Crystal structure of di-μ-chloro-bis(tetrahyrofurano)lithium bis(tetrahydrofurano)dichlorotitanate, $(THF)_2Li(\mu\text{-}Cl)_2Ti(THF)_2Cl_2$

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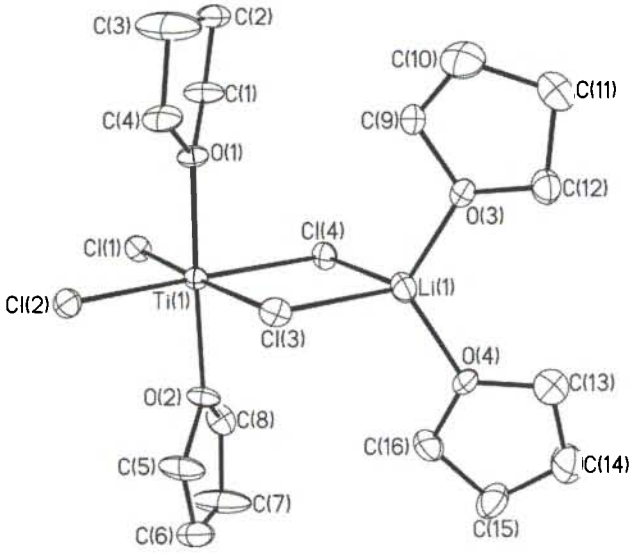

Abstract

$C_{16}H_{32}Cl_4LiO_4Ti$, monoclinic, $P12_1/c1$ (No. 14), $a = 22.4727(4)$ Å, $b = 10.2609(3)$ Å, $c = 20.0375(3)$ Å, $\beta = 77.832(1)°$, $V = 4516.6$ Å^3, $Z = 8$, $R_{gt}(F) = 0.089$, $wR(F^2) = 0.231$, $T = 173$ K.

Source of material

Addition of a solution of 2,6-dimesitylphenyllithium [1] (0.32 g, 1.0 mmol) in 10 ml tetrahydrofuran to a yellow solution of $TiCl_4(THF)_2$ (0.33 g, 1.0 mmol) in 10 ml tetrahydrofuran caused a color change to turquoise. The reaction mixture was stirred for 10 minutes and centrifuged. The solvent was removed, the residues were washed with hexanes and subsequently extracted with tetrahydrofuran. Cooling to 243 K resulted in almost complete crystallization of $(THF)_2Li(\mu\text{-}Cl)_2Ti(THF)_2Cl_2$ (**I**). Removal of the mother liquor followed by drying under vacuum gave the title compound as a turquoise microcrystalline material (0.29 g, 60%). Analytically pure complex **I** is completely insoluble in hexane and aromatic solvents, but soluble in tetrahydrofuran. Single crystals of **I** suitable for diffraction studies were grown from a THF solution by slow evaporation of solvent at ambient temperature. Alternatively, complex **I** can be prepared from $TiCl_3$ and 2,6-dimesitylphenyl-lithium (1 : 1) in tetrahydrofuran at room temperature.

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Discussion

The title compound crystallizes as two crystallographically independent but chemically equivalent molecules. The Li–Cl bond distances differ from Li(1) to Li(2) by approximately 0.13 Å on average. The contraction of the Li–Cl bond distance results in a lengthening of the Li–O bond distances by approximately 0.03 Å on average.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.15 × 0.20 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.69 cm^{-1}
Diffractometer, scan mode:	Siemens P4 equipped with a CCD area detector, φ and ω scans
$2\theta_{max}$:	48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15712, 7004
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4012
$N(param)_{refined}$:	469
Programs:	SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.2464	0.5770	0.4845	0.062
H(1B)	4e	0.2352	0.7270	0.4670	0.062
H(2A)	4e	0.1445	0.6525	0.4601	0.052
H(2B)	4e	0.1694	0.5071	0.4415	0.052
H(3A)	4e	0.1648	0.5622	0.3358	0.124
H(3B)	4e	0.1661	0.7156	0.3520	0.124
H(4A)	4e	0.2613	0.5596	0.2973	0.055
H(4B)	4e	0.2608	0.7157	0.3038	0.055
H(5A)	4e	0.5092	0.5575	0.2727	0.069
H(5B)	4e	0.5093	0.7136	0.2778	0.069
H(6A)	4e	0.5974	0.7067	0.2989	0.066
H(6B)	4e	0.5963	0.5502	0.2967	0.066
H(7A)	4e	0.5878	0.6979	0.4069	0.117
H(7B)	4e	0.5827	0.5419	0.4051	0.117
H(8A)	4e	0.4884	0.5601	0.4539	0.053
H(8B)	4e	0.4917	0.7163	0.4465	0.053
H(9A)	4e	0.2612	0.3409	0.3470	0.067
H(9B)	4e	0.2324	0.2970	0.4240	0.067
H(10A)	4e	0.2101	0.1908	0.3028	0.077
H(10B)	4e	0.1652	0.1935	0.3772	0.077
H(11A)	4e	0.2097	0.0159	0.4137	0.062
H(11B)	4e	0.2198	–0.0202	0.3338	0.062
H(12A)	4e	0.3119	–0.0032	0.3903	0.054
H(12B)	4e	0.3181	0.0422	0.3121	0.054
H(13A)	4e	0.4414	0.0009	0.3559	0.088
H(13B)	4e	0.4259	0.0407	0.4352	0.088

