

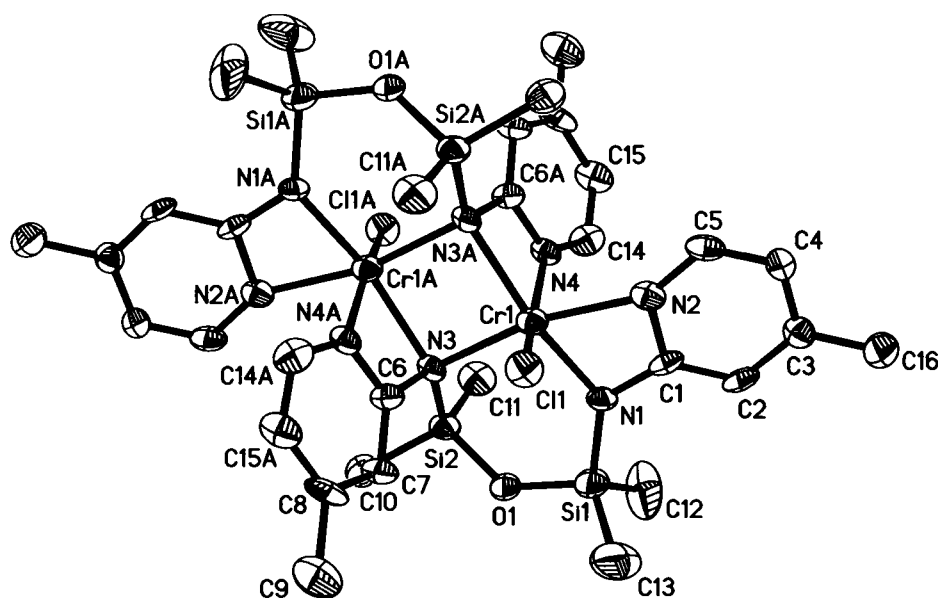
Crystal structure of bis(1,3-bis[{4-methyl-pyridin-2-yl}amido]-1,1,3,3-tetramethyldisiloxane)dichromium dichloride, $[(C_{16}H_{24}N_4OSi_2)CrCl]_2$

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Abstract

$C_{32}H_{48}Cl_2Cr_2N_8O_2Si_4$, monoclinic, $P12_1/n1$ (no. 14), $a = 12.416(2)$ Å, $b = 13.668(3)$ Å, $c = 13.172(3)$ Å, $\beta = 113.83(3)^\circ$, $V = 2044.8$ Å³, $Z = 2$, $R_{gt}(F) = 0.052$, $wR_{ref}(F^2) = 0.110$, $T = 200$ K.

Source of material

To a solution of 2.16 g (6.23 mmol) $O(SiMe_2ApH)_2$ [$O(SiMe_2ApH)_2 = O[Si(CH_3)_2NH-(4-CH_3C_5H_3N)]_2$] in 10 mL of THF was added 4.99 mL (12.46 mmol) *n*-BuLi (2.5 M in *n*-hexane) at -78°C via a syringe, stirred for 30 minutes and then allowed to warm up to -40°C . The resulting suspension was added to a suspension of 2.33 g (6.23 mmol) $[CrCl_3(thf)_3]$ in 30 mL of THF at -40°C . The dark green reaction mixture was stirred for 12 h at room temperature. After removing of the solvent the dark green residue was extracted with 10 mL of *n*-hexane and two times with 20 mL of ether. Blue-green crystals of the title compound could be obtained from the combined filtrates at -30°C (yield 1.96 g, 73 %).

Discussion

The development of amido metal chemistry of the early transition metals increased dramatically in the last decades [2]. The amido-metal bond in the complexes can be stabilized by additional N-donor functions, for instance by a pyridine moiety [3]. Recently, we developed a series of siloxane-bridged bis(2-aminopyridines) which were used as dianionic ligands after deprotonation [1].

