Crystal structure of bis(dimethylamido)bis(2-methylaminopyridinato)titanium, $C_{16}H_{26}N_6Ti$

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Table 1. Parameters used for the X-ray data collection

Crystal:	red prism, size 0.3 x 0.3 x 0.4 mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	4.60 cm ⁻¹
Diffractometer:	Enraf-Nonius CAD4-MACH3
Scan mode:	$\omega/2\theta$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{unique}}$:	1794
Criterion for I_o :	$I_o > 2 \sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	208
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{iso}
H(1A)	4a	0.348(1)	0.3205(3)	-0.121(1)	0.125
H(1B)	4a	0.454(1)	0.2783(3)	-0.086(1)	0.125
H(1C)	4a	0.442(1)	0.3073(3)	-0.246(1)	0.125
H(2A)	4a	1.036(1)	0.4301(3)	0.571(1)	0.131
H(2B)	4a	1.003(1)	0.4722(3)	0.464(1)	0.131
H(2C)	4a	1.162(1)	0.4427(3)	0.477(1)	0.131
H(3A)	4a	1.048(1)	0.3578(3)	0.547(1)	0.117
H(3B)	4a	0.986(1)	0.3148(3)	0.591(1)	0.117
H(3C)	4a	0.963(1)	0.3552(3)	0.687(1)	0.117
H(4A)	4a	0.520(1)	0.3341(3)	0.365(1)	0.127
H(4B)	4a	0.643(1)	0.3409(3)	0.576(1)	0.127
H(4C)	4a	0.666(1)	0.3005(3)	0.480(1)	0.127
H(5A)	4a	0.371(1)	0.3929(3)	-0.133(1)	0.126
H(5B)	4a	0.325(1)	0.4354(3)	-0.069(1)	0.126
H(5C)	4a	0.231(1)	0.3945(3)	-0.047(1)	0.126
H(6A)	4a	0.550(1)	0.4155(3)	0.397(1)	0.117
H(6B)	4a	0.340(1)	0.4082(3)	0.274(1)	0.117
H(6C)	4a	0.434(1)	0.4491(3)	0.252(1)	0.117
H(11)	4a	0.721(1)	0.2640(3)	-0.171(1)	0.090
H(12)	4a	1.025(2)	0.2470(3)	-0.082(2)	0.109
H(13)	4a	1.260(2)	0.2867(4)	0.128(2)	0.105
H(14)	4a	1.190(1)	0.3392(3)	0.278(1)	0.082
H(21)	4a	1.080(1)	0.4863(3)	0.196(2)	0.094
H(22)	4a	1.004(2)	0.5020(3)	-0.108(2)	0.104
H(23)	4a	0.782(1)	0.4639(3)	-0.349(1)	0.101
H(24)	4a	0.642(1)	0.4103(3)	-0.272(1)	0.085

Source of material: Tetrakis(dimethylamido)titanium (202 μ l, 0.9 mmol) was added slowly to a solution of 2-methylaminopyridine (185 μ l, 1.8 mmol) in ether (10 ml) and stirred for 2 h. The solvent was removed in vacuo and the residue was taken up with n-hexane. At 195 K, bis(dimethylamido)bis(2-methylaminopyridinato)-titanium (243 mg, 77 %) was slowly crystallized.

Highly nitrogen coordinated group 4 metal complexes that contain a low carbon to nitrogen ratio are interesting precursors for gas phase TiN formation processes. Due to the low carbon contents TiC formation can be decreased.

$C_{16}H_{26}N_6Ti$, monoclinic, $I1a1$ (No. 9), $a=8.090(1)$ Å, $b=32.252(3)$ Å, $c=8.082(1)$ Å, $\beta=116.07(1)^\circ$, $V=1894.2$ Å³, $Z=4$, $R(F)=0.048$, $R_w(F^2)=0.068$.