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(14A)	4*e*	0.5174	–0.0060	0.4392	0.112
H(14B)	4*e*	0.5347	–0.0278	0.3581	0.112
H(15A)	4*e*	0.5831	0.1525	0.3462	0.074
H(15B)	4*e*	0.5658	0.1741	0.4276	0.074
H(16A)	4*e*	0.4953	0.3162	0.4175	0.061
H(16B)	4*e*	0.5187	0.3085	0.3362	0.061
H(17A)	4*e*	0.0011	1.1529	0.5589	0.049
H(17B)	4*e*	0.0073	0.9972	0.5516	0.049
H(18A)	4*e*	–0.0941	1.1239	0.5982	0.114
H(18B)	4*e*	–0.0852	0.9693	0.6038	0.114
H(19A)	4*e*	–0.1001	0.9921	0.7103	0.056
H(19B)	4*e*	–0.0991	1.1479	0.7034	0.056
H(20A)	4*e*	–0.0110	1.1511	0.7286	0.060
H(20B)	4*e*	–0.0106	0.9945	0.7318	0.060
H(21A)	4*e*	0.2328	1.0202	0.7062	0.045
H(21B)	4*e*	0.2418	1.1737	0.6909	0.045
H(22A)	4*e*	0.3232	0.9701	0.6425	0.074
H(22B)	4*e*	0.3391	1.1164	0.6619	0.074
H(23A)	4*e*	0.3526	1.0541	0.5371	0.053

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(23B)	4*e*	0.3275	1.1972	0.5612	0.053
H(24A)	4*e*	0.2486	1.1349	0.5170	0.052
H(24B)	4*e*	0.2606	0.9825	0.5282	0.052
H(25A)	4*e*	0.2082	0.4583	0.5886	0.060
H(25B)	4*e*	0.1751	0.4642	0.6678	0.060
H(26A)	4*e*	0.2897	0.4191	0.6228	0.094
H(26B)	4*e*	0.2594	0.4605	0.6998	0.094
H(27A)	4*e*	0.3291	0.6132	0.5982	0.071
H(27B)	4*e*	0.3163	0.6353	0.6796	0.071
H(28A)	4*e*	0.2378	0.7646	0.6776	0.062
H(28B)	4*e*	0.2622	0.7710	0.5962	0.062
H(29A)	4*e*	0.0091	0.7510	0.5733	0.069
H(29B)	4*e*	–0.0165	0.7594	0.6543	0.069
H(30A)	4*e*	–0.0641	0.6131	0.5694	0.083
H(30B)	4*e*	–0.0812	0.6016	0.6514	0.083
H(31A)	4*e*	–0.0312	0.4176	0.6473	0.083
H(31B)	4*e*	–0.0192	0.4230	0.5654	0.083
H(32A)	4*e*	0.0677	0.4423	0.6331	0.058
H(32B)	4*e*	0.0741	0.4947	0.5563	0.058

