Influence of ligand backbone flexibility in group 4 complexes of tetradentate mixed tertiary amine / alkoxide ligands

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Supporting Information (45 pages)

1. Synthesis of *N*,*N*'-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane

N,*N*'-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane was synthesized in an analogous manner to $H_2\mathbf{L}^1$, using 1,4-diazacyclohexane (0.77 g, 8.94 mmol) and isolated as colourless needles. ^{1}H and ^{13}C NMR data for crystalline samples re-dissolved in chloroform-d imply that only one set of diastereomers is present; an X-ray crystallographic study indicates that this is the meso (*R*,*S*) isomer. Yield: 1.15 g, 40 %. ^{1}H NMR ($CDCl_3$, 25°C): δ 0.85 (s, 18H, ^{t}Bu), 2.25 (m, 4H, C*H*$_2$CHOH), 2.65 (br m, 8H, NCH_2) 3.26 (m ,2H, C*H*OH), 3.60 (br s, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.7 (CH_3 of ^{t}Bu), 33.3 (^{t}Bu quaternary), 53.4 (1,4-diazacyclohexane ring), 58.9 (*C*H_2CHOH), 76.9 (*C*HOH). Mass spec. (APCI) 287.1, $(M+H)^+$. IR (KBr disk, cm^{-1}) 3218, 2953, 2361, 1482, 1456, 1411, 1383, 1358, 1326, 1267, 1243, 1187, 1151, 1100, 1054, 1017, 995, 945.

2. Details of the crystal structure of $L^1Ti_2(O^iPr)_6$

Table 2/1 Crystal data and structure refinement.

Empirical formula	C35 H76 N2 O8 Ti2
Formula weight	748.78
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.0190(5) A alpha = 70.240(3) deg. b = 14.3144(6) A beta = 88.145(2) deg. c = 15.7604(8) A gamma = 71.787(2) deg.
Volume	2214.83(18) A^3
Z	2
Density (calculated)	1.123 Mg/m^3
Absorption coefficient	0.404 mm^-1
F(000)	816
Crystal size	0.20 x 0.18 x 0.15 mm
Theta range for data collection	3.05 to 25.39 deg.
Index ranges	-13<=h<=13, -17<=k<=17, -18<=l<=19
Reflections collected	31559
Independent reflections	8020 [R(int) = 0.1319]
Max. and min. transmission	0.9419 and 0.9236
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8020 / 0 / 442
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1524
R indices (all data)	R1 = 0.1451, wR2 = 0.1758
Largest diff. peak and hole	0.451 and -0.427 e.A^-3

Table 2/2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s92.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	2806(1)	2566(1)	2140(1)	36(1)
Ti(2)	447(1)	2440(1)	6304(1)	38(1)
O(1)	1414(3)	3251(2)	1284(2)	40(1)
O(2)	3924(3)	2183(2)	1379(2)	45(1)
O(3)	3576(3)	3334(2)	2510(2)	44(1)
O(4)	2905(3)	1290(2)	2961(2)	46(1)
O(5)	1252(3)	3184(2)	6715(2)	41(1)
O(6)	-359(3)	2060(3)	7306(2)	50(1)
O(7)	-935(3)	3162(3)	5466(2)	49(1)
O(8)	1389(3)	1150(2)	6291(2)	48(1)
N(1)	1064(3)	3117(3)	2980(2)	33(1)
N(2)	1724(3)	3038(3)	5115(2)	34(1)
C(1)	752(4)	4246(3)	2885(3)	40(1)
C(2)	1063(4)	4147(3)	4523(3)	39(1)
C(3)	1442(5)	4492(4)	3560(3)	46(1)
C(4)	2168(4)	2343(3)	4561(3)	36(1)
C(5)	1092(4)	2428(3)	3936(3)	37(1)
C(6)	100(4)	3530(4)	1453(3)	37(1)
C(7)	25(4)	3023(4)	2464(3)	39(1)
C(8)	-705(4)	3250(4)	847(3)	45(1)
C(9)	-215(6)	2074(4)	1000(4)	67(2)
C(10)	-577(5)	3861(4)	-153(3)	58(1)
C(11)	-2100(5)	3580(5)	1050(4)	70(2)
C(12)	4099(5)	2144(4)	485(3)	55(1)
C(13)	4175(10)	1065(6)	527(5)	145(4)
C(14)	5229(6)	2460(7)	139(4)	102(3)
C(15)	4657(4)	3677(4)	2237(3)	53(1)
C(16)	4212(7)	4763(6)	1555(6)	132(3)
C(17)	5367(6)	3621(7)	3047(5)	115(3)
C(18)	3585(4)	228(4)	3094(3)	44(1)
C(19)	2693(5)	-255(4)	2821(4)	68(2)
C(20)	4113(5)	-324(4)	4064(3)	61(1)
C(21)	2372(4)	3434(4)	6409(3)	39(1)
C(22)	2839(4)	2955(4)	5671(3)	39(1)
C(23)	3369(4)	3075(4)	7211(3)	47(1)
C(24)	4605(4)	3305(4)	6860(4)	62(2)
C(25)	3672(5)	1914(4)	7758(3)	58(1)
C(26)	2800(5)	3723(4)	7822(3)	60(2)
C(27)	-489(5)	2035(5)	8209(3)	56(1)
C(28)	283(8)	978(6)	8837(4)	113(3)
C(29)	-1872(5)	2346(6)	8369(4)	87(2)
C(30)	-2182(5)	3077(5)	5457(5)	76(2)
C(31)	-3142(5)	4070(5)	5215(6)	112(3)
C(32)	-2238(6)	2329(5)	5035(4)	80(2)
C(33)	1459(5)	94(4)	6795(3)	47(1)
C(34)	1161(6)	-394(4)	6140(4)	71(2)
C(35)	2763(6)	-486(5)	7269(5)	93(2)

