Crystal structure of dimethylamido-hexahydro-2-azepinato-bis[2-(trimethylsilylamino)-4-methylpyridinato]-titanium(IV), $C_{26}H_{46}N_6OSi_2Ti$

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Abstract

$C_{26}H_{46}N_6OSi_2Ti$, triclinic, $P\bar{1}$ (No. 2), $a = 10.178(2)$ Å, $b = 10.906(2)$ Å, $c = 16.254(3)$ Å, $\alpha = 91.82(1)^\circ$, $\beta = 102.60(2)^\circ$, $\gamma = 112.81(2)^\circ$, $V = 1609.5$ Å³, $Z = 2$, $R_g(F) = 0.046$, $wR_{obs}(F^2) = 0.116$, $T = 293$ K.

Source of material

All operations are done under exclusion of air and moisture using Ar-based Schlenk technique. To a solution of 0.48 g (1.10 mmol) of bis(dimethylamido)-bis[2-(trimethylsilylamino)-4-methylpyridinato]-titanium(IV) in 30 ml of diethylether it is added 0.13 g (1.1 mmol) of hexahydroazepine-2-on. The solution is stirred at room temperature for 2 h. Crystallization at 195 K affords 0.46 g (75 %) 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 a caprolactamato titanium complex stabilized by two aminopyridinato ligands and a dimethylamido ligand. The coordination is best described as distorted pentagonal bipyramidal. The equatorial plane is occupied by the caprolactamato ligand, one aminopyridinato ligand and the *N*-pyridine function of the second aminopyridinato ligand. This five donor atoms (N2, N3, N4, N5

and O1) form a plane (mean deviation 11 pm) from which the titanium atom is 21 pm away. The two axial positions are occupied by the *N*-amido function of the second aminopyridinato ligand and the dimethylamido ligand. The equivalence of the Ti—N and the Ti—O distances of the caprolactamato ligand indicates a delocalized binding mode. The anionic function is not localized at any of the two donor atoms.

Table 1. Data collection and handling.

Crystal:	red prism, size $0.4 \times 0.5 \times 0.5$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	3.68 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 frames, $\Delta\varphi = 2^\circ$
$2\theta_{\max}$:	48.7°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4839, 4839
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3376
$N(\text{param})_{\text{refined}}$:	325
Programs:	SHELXS-97 [4] SHELXL-93 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	2i	0.2168(5)	−0.4880(4)	0.8691(2)	0.117
H(1B)	2i	0.1701(5)	−0.3880(4)	0.9144(2)	0.117
H(1C)	2i	0.3370(5)	−0.3520(4)	0.9202(2)	0.117
H(2A)	2i	0.2613(4)	−0.0894(3)	0.7657(2)	0.099
H(2B)	2i	0.3662(4)	−0.0895(3)	0.8521(2)	0.099
H(2C)	2i	0.1993(4)	−0.1253(3)	0.8461(2)	0.099
H(3A)	2i	0.0083(4)	−0.4891(4)	0.7047(2)	0.096
H(3B)	2i	0.0206(4)	−0.3537(4)	0.6698(2)	0.096
H(3C)	2i	−0.0348(4)	−0.3887(4)	0.7523(2)	0.096
H(4A)	2i	0.9662(4)	0.1451(4)	0.9364(3)	0.133
H(4B)	2i	0.8605(4)	0.1456(4)	0.9935(3)	0.133
H(4C)	2i	0.9392(4)	0.2746(4)	0.9534(3)	0.133
H(5A)	2i	0.8793(5)	0.1640(4)	0.7480(3)	0.131
H(5B)	2i	0.8563(5)	0.2928(4)	0.7733(3)	0.131
H(5C)	2i	0.7296(5)	0.1746(4)	0.7089(3)	0.131
H(6A)	2i	0.5622(5)	0.1469(4)	0.9136(3)	0.154
H(6B)	2i	0.5229(5)	0.1638(4)	0.8171(3)	0.154
H(6C)	2i	0.6496(5)	0.2817(4)	0.8817(3)	0.154
H(8A)	2i	0.3442(4)	−0.0437(3)	0.4880(2)	0.067
H(8B)	2i	0.3391(4)	0.0391(3)	0.5671(2)	0.067
H(9A)	2i	0.1020(4)	−0.0954(4)	0.5112(2)	0.077
H(9B)	2i	0.1478(4)	−0.1648(4)	0.5885(2)	0.077
H(10A)	2i	0.1217(4)	−0.2509(4)	0.4180(2)	0.084
H(10B)	2i	0.0061(4)	−0.3228(4)	0.4693(2)	0.084

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Table 2. Continued.

