Crystal structure of bis[2-(benzylamino)-6-methylpyridinato]-bis(hexahydro-2-azepinato)zirconium(IV), $C_{38}H_{46}N_6O_2Zr$

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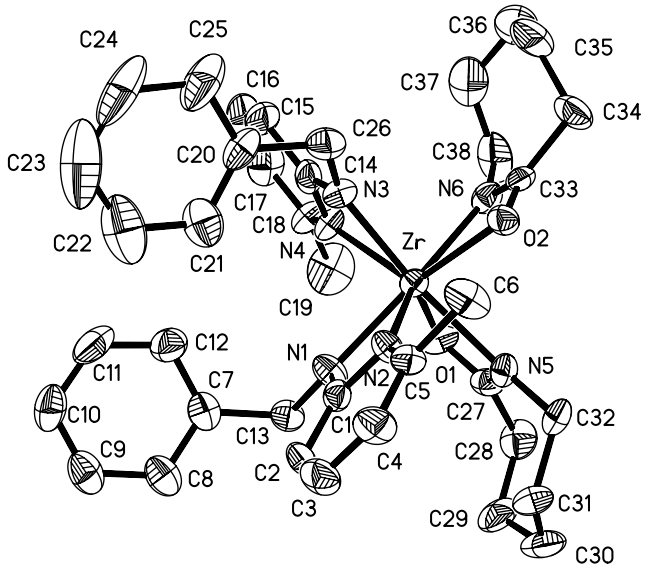

Abstract

$C_{38}H_{46}N_6O_2Zr$, monoclinic, $P12_1/c1$ (No. 14), $a = 13.575(3)$ Å, $b = 15.903(3)$ Å, $c = 17.404(3)$ Å, $\beta = 106.85(3)°$, $V = 3596.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.126$, $T = 293$ K.

Source of material

All operations are done under exclusion of air and moisture using Ar-based Schlenk-techniques. To a solution of 0.15 g (0.27 mmol) bis[2-(benzylamino)-6-methylpyridinato]-chloro-dimethylamido-zirconium(IV) in 10 ml of diethylether 0.03 g (0.3 mmol) hexahydroazepine-2-on is added. The solution is stirred at room temperature for 3 h. The volume of the solution is reduced under vacuum to 5 ml. Crystallization at 243 K affords 0.07 g (35 %) of a crystalline material. NMR data and elemental analysis are consistent with the structure of the title compound.

Discussion

Caprolactamato or hexahydro-2-azepinato transition metal complexes [1-3] have been synthesized with regard to application of such compounds as initiators for ring opening polymerization reactions. In this paper we discuss the solid state structure of the first caprolactamato zirconium compound which is also the first mononuclear biscaprolactamato complex structurally characterized with X-ray diffraction methods.