Table 2/3 Bond lengths [A] and angles [deg].

Ti(1)-O(2)	1.784(3)
Ti(1)-O(4)	1.820(3)
Ti(1)-O(3)	1.821(3)
Ti(1)-O(1)	1.853(3)
Ti(1)-N(1)	2.378(3)
Ti(2)-O(6)	1.792(3)
Ti(2)-O(8)	1.820(3)
Ti(2)-O(7)	1.831(3)
Ti(2)-O(5)	1.853(3)
Ti(2)-N(2)	2.391(3)
O(1)-C(6)	1.418(5)
O(2)-C(12)	1.433(5)
O(3)-C(15)	1.426(5)
O(4)-C(18)	1.413(5)
O(5)-C(21)	1.415(5)
O(6)-C(27)	1.415(5)
O(7)-C(30)	1.418(5)
O(8)-C(33)	1.429(5)
N(1)-C(7)	1.489(5)
N(1)-C(5)	1.491(5)
N(1)-C(1)	1.499(5)
N(2)-C(22)	1.484(5)
N(2)-C(2)	1.496(5)
N(2)-C(4)	1.498(5)
C(1)-C(3)	1.518(6)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.518(6)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.515(5)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.522(6)
C(6)-C(8)	1.549(5)
C(6)-H(6)	1.0000
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(11)	1.518(7)
C(8)-C(9)	1.533(7)
C(8)-C(10)	1.550(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(14)	1.481(7)
C(12)-C(13)	1.499(8)
C(12)-H(12)	1.0000

C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(17)	1.486(7)
C(15)-C(16)	1.498(8)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(20)	1.501(6)
C(18)-C(19)	1.511(6)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.538(5)
C(21)-C(23)	1.538(6)
C(21)-H(21)	1.0000
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(25)	1.523(7)
C(23)-C(24)	1.541(7)
C(23)-C(26)	1.544(6)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-C(29)	1.487(7)
C(27)-C(28)	1.494(8)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.415(8)
C(30)-C(32)	1.454(7)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(35)	1.488(7)

C(33)-C(34)	1.522(6)
C(33)-H(33)	1.0000
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800

O(2)-Ti(1)-O(4)	100.46(14)
O(2)-Ti(1)-O(3)	99.60(13)
O(4)-Ti(1)-O(3)	115.90(14)
O(2)-Ti(1)-O(1)	95.42(13)
O(4)-Ti(1)-O(1)	118.40(14)
O(3)-Ti(1)-O(1)	119.31(14)
O(2)-Ti(1)-N(1)	170.99(12)
O(4)-Ti(1)-N(1)	81.51(13)
O(3)-Ti(1)-N(1)	87.27(12)
O(1)-Ti(1)-N(1)	76.04(12)
O(6)-Ti(2)-O(8)	99.54(15)
O(6)-Ti(2)-O(7)	99.95(14)
O(8)-Ti(2)-O(7)	116.23(14)
O(6)-Ti(2)-O(5)	95.49(13)
O(8)-Ti(2)-O(5)	118.61(14)
O(7)-Ti(2)-O(5)	119.01(14)
O(6)-Ti(2)-N(2)	170.38(12)
O(8)-Ti(2)-N(2)	83.62(13)
O(7)-Ti(2)-N(2)	86.61(13)
O(5)-Ti(2)-N(2)	75.10(12)
C(6)-O(1)-Ti(1)	126.8(2)
C(12)-O(2)-Ti(1)	146.1(3)
C(15)-O(3)-Ti(1)	133.4(3)
C(18)-O(4)-Ti(1)	137.2(3)
C(21)-O(5)-Ti(2)	127.3(2)
C(27)-O(6)-Ti(2)	145.8(3)
C(30)-O(7)-Ti(2)	131.2(4)
C(33)-O(8)-Ti(2)	135.7(3)
C(7)-N(1)-C(5)	106.5(3)
C(7)-N(1)-C(1)	108.0(3)
C(5)-N(1)-C(1)	112.4(3)
C(7)-N(1)-Ti(1)	98.7(2)
C(5)-N(1)-Ti(1)	117.3(2)
C(1)-N(1)-Ti(1)	112.4(2)
C(22)-N(2)-C(2)	111.5(3)
C(22)-N(2)-C(4)	109.1(3)
C(2)-N(2)-C(4)	110.9(3)
C(22)-N(2)-Ti(2)	99.0(2)
C(2)-N(2)-Ti(2)	111.5(2)
C(4)-N(2)-Ti(2)	114.3(2)
N(1)-C(1)-C(3)	117.3(4)
N(1)-C(1)-H(1A)	108.0
C(3)-C(1)-H(1A)	108.0
N(1)-C(1)-H(1B)	108.0
C(3)-C(1)-H(1B)	108.0
H(1A)-C(1)-H(1B)	107.2
N(2)-C(2)-C(3)	117.4(3)
N(2)-C(2)-H(2A)	108.0
C(3)-C(2)-H(2A)	108.0
N(2)-C(2)-H(2B)	108.0
C(3)-C(2)-H(2B)	108.0