Atom	Site	x	y	z	<i>U</i> _{iso}
H(11A)	2i	0.1447(4)	−0.4453(4)	0.4627(2)	0.082
H(11B)	2i	0.1769(4)	−0.3870(4)	0.5576(2)	0.082
H(12A)	2i	0.3890(4)	−0.3735(4)	0.5052(2)	0.077
H(12B)	2i	0.3710(4)	−0.2560(4)	0.4578(2)	0.077
H(14)	2i	0.1758(3)	−0.5890(3)	0.7164(2)	0.053
H(16)	2i	0.4560(4)	−0.7025(3)	0.6292(2)	0.072
H(17)	2i	0.6065(4)	−0.4822(3)	0.6345(2)	0.066
H(19)	2i	0.7080(4)	−0.0600(4)	0.9990(2)	0.066
H(21)	2i	0.6700(4)	−0.4401(4)	0.9823(2)	0.081
H(22)	2i	0.6211(4)	−0.4494(4)	0.8372(2)	0.072
H(23A)	2i	0.6589(4)	−0.2327(4)	0.5568(2)	0.118

Table 2. Continued.

Atom	Site	x	y	z	<i>U</i> _{iso}
H(23B)	2i	0.7876(4)	−0.2708(4)	0.6025(2)	0.118
H(23C)	2i	0.8223(4)	−0.1272(4)	0.5752(2)	0.118
H(24A)	2i	0.8832(4)	−0.0705(4)	0.7923(3)	0.128
H(24B)	2i	0.9577(4)	−0.0297(4)	0.7168(3)	0.128
H(24C)	2i	0.9233(4)	−0.1730(4)	0.7445(3)	0.128
H(25A)	2i	0.2365(4)	−0.8718(3)	0.6455(2)	0.102
H(25B)	2i	0.1014(4)	−0.8321(3)	0.6289(2)	0.102
H(25C)	2i	0.1823(4)	−0.8351(3)	0.7222(2)	0.102
H(26A)	2i	0.7383(5)	−0.1550(5)	1.1259(2)	0.129
H(26B)	2i	0.8093(5)	−0.2592(5)	1.1240(2)	0.129
H(26C)	2i	0.6400(5)	−0.3089(5)	1.1167(2)	0.129

