)	0.089(3)	0.029(2)	–0.034(2)	–0.002(1)	–0.009(2)
C(50)	2*i*	0.9661(3)	0.5145(4)	0.1491(2)	0.058(2)	0.102(3)	0.039(2)	–0.034(2)	0.010(2)	–0.032(2)
C(51)	2*i*	0.9920(3)	0.4313(3)	0.2058(2)	0.056(2)	0.076(3)	0.058(2)	–0.021(2)	0.014(2)	–0.042(2)
C(52)	2*i*	0.9455(3)	0.4502(3)	0.2900(2)	0.050(2)	0.047(2)	0.049(2)	–0.019(2)	0.003(1)	–0.020(1)
C(53)	2*i*	0.8717(2)	0.5578(2)	0.3149(2)	0.038(1)	0.048(2)	0.029(1)	–0.021(1)	0.004(1)	–0.013(1)

References

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