H(2A)-C(2)-H(2B)	107.2
C(1)-C(3)-C(2)	115.3(4)
C(1)-C(3)-H(3A)	108.5
C(2)-C(3)-H(3A)	108.5
C(1)-C(3)-H(3B)	108.5
C(2)-C(3)-H(3B)	108.5
H(3A)-C(3)-H(3B)	107.5
N(2)-C(4)-C(5)	112.2(3)
N(2)-C(4)-H(4A)	109.2
C(5)-C(4)-H(4A)	109.2
N(2)-C(4)-H(4B)	109.2
C(5)-C(4)-H(4B)	109.2
H(4A)-C(4)-H(4B)	107.9
N(1)-C(5)-C(4)	114.7(3)
N(1)-C(5)-H(5A)	108.6
C(4)-C(5)-H(5A)	108.6
N(1)-C(5)-H(5B)	108.6
C(4)-C(5)-H(5B)	108.6
H(5A)-C(5)-H(5B)	107.6
O(1)-C(6)-C(7)	107.4(3)
O(1)-C(6)-C(8)	111.7(3)
C(7)-C(6)-C(8)	114.3(4)
O(1)-C(6)-H(6)	107.7
C(7)-C(6)-H(6)	107.7
C(8)-C(6)-H(6)	107.7
N(1)-C(7)-C(6)	109.9(3)
N(1)-C(7)-H(7A)	109.7
C(6)-C(7)-H(7A)	109.7
N(1)-C(7)-H(7B)	109.7
C(6)-C(7)-H(7B)	109.7
H(7A)-C(7)-H(7B)	108.2
C(11)-C(8)-C(9)	110.4(4)
C(11)-C(8)-C(6)	109.2(4)
C(9)-C(8)-C(6)	111.1(4)
C(11)-C(8)-C(10)	109.5(4)
C(9)-C(8)-C(10)	108.7(4)
C(6)-C(8)-C(10)	108.0(4)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(2)-C(12)-C(14)	109.9(4)
O(2)-C(12)-C(13)	107.5(4)
C(14)-C(12)-C(13)	114.6(6)
O(2)-C(12)-H(12)	108.2
C(14)-C(12)-H(12)	108.2

C(13)-C(12)-H(12)	108.2
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(3)-C(15)-C(17)	109.2(4)
O(3)-C(15)-C(16)	109.3(4)
C(17)-C(15)-C(16)	112.0(6)
O(3)-C(15)-H(15)	108.8
C(17)-C(15)-H(15)	108.8
C(16)-C(15)-H(15)	108.8
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(4)-C(18)-C(20)	109.1(4)
O(4)-C(18)-C(19)	108.7(4)
C(20)-C(18)-C(19)	112.4(4)
O(4)-C(18)-H(18)	108.8
C(20)-C(18)-H(18)	108.8
C(19)-C(18)-H(18)	108.8
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(5)-C(21)-C(22)	107.6(3)
O(5)-C(21)-C(23)	110.4(4)
C(22)-C(21)-C(23)	114.5(4)
O(5)-C(21)-H(21)	108.1
C(22)-C(21)-H(21)	108.1
C(23)-C(21)-H(21)	108.1
N(2)-C(22)-C(21)	109.9(3)
N(2)-C(22)-H(22A)	109.7
C(21)-C(22)-H(22A)	109.7
N(2)-C(22)-H(22B)	109.7
C(21)-C(22)-H(22B)	109.7

H(22A)-C(22)-H(22B)	108.2
C(25)-C(23)-C(21)	111.8(4)
C(25)-C(23)-C(24)	110.0(4)
C(21)-C(23)-C(24)	109.6(4)
C(25)-C(23)-C(26)	109.3(4)
C(21)-C(23)-C(26)	107.4(4)
C(24)-C(23)-C(26)	108.7(4)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
O(6)-C(27)-C(29)	109.4(4)
O(6)-C(27)-C(28)	109.2(4)
C(29)-C(27)-C(28)	113.9(6)
O(6)-C(27)-H(27)	108.1
C(29)-C(27)-H(27)	108.1
C(28)-C(27)-H(27)	108.1
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(31)-C(30)-O(7)	111.7(5)
C(31)-C(30)-C(32)	120.1(6)
O(7)-C(30)-C(32)	111.2(5)
C(31)-C(30)-H(30)	103.9
O(7)-C(30)-H(30)	103.9
C(32)-C(30)-H(30)	103.9
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5