The title compound is a dinuclear dichloro chromium(III) complex. Each of the chromium atoms adopt an octahedral coordination, as preferred by Cr(III) complexes [4]. Both chromium atoms are axial coordinated by one chloro ligand in a *transoid* arrangement. Each siloxane-bridged bis(aminopyridinato) ligand uses a pair of adjacent pyridyl and amido N donor atoms to chelate one chromium atom equatorial to the Cr1, N3, Cr1A, N3A plane, while the second amido nitrogen atom bridged both chromium atoms. The second N atom on the other pyridyl group is used for coordination of the second chromium atom. The chelating N3A–Cr–N4 angle (65.31°) is much smaller than the chelating N1–Cr–N2 angle (66.04°). The bond lengths observed for N3–Cr1 (2.139 Å) and N3–Cr1A (2.170 Å) reflect delocalized bonding mode. The two Cr atoms are separated by a distance of 3.185 Å. The length of the Cr1–N2_{pyridinato} bond is almost 0.103 Å longer than the Cr1–N1_{amido} bond. This difference indicates a localized bonding mode.

Table 1. Data collection and handling.

Crystal:	blue-green prism, size $0.2 \times 0.3 \times 0.4$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	8.19 cm^{-1}
Diffractionmeter, scan mode:	Stoe IPDS I, φ
$2\theta_{\text{max}}$:	42.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4054, 2095
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1256
$N(\text{param})_{\text{refined}}$:	226
Programs:	SHELXS-86 [5], SHELXL-93 [6]

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

Atom	Site	x	y	z	U _{iso}
H(2)	4e	1.1647	0.4243	0.1397	0.038
H(4)	4e	0.8348	0.3225	-0.0117	0.043
H(5)	4e	0.7953	0.3765	0.1342	0.040
H(7)	4e	1.2035	0.7295	0.5228	0.038
H(9A)	4e	1.1063	0.9718	0.5492	0.083
H(9B)	4e	1.1480	0.9176	0.4635	0.083
H(9C)	4e	1.2304	0.9163	0.5934	0.083
H(10A)	4e	1.3243	0.5713	0.7784	0.062
H(10B)	4e	1.3333	0.6636	0.7073	0.062
H(10C)	4e	1.4334	0.5812	0.7436	0.062
H(11A)	4e	1.2745	0.3702	0.6720	0.066
H(11B)	4e	1.3847	0.3839	0.6396	0.066

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(11C)	4e	1.2578	0.3585	0.5456	0.066
H(12A)	4e	1.3575	0.4203	0.2821	0.141
H(12B)	4e	1.3746	0.3811	0.4022	0.141
H(12C)	4e	1.4591	0.4650	0.3910	0.141
H(13A)	4e	1.2643	0.6247	0.2128	0.137
H(13B)	4e	1.3655	0.6676	0.3232	0.137
H(13C)	4e	1.2303	0.6920	0.2948	0.137
H(14)	4e	1.1275	0.2623	0.4007	0.045
H(15)	4e	1.0431	0.1168	0.4159	0.045
H(16A)	4e	0.9598	0.3016	-0.1027	0.072
H(16B)	4e	1.0947	0.2843	-0.0213	0.072
H(16C)	4e	1.0536	0.3878	-0.0815	0.072