Due to the strained coordination of the aminopyridinato ligands and the caprolactamato ligands the coordination cannot be described as ideal square antiprismatic or cubic. The two *N*-donor atoms of each of the two aminopyridinato ligands are forming a plane with the *N*,*O*-donor set of the "opposite" bound caprolactamato ligand and the zirconium atom. The dihedral angle between these two planes (N1/N2/N6/O2/Zr, maximal deviation of 1.4 pm and N3/N4/N5/O1/Zr maximal deviation of 0.9 pm) is 88°. The equivalence of the Zr—N and the Zr—O distances of the caprolactamato ligands indicate a delocalized binding mode. The anionic function is not localized at any of the donor atoms.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.1 × 0.5 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.47 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ/ω
$2\theta_{max}$:	48.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10588, 5450
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3912
$N(param)_{refined}$:	424
Programs:	SHELXS-97 [4] SHELXL-93 [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.4514	–0.1114	0.2246	0.042
H(3)	4*e*	0.5866	–0.1285	0.3400	0.051
H(4)	4*e*	0.6231	–0.0245	0.4378	0.050
H(6A)	4*e*	0.4897	0.1711	0.4185	0.065
H(6B)	4*e*	0.6055	0.1439	0.4496	0.065
H(6C)	4*e*	0.5243	0.1039	0.4869	0.065
H(8)	4*e*	0.3238	–0.1790	0.0758	0.055
H(9)	4*e*	0.2379	–0.2997	0.0957	0.061
H(10)	4*e*	0.1112	–0.2937	0.1574	0.065
H(11)	4*e*	0.0711	–0.1661	0.2011	0.072
H(12)	4*e*	0.1513	–0.0450	0.1842	0.058
H(13A)	4*e*	0.3664	–0.0369	0.1022	0.044
H(13B)	4*e*	0.2625	0.0127	0.0728	0.044
H(15)	4*e*	0.0192	0.1225	0.2987	0.055
H(16)	4*e*	–0.1187	0.1336	0.1853	0.069
H(17)	4*e*	–0.0933	0.1469	0.0597	0.067
H(19A)	4*e*	0.1553	0.1581	0.0281	0.118
H(19B)	4*e*	0.0514	0.2070	–0.0056	0.118
H(19C)	4*e*	0.0535	0.1087	–0.0126	0.118
H(21)	4*e*	0.2584	–0.0265	0.3326	0.064
H(22)	4*e*	0.2113	–0.1567	0.3665	0.097
H(23)	4*e*	0.1266	–0.1716	0.4624	0.122
H(24)	4*e*	0.0902	–0.0542	0.5246	0.110
H(25)	4*e*	0.1283	0.0791	0.4885	0.088
H(26A)	4*e*	0.1781	0.1678	0.3921	0.051
H(26B)	4*e*	0.2933	0.1395	0.4132	0.051

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(28A)	4*e*	0.5035	0.2588	0.0555	0.060
H(28B)	4*e*	0.4097	0.2123	–0.0036	0.060
H(29A)	4*e*	0.4978	0.0807	0.0504	0.067
H(29B)	4*e*	0.5443	0.1306	–0.0086	0.067
H(30A)	4*e*	0.6796	0.0897	0.0991	0.073
H(30B)	4*e*	0.6712	0.1877	0.1024	0.073
H(31A)	4*e*	0.7016	0.1281	0.2301	0.059
H(31B)	4*e*	0.5990	0.0771	0.2005	0.059
H(32A)	4*e*	0.5939	0.2028	0.2778	0.045
H(32B)	4*e*	0.5965	0.2537	0.2015	0.045

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(34A)	4*e*	0.3354	0.4405	0.3057	0.057
H(34B)	4*e*	0.3806	0.3917	0.3866	0.057
H(35A)	4*e*	0.2041	0.3483	0.3740	0.092
H(35B)	4*e*	0.2314	0.4417	0.3995	0.092
H(36A)	4*e*	0.1516	0.4863	0.2694	0.105
H(36B)	4*e*	0.0740	0.4384	0.3049	0.105
H(37A)	4*e*	0.0847	0.3195	0.2300	0.098
H(37B)	4*e*	0.0482	0.3968	0.1734	0.098
H(38A)	4*e*	0.1594	0.3327	0.1208	0.071
H(38B)	4*e*	0.2231	0.4085	0.1675	0.071