H(32B)-C(32)-H(32C)	109.5
O(8)-C(33)-C(35)	109.1(4)
O(8)-C(33)-C(34)	108.1(4)
C(35)-C(33)-C(34)	111.6(5)
O(8)-C(33)-H(33)	109.3
C(35)-C(33)-H(33)	109.3
C(34)-C(33)-H(33)	109.3
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 2/4 Anisotropic displacement parameters (A^2 x 10^3).

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ti(1)	36(1)	39(1)	37(1)	-17(1)	6(1)	-15(1)
Ti(2)	36(1)	46(1)	38(1)	-20(1)	7(1)	-15(1)
O(1)	40(2)	53(2)	35(2)	-19(2)	5(1)	-19(2)
O(2)	45(2)	57(2)	41(2)	-26(2)	11(2)	-18(2)
O(3)	40(2)	59(2)	49(2)	-30(2)	12(2)	-26(2)
O(4)	51(2)	33(2)	50(2)	-16(2)	18(2)	-8(2)
O(5)	40(2)	51(2)	42(2)	-27(2)	4(1)	-14(2)
O(6)	57(2)	64(2)	42(2)	-26(2)	14(2)	-28(2)
O(7)	30(2)	69(2)	52(2)	-25(2)	3(2)	-16(2)
O(8)	56(2)	39(2)	50(2)	-18(2)	18(2)	-17(2)
N(1)	34(2)	34(2)	32(2)	-12(2)	4(2)	-13(2)
N(2)	36(2)	31(2)	35(2)	-16(2)	5(2)	-6(2)
C(1)	43(3)	36(3)	39(3)	-16(2)	8(2)	-7(2)
C(2)	40(3)	31(3)	46(3)	-18(2)	3(2)	-5(2)
C(3)	56(3)	38(3)	48(3)	-19(2)	2(2)	-14(2)
C(4)	43(3)	30(3)	34(2)	-15(2)	6(2)	-7(2)
C(5)	37(3)	38(3)	38(3)	-18(2)	10(2)	-11(2)
C(6)	35(3)	41(3)	34(2)	-12(2)	3(2)	-14(2)
C(7)	35(3)	40(3)	44(3)	-14(2)	2(2)	-14(2)
C(8)	44(3)	50(3)	44(3)	-14(2)	-5(2)	-21(3)
C(9)	96(5)	63(4)	53(3)	-20(3)	-13(3)	-40(3)
C(10)	69(4)	61(4)	45(3)	-11(3)	-10(3)	-29(3)
C(11)	54(4)	95(5)	65(4)	-21(3)	-6(3)	-35(3)
C(12)	55(3)	71(4)	41(3)	-25(3)	9(3)	-20(3)
C(13)	288(12)	111(7)	79(5)	-71(5)	75(6)	-88(7)
C(14)	65(4)	202(9)	57(4)	-53(5)	28(3)	-60(5)
C(15)	36(3)	61(4)	71(4)	-28(3)	3(3)	-23(3)
C(16)	86(5)	76(6)	193(9)	11(6)	25(6)	-35(5)
C(17)	74(5)	210(9)	122(6)	-95(6)	24(4)	-87(6)
C(18)	42(3)	37(3)	50(3)	-15(2)	9(2)	-7(2)
C(19)	69(4)	49(4)	85(4)	-22(3)	-8(3)	-18(3)
C(20)	61(4)	53(4)	59(3)	-12(3)	5(3)	-10(3)
C(21)	32(3)	37(3)	46(3)	-19(2)	2(2)	-6(2)
C(22)	33(3)	42(3)	45(3)	-20(2)	5(2)	-12(2)
C(23)	44(3)	45(3)	49(3)	-23(3)	-6(2)	-4(2)
C(24)	37(3)	74(4)	84(4)	-37(3)	-3(3)	-18(3)
C(25)	65(4)	50(4)	53(3)	-19(3)	-16(3)	-5(3)
C(26)	53(3)	64(4)	62(3)	-35(3)	-18(3)	-1(3)
C(27)	62(4)	74(4)	45(3)	-30(3)	15(3)	-30(3)
C(28)	148(7)	113(7)	48(4)	-23(4)	28(4)	-8(6)
C(29)	64(4)	152(7)	80(4)	-77(5)	30(3)	-42(4)
C(30)	37(3)	93(5)	124(5)	-70(4)	3(3)	-18(3)
C(31)	42(4)	52(4)	220(9)	-23(5)	7(5)	-11(3)
C(32)	77(4)	77(5)	97(5)	-25(4)	-6(4)	-47(4)
C(33)	59(3)	41(3)	47(3)	-17(3)	12(2)	-21(3)
C(34)	93(5)	64(4)	79(4)	-37(3)	26(3)	-44(4)
C(35)	74(5)	63(4)	116(6)	3(4)	-26(4)	-22(4)