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4a	0.452(1)	0.3066(3)	-0.124(1)	0.073(6)	0.084(7)	0.087(7)	-0.025(6)	0.029(6)	-0.022(6)
C(2)	4a	1.039(1)	0.4438(3)	0.467(1)	0.070(6)	0.101(8)	0.084(7)	-0.017(6)	0.027(6)	-0.022(7)
C(3)	4a	0.959(1)	0.3440(3)	0.575(1)	0.072(6)	0.090(7)	0.049(5)	0.005(5)	0.005(5)	0.014(5)

Table 3. (Continued)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(4)	4a	0.640(1)	0.3297(3)	0.465(1)	0.075(6)	0.073(7)	0.099(8)	0.004(5)	0.030(6)	0.016(6)
C(5)	4a	0.342(1)	0.4062(3)	−0.043(1)	0.062(6)	0.093(7)	0.069(7)	0.001(5)	0.003(5)	0.006(6)
C(6)	4a	0.450(1)	0.4199(3)	0.277(1)	0.079(7)	0.064(6)	0.079(7)	0.015(5)	0.024(6)	−0.009(5)
C(10)	4a	0.781(1)	0.3118(3)	0.016(1)	0.072(6)	0.060(6)	0.051(5)	−0.016(5)	0.027(5)	0.000(5)
C(11)	4a	0.816(1)	0.2787(3)	−0.079(1)	0.101(8)	0.058(6)	0.072(6)	0.000(5)	0.043(6)	−0.001(5)
C(12)	4a	0.997(2)	0.2697(3)	−0.028(2)	0.13(1)	0.063(8)	0.11(1)	0.021(7)	0.085(9)	0.012(6)
C(13)	4a	1.139(2)	0.2926(4)	0.101(2)	0.081(8)	0.093(8)	0.12(1)	0.018(6)	0.069(8)	0.026(7)
C(14)	4a	1.095(1)	0.3242(3)	0.187(1)	0.063(6)	0.075(7)	0.068(6)	0.001(5)	0.029(5)	0.011(5)
C(20)	4a	0.899(1)	0.4380(3)	0.136(1)	0.058(5)	0.056(5)	0.057(6)	0.003(4)	0.029(5)	−0.002(5)
C(21)	4a	0.991(1)	0.4711(3)	0.101(2)	0.077(6)	0.073(7)	0.096(8)	0.005(5)	0.049(6)	−0.011(6)
C(22)	4a	0.945(2)	0.4801(3)	−0.082(2)	0.111(9)	0.060(7)	0.12(1)	0.018(6)	0.078(9)	0.013(7)
C(23)	4a	0.813(1)	0.4577(3)	−0.227(1)	0.121(9)	0.086(8)	0.059(7)	0.015(7)	0.052(7)	0.014(6)
C(24)	4a	0.731(1)	0.4259(3)	−0.178(1)	0.088(6)	0.070(7)	0.067(6)	0.012(5)	0.046(6)	−0.002(5)
N(1)	4a	0.6212(9)	0.3273(2)	0.0020(9)	0.048(4)	0.075(5)	0.054(4)	−0.013(4)	0.015(4)	−0.016(4)
N(2)	4a	0.9205(9)	0.3343(2)	0.1440(9)	0.043(4)	0.062(4)	0.065(5)	0.000(3)	0.024(4)	0.008(4)
N(3)	4a	0.9120(8)	0.4229(2)	0.2958(9)	0.056(4)	0.071(5)	0.043(4)	−0.006(4)	0.017(3)	−0.002(4)
N(4)	4a	0.7706(9)	0.4158(2)	−0.0044(9)	0.073(5)	0.059(4)	0.049(4)	0.002(4)	0.027(4)	−0.003(4)
N(5)	4a	0.7766(8)	0.3501(2)	0.4255(8)	0.046(4)	0.061(4)	0.051(4)	−0.004(3)	0.010(3)	0.003(4)
N(6)	4a	0.4916(8)	0.4001(2)	0.1392(9)	0.048(4)	0.066(5)	0.052(4)	0.005(3)	0.014(4)	−0.004(4)
Ti	4a	0.7231(2)	0.37500(5)	0.1933(2)	0.0456(7)	0.0640(8)	0.0487(8)	−0.0033(9)	0.0146(6)	−0.002(1)

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References

1. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Large Structures. *Acta Crystallogr. A* **46** (1990) 467–473.
2. Sheldrick, G. M.: SHELXL-93, a program for refining crystal structures. University of Göttingen, Germany 1993.