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}
Zr	4*e*	0.32185(3)	0.16304(3)	0.22390(2)	0.0234(2)	0.0276(2)	0.0254(2)	0.0017(2)	0.0056(2)	0.0025(2)
N(1)	4*e*	0.3369(3)	0.0329(2)	0.1881(2)	0.046(2)	0.031(2)	0.025(2)	0.002(2)	0.003(2)	–0.007(2)
N(2)	4*e*	0.4385(2)	0.0676(2)	0.3087(2)	0.033(2)	0.022(2)	0.026(2)	0.005(2)	0.001(2)	0.002(2)
C(1)	4*e*	0.4155(3)	0.0065(3)	0.2513(2)	0.032(2)	0.027(2)	0.029(2)	–0.004(2)	0.012(2)	0.001(2)
C(2)	4*e*	0.4688(3)	–0.0688(3)	0.2628(3)	0.042(3)	0.020(2)	0.042(3)	0.001(2)	0.011(2)	–0.003(2)
C(3)	4*e*	0.5480(3)	–0.0793(3)	0.3320(3)	0.043(3)	0.029(3)	0.053(3)	0.012(2)	0.010(2)	0.006(2)
C(4)	4*e*	0.5708(3)	–0.0167(3)	0.3902(3)	0.033(2)	0.041(3)	0.043(3)	0.011(2)	0.001(2)	0.002(2)
C(5)	4*e*	0.5158(3)	0.0563(3)	0.3768(2)	0.028(2)	0.031(3)	0.029(2)	0.005(2)	0.008(2)	–0.001(2)
C(6)	4*e*	0.5356(4)	0.1250(3)	0.4385(3)	0.043(3)	0.043(3)	0.033(2)	0.011(2)	–0.005(2)	–0.007(2)
C(7)	4*e*	0.2466(3)	–0.0990(3)	0.1283(2)	0.037(2)	0.039(3)	0.022(2)	–0.006(2)	–0.006(2)	–0.004(2)
C(8)	4*e*	0.2725(4)	–0.1758(3)	0.1014(3)	0.055(3)	0.040(3)	0.035(3)	–0.003(2)	0.001(2)	–0.009(2)
C(9)	4*e*	0.2204(4)	–0.2482(3)	0.1134(3)	0.048(3)	0.039(3)	0.053(3)	–0.005(2)	–0.005(3)	–0.008(3)
C(10)	4*e*	0.1458(4)	–0.2453(4)	0.1499(3)	0.039(3)	0.055(4)	0.062(3)	–0.019(3)	0.004(3)	0.003(3)
C(11)	4*e*	0.1224(4)	–0.1686(4)	0.1756(3)	0.039(3)	0.082(5)	0.067(4)	–0.012(3)	0.030(3)	–0.005(3)
C(12)	4*e*	0.1699(4)	–0.0958(3)	0.1659(3)	0.047(3)	0.055(4)	0.049(3)	–0.008(3)	0.023(3)	–0.013(3)
C(13)	4*e*	0.3056(3)	–0.0200(3)	0.1169(2)	0.045(3)	0.040(3)	0.027(2)	–0.003(2)	0.014(2)	–0.009(2)
N(3)	4*e*	0.2203(3)	0.1331(2)	0.2968(2)	0.028(2)	0.039(2)	0.033(2)	0.003(2)	0.011(2)	0.001(2)
N(4)	4*e*	0.1416(2)	0.1433(2)	0.1661(2)	0.023(2)	0.043(3)	0.034(2)	–0.004(2)	0.010(2)	0.006(2)
C(14)	4*e*	0.1292(3)	0.1342(3)	0.2402(3)	0.033(2)	0.023(2)	0.050(3)	–0.001(2)	0.011(2)	0.005(2)
C(15)	4*e*	0.0294(3)	0.1295(3)	0.2485(3)	0.029(2)	0.044(3)	0.066(3)	0.004(2)	0.019(3)	0.003(3)
C(16)	4*e*	–0.0520(4)	0.1354(3)	0.1809(4)	0.026(3)	0.044(3)	0.093(4)	0.003(2)	0.004(3)	0.006(3)
C(17)	4*e*	–0.0373(4)	0.1441(3)	0.1056(3)	0.032(3)	0.062(4)	0.062(3)	0.000(2)	–0.005(3)	0.009(3)
C(18)	4*e*	0.0618(3)	0.1483(3)	0.1001(3)	0.027(2)	0.056(3)	0.042(3)	0.000(2)	0.013(2)	0.007(2)