Table 2/5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(1A)	-182	4530	2928	48
H(1B)	937	4629	2270	48
H(2A)	1216	4613	4820	47
H(2B)	129	4260	4496	47
H(3A)	1280	5258	3348	56
H(3B)	2375	4152	3563	56
H(4A)	2530	1607	4971	43
H(4B)	2858	2536	4196	43
H(5A)	1170	1717	3944	44
H(5B)	265	2699	4175	44
H(6)	-227	4307	1303	44
H(7A)	-819	3372	2640	47
H(7B)	116	2275	2608	47
H(9A)	-315	1679	1626	100
H(9B)	693	1868	885	100
H(9C)	-709	1923	586	100
H(10A)	-1052	3675	-551	87
H(10B)	330	3680	-274	87
H(10C)	-927	4616	-267	87
H(11A)	-2622	3446	640	105
H(11B)	-2394	4329	964	105
H(11C)	-2185	3177	1677	105
H(12)	3324	2656	82	65
H(13A)	4905	548	944	217
H(13B)	4287	1015	-77	217
H(13C)	3382	927	741	217
H(14A)	5097	3176	123	153
H(14B)	5341	2434	-473	153
H(14C)	5996	1981	538	153
H(15)	5235	3197	1950	63
H(16A)	3834	4752	1005	198
H(16B)	4943	5025	1407	198
H(16C)	3567	5224	1805	198
H(17A)	4815	4101	3326	173
H(17B)	6134	3822	2867	173
H(17C)	5619	2904	3483	173
H(18)	4314	196	2699	53
H(19A)	1960	-206	3191	102
H(19B)	3153	-993	2913	102
H(19C)	2388	121	2181	102
H(20A)	4707	0	4203	92
H(20B)	4570	-1065	4163	92
H(20C)	3409	-269	4459	92
H(21)	2131	4213	6125	46
H(22A)	3383	3330	5281	47
H(22B)	3361	2210	5956	47
H(24A)	5209	3135	7374	94
H(24B)	4397	4049	6492	94
H(24C)	4993	2877	6490	94
H(25A)	4278	1722	8277	88
H(25B)	4053	1500	7375	88
H(25C)	2880	1774	7972	88

H(26A)	1997	3602	8032	90
H(26B)	2631	4470	7477	90
H(26C)	3411	3509	8344	90
H(27)	-128	2563	8289	67
H(28A)	-220	498	8947	169
H(28B)	506	1032	9412	169
H(28C)	1069	709	8566	169
H(29A)	-2308	3059	7956	131
H(29B)	-1963	2323	8996	131
H(29C)	-2257	1861	8260	131
H(30)	-2289	2728	6108	92
H(31A)	-3080	4405	5653	168
H(31B)	-3989	3981	5212	168
H(31C)	-3023	4510	4610	168
H(32A)	-2025	2567	4406	119
H(32B)	-3104	2276	5050	119
H(32C)	-1621	1641	5366	119
H(33)	808	93	7252	57
H(34A)	285	-11	5859	106
H(34B)	1238	-1129	6469	106
H(34C)	1767	-356	5670	106
H(35A)	3399	-517	6822	139
H(35B)	2801	-1199	7645	139
H(35C)	2947	-124	7653	139

3. Details of the crystal structure of $L^1{}_2Ti_2(OEt)_2(\mu\text{-}O)$

Table 3/1 Crystal data and structure refinement.

Empirical formula	$C_{38}H_{78}N_4O_7Ti_2$
Formula weight	798.84
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 19.7850(10) Å
	b = 11.7253(4) Å
	c = 19.6134(7) Å
Volume	4550.0(3) Å^3
Z	4
Density (calculated)	1.166 Mg / m^3
Absorption coefficient	0.397 mm^{-1}
F(000)	1736
Crystal	Colourless Block
Crystal size	0.20 × 0.15 × 0.05 mm^3
θ range for data collection	2.92 – 25.02°
Index ranges	$-23 \le h \le 18$, $-10 \le k \le 13$, $-23 \le l \le 21$
Reflections collected	22572
Independent reflections	7502 [R_{int} = 0.0809]
Completeness to θ = 25.02°	99.2 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9804 and 0.9249
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7502 / 9 / 471
Goodness-of-fit on F^2	1.008
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0607, $wR2$ = 0.1248
R indices (all data)	$R1$ = 0.1033, $wR2$ = 0.1410
Absolute structure parameter	0.40(3)
Largest diff. peak and hole	0.618 and –0.314 e Å^{-3}

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: Refined as a racemic twin

Table 3/2 Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors.