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}
Ti(1)	4*e*	0.37529(6)	0.6293(1)	0.37560(7)	0.0251(8)	0.0292(8)	0.0194(7)	–0.0002(6)	–0.0033(6)	–0.0004(6)
Li(1)	4*e*	0.3765(6)	0.288(1)	0.3742(8)	0.044(9)	0.034(7)	0.043(8)	–0.005(7)	–0.002(7)	0.006(7)
Cl(1)	4*e*	0.36512(9)	0.7853(2)	0.46359(9)	0.039(1)	0.033(1)	0.028(1)	–0.0028(9)	–0.0019(9)	–0.0068(9)
Cl(2)	4*e*	0.38504(9)	0.7888(2)	0.2898(1)	0.042(1)	0.044(1)	0.029(1)	0.006(1)	–0.002(1)	0.009(1)
Cl(3)	4*e*	0.38584(9)	0.4541(2)	0.2910(1)	0.038(1)	0.040(1)	0.027(1)	–0.0023(9)	–0.0049(9)	–0.0074(9)
Cl(4)	4*e*	0.36562(9)	0.4525(2)	0.4597(1)	0.041(1)	0.036(1)	0.024(1)	–0.0006(9)	–0.0046(9)	0.0047(9)
O(1)	4*e*	0.2815(2)	0.6242(5)	0.3846(3)	0.023(3)	0.043(3)	0.027(3)	0.002(2)	–0.006(2)	–0.008(3)
O(2)	4*e*	0.4699(2)	0.6256(5)	0.3653(3)	0.021(3)	0.059(4)	0.020(3)	–0.004(3)	–0.001(2)	0.001(3)
O(3)	4*e*	0.3043(2)	0.1912(5)	0.3793(3)	0.033(3)	0.029(3)	0.075(5)	0.004(3)	–0.011(3)	0.002(3)
O(4)	4*e*	0.4485(2)	0.1913(5)	0.3722(3)	0.027(3)	0.030(3)	0.075(4)	0.007(2)	–0.010(3)	0.001(3)
C(1)	4*e*	0.2365(3)	0.6366(9)	0.4495(5)	0.022(5)	0.082(7)	0.047(6)	0.002(5)	0.003(4)	–0.006(5)
C(2)	4*e*	0.1781(3)	0.6009(8)	0.4326(5)	0.024(5)	0.041(5)	0.063(7)	0.000(4)	–0.006(4)	–0.021(5)
C(3)	4*e*	0.1848(4)	0.630(2)	0.3583(6)	0.034(6)	0.21(2)	0.067(9)	–0.009(8)	–0.019(6)	0.020(9)
C(4)	4*e*	0.2499(3)	0.6335(9)	0.3292(4)	0.029(5)	0.080(7)	0.032(5)	0.002(5)	–0.016(4)	0.009(5)
C(5)	4*e*	0.5145(4)	0.632(1)	0.3023(4)	0.036(5)	0.110(8)	0.022(5)	–0.003(5)	0.008(4)	0.001(5)
C(6)	4*e*	0.5739(4)	0.628(1)	0.3174(5)	0.033(5)	0.079(7)	0.048(6)	0.008(5)	–0.001(5)	0.008(5)
C(7)	4*e*	0.5659(4)	0.624(1)	0.3911(6)	0.023(6)	0.20(2)	0.065(9)	–0.003(7)	–0.007(5)	–0.002(9)
C(8)	4*e*	0.5010(4)	0.6329(8)	0.4216(4)	0.051(6)	0.046(5)	0.038(5)	–0.012(4)	–0.016(5)	0.000(4)
C(9)	4*e*	0.2509(4)	0.2649(8)	0.3777(5)	0.039(5)	0.033(5)	0.091(8)	0.002(4)	–0.002(5)	0.022(5)
C(10)	4*e*	0.2076(4)	0.178(1)	0.3523(5)	0.053(7)	0.087(8)	0.061(7)	0.001(6)	–0.031(5)	0.009(6)
C(11)	4*e*	0.2292(4)	0.0442(9)	0.3669(5)	0.059(6)	0.057(6)	0.042(6)	–0.016(5)	–0.017(5)	0.006(5)
C(12)	4*e*	0.2965(4)	0.0583(8)	0.3598(5)	0.050(6)	0.037(5)	0.049(6)	–0.002(4)	–0.011(5)	0.006(4)
C(13)	4*e*	0.4533(5)	0.058(1)	0.3906(6)	0.063(7)	0.062(7)	0.088(9)	0.001(6)	0.000(6)	0.009(6)
C(14)	4*e*	0.5159(5)	0.034(1)	0.3946(7)	0.064(8)	0.055(7)	0.16(1)	0.003(6)	–0.026(8)	0.029(8)
C(15)	4*e*	0.5491(4)	0.1554(9)	0.3867(6)	0.058(7)	0.051(6)	0.081(8)	0.016(5)	–0.026(6)	0.001(6)
C(16)	4*e*	0.5032(4)	0.2566(8)	0.3778(5)	0.048(6)	0.040(5)	0.062(6)	–0.013(4)	–0.007(5)	–0.003(5)