Table 3. 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)	4e	1.0653(6)	0.4452(5)	0.2270(7)	0.023(5)	0.026(4)	0.040(7)	0.004(4)	0.021(5)	0.009(4)
C(2)	4e	1.0886(6)	0.4137(5)	0.1384(7)	0.021(4)	0.038(5)	0.048(7)	0.001(4)	0.024(5)	0.006(5)
C(3)	4e	1.0055(7)	0.3678(5)	0.0489(7)	0.029(5)	0.029(5)	0.034(6)	0.002(4)	0.012(5)	-0.003(4)
C(4)	4e	0.8947(7)	0.3542(5)	0.0491(7)	0.036(5)	0.041(5)	0.031(6)	-0.008(4)	0.015(5)	-0.009(4)
C(5)	4e	0.8718(6)	0.3861(5)	0.1359(7)	0.016(4)	0.036(5)	0.044(7)	-0.003(4)	0.008(5)	0.002(4)
C(6)	4e	1.0807(6)	0.6469(5)	0.5498(6)	0.025(5)	0.028(5)	0.036(6)	-0.003(4)	0.014(4)	0.001(4)
C(7)	4e	1.1355(6)	0.7327(5)	0.5387(7)	0.023(4)	0.026(5)	0.043(6)	-0.005(4)	0.012(4)	-0.001(4)
C(8)	4e	1.0905(7)	0.8233(5)	0.5508(7)	0.036(5)	0.015(5)	0.043(6)	-0.008(4)	0.002(4)	0.005(4)
C(9)	4e	1.1488(7)	0.9151(5)	0.5381(8)	0.048(5)	0.040(6)	0.068(8)	0.000(4)	0.013(5)	-0.003(5)
C(10)	4e	1.3489(6)	0.5934(5)	0.7202(7)	0.028(5)	0.049(5)	0.050(7)	0.002(4)	0.018(5)	-0.003(4)
C(11)	4e	1.2998(6)	0.3942(5)	0.6150(7)	0.023(4)	0.050(5)	0.053(7)	0.008(4)	0.009(4)	-0.001(5)
C(12)	4e	1.3788(7)	0.4388(9)	0.3597(9)	0.029(5)	0.17(1)	0.077(9)	0.011(6)	0.020(6)	-0.057(8)
C(13)	4e	1.2849(9)	0.6420(7)	0.2906(8)	0.090(8)	0.12(1)	0.037(8)	-0.063(7)	0.002(6)	0.007(6)
C(14)	4e	1.0593(7)	0.2636(6)	0.4165(7)	0.027(5)	0.043(6)	0.039(7)	0.006(4)	0.011(5)	0.009(4)
C(15)	4e	1.0098(7)	0.1768(5)	0.4256(7)	0.031(5)	0.021(5)	0.055(7)	0.008(4)	0.011(5)	0.001(4)
C(16)	4e	1.0306(7)	0.3323(6)	-0.0476(7)	0.040(5)	0.065(6)	0.044(7)	-0.008(4)	0.021(5)	-0.009(5)
N(1)	4e	1.1346(5)	0.4879(4)	0.3248(6)	0.018(3)	0.032(4)	0.033(5)	-0.006(3)	0.011(3)	-0.004(3)
N(2)	4e	0.9538(5)	0.4308(4)	0.2242(5)	0.021(4)	0.027(4)	0.039(5)	0.002(3)	0.009(4)	0.000(3)
N(3)	4e	1.1142(4)	0.5477(4)	0.5453(5)	0.020(3)	0.018(3)	0.040(5)	0.001(3)	0.013(3)	-0.010(3)
N(4)	4e	1.0170(5)	0.3496(4)	0.4288(5)	0.021(4)	0.019(4)	0.038(5)	0.002(3)	0.010(3)	-0.006(3)
O(1)	4e	1.3098(4)	0.5647(3)	0.4961(4)	0.021(3)	0.048(3)	0.035(4)	-0.008(2)	0.013(3)	-0.007(3)
Si(1)	4e	1.2750(2)	0.5334(2)	0.3670(2)	0.025(1)	0.062(2)	0.041(2)	-0.011(1)	0.015(1)	-0.007(1)
Si(2)	4e	1.2666(2)	0.5262(2)	0.5920(2)	0.019(1)	0.034(1)	0.038(2)	-0.0015(9)	0.011(1)	-0.004(1)
Cl(1)	4e	0.9331(2)	0.6413(1)	0.3020(2)	0.041(1)	0.032(1)	0.039(2)	0.0031(9)	0.015(1)	0.004(1)
Cr(1)	4e	1.00877(9)	0.49344(8)	0.3829(1)	0.0204(7)	0.0275(7)	0.0328(9)	0.0009(5)	0.0104(6)	-0.0001(6)

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References

- Oberthür, M.; Arndt, P.; Kempe, R.: Synthesis and Structure of Mononuclear Titanium Complexes Containing *ansa*-Aminopyridinato Ligands. *Chem. Ber.* **129** (1996) 1087-1091.
- Kempe, R.: Highlights in the Renaissance of Amidometal Chemistry. *Angew. Chem., Int. Ed.* **39** (2000) 468-493.
- Kempe, R.: The Strained μ_2 -*N*-Amido-*N*-Pyridine Coordination of Aminopyridinato Ligands. *Eur. J. Inorg. Chem.* (2003) 791-803.
- Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M.: *Advanced Inorganic Chemistry*. John Wiley & Sons, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto 1999, p. 737-747.
- Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46** (1990) 467-473.
- Sheldrick, G. M.: SHELXL-93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1993.