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
Ti1	1357(1)	1454(1)	1998(1)	24(1)	1
Ti2	1144(1)	3625(1)	694(1)	23(1)	1
N1	1668(2)	3061(3)	2780(2)	22(1)	1
N2	2255(2)	608(3)	1049(2)	27(1)	1
N3	1636(2)	2218(3)	−80(2)	24(1)	1
N4	2039(2)	4857(3)	1655(2)	27(1)	1
O1	681(2)	1549(3)	2654(2)	29(1)	1
O2	2121(2)	848(3)	2415(2)	29(1)	1
O3	917(2)	248(3)	1600(2)	36(1)	1
O4	471(2)	3263(3)	75(2)	29(1)	1
O5	1781(2)	4529(3)	275(2)	28(1)	1
O6	589(2)	4633(3)	1131(2)	33(1)	1
O7	1322(2)	2572(3)	1350(2)	23(1)	1
C1	665(3)	2180(5)	3270(3)	28(1)	1
C2	1381(3)	2574(5)	3409(3)	26(1)	1
C3	359(3)	1464(5)	3861(3)	30(1)	1
C4	322(3)	2197(5)	4500(3)	42(2)	1
C5	766(3)	382(5)	4008(3)	40(2)	1
C6	−358(3)	1132(5)	3650(3)	43(2)	1
C7	2597(3)	32(4)	2207(3)	30(1)	1
C8	2444(3)	−366(4)	1486(3)	32(1)	1
C9	2619(3)	−964(4)	2732(3)	30(1)	1
C10	2806(3)	−466(4)	3427(3)	37(2)	1
C11	1936(3)	−1571(4)	2787(3)	39(2)	1
C12	3169(3)	−1823(5)	2519(3)	39(2)	1
C15	1280(3)	4123(4)	2612(3)	26(1)	1
C16	1651(3)	5124(4)	2276(3)	27(1)	1
C17	2399(3)	3269(4)	2883(3)	27(1)	1
C18	2796(3)	3405(5)	2217(3)	30(1)	1
C19	2730(3)	4547(4)	1849(3)	30(1)	1
C20	1910(3)	219(4)	427(3)	25(1)	1
C21	1405(3)	1038(4)	107(3)	26(1)	1
C22	2882(3)	1235(4)	862(3)	28(1)	1
C23	2769(3)	2341(4)	490(3)	30(1)	1
C24	2372(3)	2300(4)	−172(3)	27(1)	1
C25	533(3)	2680(5)	−556(3)	28(1)	1
C26	1281(3)	2574(4)	−709(3)	27(1)	1
C27	127(3)	3300(5)	−1121(3)	30(1)	1
C28	181(3)	2619(5)	−1791(3)	45(2)	1
C29	−614(3)	3338(5)	−912(3)	41(2)	1
C30	380(3)	4514(5)	−1232(3)	44(2)	1
C31	2222(3)	5417(4)	464(3)	24(1)	1

C32	2054(3)	5813(4)	1181(3)	30(1)	1
C33	2234(3)	6364(4)	−80(3)	29(1)	1
C34	2400(3)	5819(5)	−773(3)	40(2)	1
C35	1540(3)	6934(5)	−133(3)	41(2)	1
C36	2782(3)	7248(4)	86(3)	34(1)	1
C13A	317(3)	−417(7)	1749(5)	46(2)	0.70
C14A	−232(4)	215(8)	1339(5)	61(3)	0.70
C13B	237(5)	−199(15)	1677(15)	46(2)	0.30
C14B	291(12)	−1461(16)	1466(12)	61(3)	0.30
C37A	−114(4)	4951(14)	1219(13)	102(4)	0.48
C38A	−511(8)	3985(13)	1569(8)	67(3)	0.48
C37B	−124(3)	4849(12)	1020(12)	102(4)	0.52
C38B	−308(7)	6076(11)	1226(8)	67(3)	0.52

Table 3/3 Bond lengths [Å] and angles [°].

Ti1–O7	1.826(4)
Ti1–O3	1.835(3)
Ti1–O1	1.860(4)
Ti1–O2	1.860(4)
Ti1–N1	2.506(4)
Ti2–O7	1.818(4)
Ti2–O6	1.827(4)
Ti2–O5	1.840(4)
Ti2–O4	1.852(3)
Ti2–N3	2.443(4)
N1–C2	1.474(6)
N1–C17	1.480(6)
N1–C15	1.499(6)
N2–C20	1.470(6)
N2–C8	1.477(6)
N2–C22	1.488(6)
N3–C24	1.472(6)
N3–C26	1.479(6)
N3–C21	1.502(6)
N4–C32	1.456(6)
N4–C19	1.463(6)
N4–C16	1.474(6)
O1–C1	1.418(6)
O2–C7	1.404(6)
O3–C13A	1.449(2)
O3–C13B	1.450(2)
O4–C25	1.419(6)
O5–C31	1.408(6)
O6–C37B	1.449(2)
O6–C37A	1.451(2)
C1–C2	1.516(8)
C1–C3	1.553(7)
C3–C4	1.522(8)
C3–C6	1.529(8)
C3–C5	1.531(8)
C7–C8	1.519(8)
C7–C9	1.556(7)
C9–C10	1.530(7)
C9–C11	1.531(8)
C9–C12	1.542(8)
C15–C16	1.533(7)
C17–C18	1.532(7)
C18–C19	1.528(7)
C20–C21	1.522(7)