Ti(2)	4*e*	0.12109(6)	1.0743(1)	0.62582(7)	0.0244(8)	0.0231(7)	0.0214(8)	–0.0005(6)	–0.0031(6)	–0.0004(6)
Li(2)	4*e*	0.1236(6)	0.734(1)	0.6278(8)	0.028(7)	0.032(7)	0.057(9)	–0.008(6)	–0.010(7)	0.005(7)
Cl(5)	4*e*	0.12791(9)	1.2274(2)	0.5372(1)	0.043(1)	0.030(1)	0.032(1)	0.0056(9)	–0.0004(9)	0.0066(9)
Cl(6)	4*e*	0.11247(9)	1.2357(2)	0.71108(9)	0.041(1)	0.027(1)	0.031(1)	–0.0073(9)	–0.0019(9)	–0.0086(9)
Cl(7)	4*e*	0.11267(9)	0.9003(2)	0.7106(1)	0.036(1)	0.029(1)	0.027(1)	–0.0029(8)	–0.0045(9)	0.0034(8)
Cl(8)	4*e*	0.13188(9)	0.8968(2)	0.5423(1)	0.038(1)	0.028(1)	0.027(1)	–0.0013(8)	–0.0061(9)	–0.0061(8)
O(5)	4*e*	0.0271(2)	1.0665(5)	0.6389(3)	0.032(3)	0.039(3)	0.021(3)	–0.003(2)	–0.010(2)	0.000(2)
O(6)	4*e*	0.2154(2)	1.0737(5)	0.6146(3)	0.022(3)	0.042(3)	0.025(3)	–0.005(2)	–0.003(2)	0.003(2)
O(7)	4*e*	0.1966(2)	0.6377(5)	0.6259(3)	0.033(3)	0.035(3)	0.056(4)	0.000(3)	–0.013(3)	0.005(3)
O(8)	4*e*	0.0525(2)	0.6334(5)	0.6272(3)	0.035(3)	0.029(3)	0.055(4)	0.001(3)	–0.010(3)	–0.001(3)
C(17)	4*e*	–0.0062(3)	1.0694(9)	0.5841(4)	0.034(5)	0.055(6)	0.035(5)	–0.005(4)	–0.011(4)	–0.006(4)
C(18)	4*e*	–0.0702(4)	1.055(1)	0.6153(5)	0.032(6)	0.22(2)	0.037(7)	0.002(8)	–0.015(5)	0.004(8)
C(19)	4*e*	–0.0767(4)	1.0670(9)	0.6871(5)	0.029(5)	0.060(6)	0.048(6)	–0.002(4)	–0.005(4)	0.003(5)
C(20)	4*e*	–0.0162(3)	1.070(1)	0.7033(4)	0.022(5)	0.088(7)	0.037(6)	0.007(5)	0.000(4)	–0.014(5)
C(21)	4*e*	0.2477(4)	1.0857(8)	0.6703(4)	0.044(5)	0.048(5)	0.024(5)	–0.010(4)	–0.020(4)	0.003(4)
C(22)	4*e*	0.3125(4)	1.063(1)	0.6391(5)	0.039(6)	0.092(8)	0.059(7)	–0.006(5)	–0.017(5)	0.006(6)
C(23)	4*e*	0.3190(4)	1.1027(8)	0.5667(4)	0.043(5)	0.043(5)	0.040(6)	–0.008(4)	0.009(4)	–0.005(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(24)	4*e*	0.2593(3)	1.0701(9)	0.5491(4)	0.036(5)	0.060(6)	0.030(5)	–0.002(4)	0.003(4)	–0.001(4)
C(25)	4*e*	0.2078(4)	0.5031(7)	0.6325(5)	0.062(7)	0.018(4)	0.067(7)	0.002(4)	–0.005(5)	0.005(4)
C(26)	4*e*	0.2654(4)	0.4871(9)	0.6514(7)	0.060(7)	0.043(6)	0.14(1)	0.002(5)	–0.035(7)	0.011(6)
C(27)	4*e*	0.2972(4)	0.6142(9)	0.6407(6)	0.047(6)	0.060(6)	0.076(8)	–0.002(5)	–0.024(6)	0.014(6)
C(28)	4*e*	0.2482(4)	0.7117(9)	0.6354(5)	0.047(6)	0.057(6)	0.055(6)	–0.009(5)	–0.023(5)	–0.004(5)
C(29)	4*e*	–0.0008(4)	0.6994(8)	0.6159(6)	0.036(5)	0.036(5)	0.103(9)	0.010(4)	–0.018(5)	0.021(5)
C(30)	4*e*	–0.0474(4)	0.599(1)	0.6108(6)	0.036(6)	0.069(7)	0.10(1)	0.003(5)	–0.013(6)	–0.016(7)
C(31)	4*e*	–0.0147(4)	0.4716(9)	0.6067(6)	0.053(7)	0.056(6)	0.099(9)	–0.023(5)	–0.019(6)	–0.015(6)
C(32)	4*e*	0.0503(4)	0.5028(7)	0.6037(5)	0.061(6)	0.021(4)	0.063(7)	0.003(4)	–0.016(5)	–0.013(4)

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