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	2i	0.2389(5)	−0.3951(4)	0.8844(2)	0.105(3)	0.094(3)	0.057(2)	0.055(3)	0.034(2)	0.025(2)
C(2)	2i	0.2682(4)	−0.1324(3)	0.8162(2)	0.070(2)	0.055(2)	0.081(3)	0.028(2)	0.028(2)	0.000(2)
C(3)	2i	0.0312(4)	−0.3961(4)	0.7203(2)	0.054(2)	0.061(2)	0.078(2)	0.025(2)	0.018(2)	0.009(2)
C(4)	2i	0.8948(4)	0.1784(4)	0.9446(3)	0.077(3)	0.077(3)	0.078(3)	0.007(2)	0.000(2)	−0.006(2)
C(5)	2i	0.8092(5)	0.1971(4)	0.7588(3)	0.108(4)	0.056(3)	0.078(3)	0.010(2)	0.024(3)	0.018(2)
C(6)	2i	0.6015(5)	0.1860(4)	0.8675(3)	0.088(3)	0.058(3)	0.157(5)	0.031(2)	0.021(3)	−0.018(3)
C(7)	2i	0.4250(3)	−0.0986(3)	0.6006(2)	0.045(2)	0.047(2)	0.045(2)	0.018(2)	0.013(2)	0.018(2)
C(8)	2i	0.3226(4)	−0.0500(3)	0.5434(2)	0.059(2)	0.054(2)	0.056(2)	0.027(2)	0.009(2)	0.019(2)
C(9)	2i	0.1627(4)	−0.1429(4)	0.5329(2)	0.052(2)	0.071(3)	0.066(2)	0.025(2)	0.008(2)	0.020(2)
C(10)	2i	0.1103(4)	−0.2728(4)	0.4741(2)	0.057(2)	0.076(3)	0.062(2)	0.017(2)	0.001(2)	0.016(2)
C(11)	2i	0.1904(4)	−0.3632(4)	0.5021(2)	0.077(3)	0.055(2)	0.050(2)	0.013(2)	−0.002(2)	−0.003(2)
C(12)	2i	0.3553(4)	−0.3018(4)	0.5072(2)	0.086(3)	0.075(3)	0.042(2)	0.045(2)	0.015(2)	0.003(2)
C(13)	2i	0.3612(3)	−0.4326(3)	0.7047(2)	0.047(2)	0.040(2)	0.033(2)	0.020(2)	0.007(1)	0.007(1)
C(14)	2i	0.2633(3)	−0.5684(3)	0.7001(2)	0.050(2)	0.043(2)	0.041(2)	0.018(2)	0.013(2)	0.006(1)
C(15)	2i	0.2976(4)	−0.6699(3)	0.6716(2)	0.067(2)	0.040(2)	0.044(2)	0.021(2)	0.014(2)	0.003(2)
C(16)	2i	0.4294(4)	−0.6358(3)	0.6475(2)	0.077(3)	0.044(2)	0.068(2)	0.029(2)	0.028(2)	0.002(2)
C(17)	2i	0.5192(4)	−0.5038(3)	0.6511(2)	0.067(2)	0.052(2)	0.061(2)	0.031(2)	0.030(2)	0.006(2)
C(18)	2i	0.6695(3)	−0.1469(3)	0.8779(2)	0.040(2)	0.055(2)	0.047(2)	0.019(2)	0.005(2)	0.010(2)
C(19)	2i	0.6933(4)	−0.1386(4)	0.9671(2)	0.062(2)	0.063(2)	0.045(2)	0.031(2)	0.010(2)	0.008(2)
C(20)	2i	0.6944(4)	−0.2494(4)	1.0068(2)	0.060(2)	0.083(3)	0.045(2)	0.039(2)	0.011(2)	0.018(2)
C(21)	2i	0.6688(4)	−0.3651(4)	0.9570(2)	0.084(3)	0.069(3)	0.058(2)	0.041(2)	0.012(2)	0.028(2)
C(22)	2i	0.6416(4)	−0.3697(4)	0.8701(2)	0.073(3)	0.053(2)	0.056(2)	0.034(2)	0.004(2)	0.015(2)
C(23)	2i	0.7540(4)	−0.1998(4)	0.5962(2)	0.080(3)	0.108(4)	0.078(3)	0.057(3)	0.042(2)	0.041(2)
C(24)	2i	0.8896(4)	−0.1021(4)	0.7381(3)	0.053(2)	0.087(3)	0.112(4)	0.028(2)	0.016(2)	0.003(3)
C(25)	2i	0.1951(4)	−0.8155(3)	0.6666(2)	0.085(3)	0.043(2)	0.074(2)	0.022(2)	0.025(2)	0.002(2)
C(26)	2i	0.7231(5)	−0.2425(5)	1.1019(2)	0.110(4)	0.119(4)	0.051(2)	0.068(3)	0.019(2)	0.031(2)
N(1)	2i	0.3519(3)	−0.3191(2)	0.7331(1)	0.049(2)	0.035(2)	0.042(1)	0.019(1)	0.011(1)	0.002(1)
N(2)	2i	0.4861(3)	−0.4040(2)	0.6776(2)	0.048(2)	0.045(2)	0.042(1)	0.022(1)	0.013(1)	0.009(1)
N(3)	2i	0.6613(3)	−0.0535(3)	0.8251(2)	0.051(2)	0.042(2)	0.043(1)	0.019(1)	0.006(1)	0.010(1)
N(4)	2i	0.6439(3)	−0.2627(3)	0.8317(2)	0.056(2)	0.044(2)	0.047(2)	0.021(1)	0.005(1)	0.009(1)
N(5)	2i	0.4443(3)	−0.2068(3)	0.5840(2)	0.056(2)	0.052(2)	0.038(1)	0.026(1)	0.011(1)	0.007(1)
N(6)	2i	0.7436(3)	−0.1528(3)	0.6781(2)	0.048(2)	0.057(2)	0.066(2)	0.025(2)	0.020(2)	0.019(2)
O(1)	2i	0.4977(2)	−0.0349(2)	0.6756(1)	0.059(1)	0.042(1)	0.048(1)	0.021(1)	0.002(1)	0.004(1)
Si(1)	2i	0.2251(1)	−0.31194(9)	0.78646(5)	0.0509(5)	0.0440(5)	0.0420(5)	0.0227(4)	0.0147(4)	0.0073(4)
Si(2)	2i	0.7362(1)	0.1195(1)	0.84857(6)	0.0551(6)	0.0457(6)	0.0574(6)	0.0154(5)	0.0098(5)	0.0018(5)
Ti(1)	2i	0.56550(6)	−0.18936(5)	0.71353(3)	0.0429(3)	0.0400(4)	0.0397(3)	0.0178(3)	0.0082(3)	0.0085(2)

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