C22–C23	1.505(7)
C23–C24	1.518(7)
C25–C26	1.515(7)
C25–C27	1.549(7)
C27–C29	1.523(8)
C27–C30	1.525(7)
C27–C28	1.541(8)
C31–C32	1.519(7)
C31–C33	1.541(7)
C33–C35	1.531(8)
C33–C36	1.535(7)
C33–C34	1.536(8)
C13A–C14A	1.542(2)
C13B–C14B	1.541(2)
C37A–C38A	1.541(2)
C37B–C38B	1.538(2)

O7–Ti1–O3	103.87(16)
O7–Ti1–O1	114.34(16)
O3–Ti1–O1	89.93(16)
O7–Ti1–O2	127.63(16)
O3–Ti1–O2	106.15(16)
O1–Ti1–O2	107.61(15)
O7–Ti1–N1	84.01(15)
O3–Ti1–N1	162.97(16)
O1–Ti1–N1	73.04(14)
O2–Ti1–N1	79.52(14)
O7–Ti2–O6	102.94(17)
O7–Ti2–O5	125.04(16)
O6–Ti2–O5	104.41(16)
O7–Ti2–O4	116.57(16)
O6–Ti2–O4	91.36(16)
O5–Ti2–O4	109.42(16)
O7–Ti2–N3	84.45(15)
O6–Ti2–N3	165.34(16)
O5–Ti2–N3	80.75(14)
O4–Ti2–N3	73.98(15)
C2–N1–C17	109.0(4)
C2–N1–C15	108.0(4)
C17–N1–C15	113.1(4)
C2–N1–Ti1	97.3(3)
C17–N1–Ti1	116.6(3)
C15–N1–Ti1	111.4(3)
C20–N2–C8	111.0(4)
C20–N2–C22	109.6(4)
C8–N2–C22	108.3(4)
C24–N3–C26	110.3(4)

C24–N3–C21	113.0(4)
C26–N3–C21	108.6(4)
C24–N3–Ti2	115.3(3)
C26–N3–Ti2	98.0(3)
C21–N3–Ti2	110.5(3)
C32–N4–C19	109.8(4)
C32–N4–C16	111.9(4)
C19–N4–C16	108.9(4)
C1–O1–Ti1	129.6(3)
C7–O2–Ti1	132.7(3)
C13A–O3–C13B	13.2(11)
C13A–O3–Ti1	135.8(5)
C13B–O3–Ti1	132.3(9)
C25–O4–Ti2	128.4(3)
C31–O5–Ti2	137.1(3)
C37B–O6–C37A	16.2(17)
C37B–O6–Ti2	128.9(7)
C37A–O6–Ti2	143.0(11)
Ti2–O7–Ti1	170.7(2)
O1–C1–C2	106.9(4)
O1–C1–C3	111.3(4)
C2–C1–C3	113.3(4)
N1–C2–C1	109.2(4)
C4–C3–C6	108.8(5)
C4–C3–C5	109.7(5)
C6–C3–C5	109.2(5)
C4–C3–C1	109.2(4)
C6–C3–C1	107.3(4)
C5–C3–C1	112.6(4)
O2–C7–C8	110.2(4)
O2–C7–C9	109.7(4)
C8–C7–C9	113.0(4)
N2–C8–C7	110.7(4)
C10–C9–C11	109.1(5)
C10–C9–C12	108.6(5)
C11–C9–C12	109.8(4)
C10–C9–C7	108.1(4)
C11–C9–C7	111.8(4)
C12–C9–C7	109.3(4)
N1–C15–C16	119.1(4)
N4–C16–C15	116.3(4)
N1–C17–C18	113.6(4)
C19–C18–C17	116.8(5)
N4–C19–C18	114.9(4)
N2–C20–C21	116.8(4)
N3–C21–C20	118.9(4)
N2–C22–C23	114.8(4)

C22–C23–C24	117.8(5)
N3–C24–C23	114.0(4)
O4–C25–C26	107.2(4)
O4–C25–C27	110.6(4)
C26–C25–C27	113.8(4)
N3–C26–C25	108.8(4)
C29–C27–C30	109.1(5)
C29–C27–C28	108.1(5)
C30–C27–C28	109.8(5)
C29–C27–C25	108.7(4)
C30–C27–C25	111.8(5)
C28–C27–C25	109.3(4)
O5–C31–C32	109.5(4)
O5–C31–C33	111.1(4)
C32–C31–C33	115.1(4)
N4–C32–C31	111.0(4)
C35–C33–C36	110.7(4)
C35–C33–C34	108.3(5)
C36–C33–C34	108.5(5)
C35–C33–C31	110.4(4)
C36–C33–C31	110.5(4)
C34–C33–C31	108.4(4)
O3–C13A–C14A	102.3(6)
O3–C13B–C14B	104.7(13)
O6–C37A–C38A	110.7(10)
O6–C37B–C38B	110.8(9)

Table 3/4 Anisotropic displacement parameters [$Å^2 \times 10^3$].