C(19)	4*e*	0.0823(4)	0.1562(4)	0.0203(3)	0.065(4)	0.109(6)	0.043(3)	–0.005(4)	–0.014(3)	0.011(4)
C(20)	4*e*	0.1948(3)	0.0404(3)	0.4053(2)	0.028(2)	0.062(3)	0.029(2)	–0.009(2)	0.005(2)	0.008(2)
C(21)	4*e*	0.2221(4)	–0.0314(3)	0.3703(3)	0.065(3)	0.045(3)	0.046(3)	–0.002(3)	0.007(3)	0.007(3)
C(22)	4*e*	0.1950(5)	–0.1092(4)	0.3915(4)	0.088(5)	0.052(4)	0.075(4)	–0.005(3)	–0.019(4)	0.023(3)
C(23)	4*e*	0.1448(6)	–0.1186(5)	0.4485(4)	0.110(6)	0.091(6)	0.066(5)	–0.046(5)	–0.032(4)	0.053(5)
C(24)	4*e*	0.1224(5)	–0.0484(6)	0.4844(4)	0.077(4)	0.144(8)	0.058(4)	–0.045(5)	0.026(4)	0.035(5)
C(25)	4*e*	0.1457(4)	0.0320(4)	0.4635(3)	0.074(4)	0.106(5)	0.045(3)	–0.038(4)	0.027(3)	0.005(3)
C(26)	4*e*	0.2241(4)	0.1261(3)	0.3806(3)	0.049(3)	0.046(3)	0.036(3)	0.001(2)	0.020(2)	–0.006(2)
O(1)	4*e*	0.3154(2)	0.1883(2)	0.0958(2)	0.029(2)	0.053(2)	0.032(2)	0.008(1)	0.012(1)	0.005(1)
N(5)	4*e*	0.4642(3)	0.1961(2)	0.1898(2)	0.029(2)	0.029(2)	0.034(2)	–0.003(2)	0.007(2)	0.005(2)
C(27)	4*e*	0.4144(3)	0.1976(3)	0.1134(3)	0.044(3)	0.029(3)	0.036(3)	0.008(2)	0.020(2)	0.006(2)
C(28)	4*e*	0.4631(4)	0.2075(3)	0.0473(3)	0.061(3)	0.056(3)	0.036(3)	–0.006(3)	0.019(2)	0.008(2)
C(29)	4*e*	0.5329(4)	0.1322(4)	0.0439(3)	0.047(3)	0.080(4)	0.053(3)	–0.011(3)	0.035(3)	–0.013(3)
C(30)	4*e*	0.6373(4)	0.1355(4)	0.1084(3)	0.044(3)	0.072(4)	0.077(4)	0.008(3)	0.034(3)	–0.020(3)
C(31)	4*e*	0.6320(3)	0.1296(3)	0.1942(3)	0.027(2)	0.052(3)	0.072(4)	0.010(2)	0.018(3)	–0.003(3)
C(32)	4*e*	0.5745(3)	0.2012(3)	0.2196(3)	0.028(2)	0.042(3)	0.044(3)	–0.009(2)	0.013(2)	0.005(2)
O(2)	4*e*	0.3896(2)	0.2535(2)	0.3243(2)	0.029(2)	0.027(2)	0.035(2)	0.005(1)	0.008(1)	0.000(1)
N(6)	4*e*	0.2698(3)	0.2976(2)	0.2186(2)	0.029(2)	0.035(2)	0.039(2)	0.002(2)	0.012(2)	0.010(2)
C(33)	4*e*	0.3287(3)	0.3136(3)	0.2909(3)	0.031(2)	0.027(3)	0.047(3)	0.001(2)	0.026(2)	0.002(2)
C(34)	4*e*	0.3251(4)	0.3925(3)	0.3368(3)	0.061(3)	0.026(3)	0.057(3)	0.008(2)	0.021(3)	–0.006(2)
C(35)	4*e*	0.2224(5)	0.4021(4)	0.3557(4)	0.104(5)	0.032(3)	0.111(5)	0.004(3)	0.059(5)	–0.015(3)
C(36)	4*e*	0.1344(5)	0.4315(4)	0.2863(5)	0.067(4)	0.045(4)	0.165(7)	0.016(3)	0.057(5)	–0.010(4)
C(37)	4*e*	0.1067(4)	0.3729(4)	0.2135(4)	0.037(3)	0.045(4)	0.154(7)	0.016(3)	0.014(4)	0.012(4)
C(38)	4*e*	0.1907(4)	0.3556(3)	0.1740(3)	0.052(3)	0.030(3)	0.078(4)	0.008(2)	–0.009(3)	0.024(3)

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