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti1	31(1)	21(1)	20(1)	1(1)	−2(1)	−2(1)
Ti2	28(1)	20(1)	20(1)	−1(1)	0(1)	2(1)
N1	25(3)	20(2)	20(2)	2(2)	−2(2)	1(2)
N2	34(3)	22(2)	25(2)	−1(2)	−4(2)	3(2)
N3	27(3)	21(2)	23(3)	3(2)	−2(2)	−4(2)
N4	30(3)	22(2)	29(3)	1(2)	2(2)	1(2)
O1	33(2)	35(2)	18(2)	0(2)	−2(2)	−6(2)
O2	42(2)	19(2)	25(2)	0(2)	−4(2)	6(2)
O3	45(3)	31(2)	30(2)	−2(2)	−4(2)	−13(2)
O4	28(2)	34(2)	25(2)	−4(2)	−2(2)	5(2)
O5	39(2)	20(2)	26(2)	0(1)	2(2)	−3(2)
O6	36(2)	36(2)	28(2)	−4(2)	−2(2)	13(2)
O7	27(2)	25(2)	17(2)	−2(1)	2(2)	−2(2)
C1	31(4)	31(3)	23(3)	2(2)	0(2)	8(3)
C2	34(3)	29(3)	15(3)	3(2)	−1(2)	6(3)
C3	21(3)	39(3)	29(3)	2(3)	2(2)	−3(3)
C4	40(4)	61(4)	23(3)	8(3)	8(3)	−6(3)
C5	40(4)	43(4)	37(4)	10(3)	4(3)	−4(3)
C6	36(4)	62(4)	30(4)	9(3)	1(3)	−17(3)
C7	33(3)	27(3)	29(3)	−4(2)	−3(2)	8(3)
C8	38(4)	21(3)	38(4)	1(2)	1(3)	9(3)
C9	37(4)	25(3)	28(3)	−1(2)	−4(2)	3(3)
C10	57(4)	22(3)	32(3)	4(2)	−13(3)	8(3)
C11	60(5)	23(3)	35(4)	4(2)	−1(3)	8(3)
C12	56(4)	28(3)	33(3)	1(2)	−11(3)	12(3)
C15	34(3)	20(3)	23(3)	1(2)	0(2)	−2(2)
C16	35(3)	21(3)	25(3)	−4(2)	−1(2)	2(2)
C17	29(3)	29(3)	22(3)	0(2)	−6(2)	−1(2)
C18	25(3)	43(3)	23(3)	−4(2)	−2(2)	4(3)
C19	22(3)	35(3)	32(3)	2(2)	3(2)	−8(2)
C20	32(3)	15(3)	28(3)	−5(2)	2(2)	−5(2)
C21	42(4)	21(3)	16(3)	−3(2)	−9(2)	−1(2)
C22	21(3)	37(3)	26(3)	1(2)	1(2)	−2(2)
C23	28(3)	33(3)	28(3)	−3(2)	1(2)	−3(2)
C24	34(4)	25(3)	22(3)	2(2)	2(2)	4(2)
C25	34(4)	28(3)	22(3)	0(2)	−7(2)	0(3)
C26	43(4)	19(3)	18(3)	−1(2)	−4(2)	5(2)
C27	34(4)	35(3)	22(3)	4(2)	−5(2)	2(3)
C28	51(4)	56(4)	28(4)	1(3)	−10(3)	−4(3)
C29	29(4)	58(4)	37(4)	6(3)	−7(3)	2(3)

C30	45(4)	39(4)	48(4)	19(3)	−14(3)	−2(3)
C31	26(3)	19(3)	27(3)	−1(2)	−1(2)	−6(2)
C32	42(4)	21(3)	27(3)	0(2)	0(3)	−1(3)
C33	35(4)	25(3)	28(3)	0(2)	3(2)	−4(3)
C34	58(4)	32(4)	29(3)	0(2)	5(3)	−9(3)
C35	43(4)	35(3)	44(4)	13(3)	1(3)	−1(3)
C36	42(4)	27(3)	33(3)	4(2)	3(3)	−6(3)

Table 3/5 Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H1	374	2868	3200	34	1
H2A	1381	3156	3774	31	1
H2B	1660	1921	3562	31	1
H4A	60	1798	4851	62	1
H4B	102	2924	4392	62	1
H4C	780	2341	4670	62	1
H5A	547	–49	4375	60	1
H5B	1225	591	4149	60	1
H5C	788	–88	3596	60	1
H6A	–341	685	3228	64	1
H6B	–627	1822	3575	64	1
H6C	–566	674	4011	64	1
H7	3052	404	2203	35	1
H8A	2846	–751	1294	39	1
H8B	2068	–924	1497	39	1
H10A	2857	–1086	3758	55	1
H10B	2448	52	3580	55	1
H10C	3233	–46	3390	55	1
H11A	1950	–2117	3165	59	1
H11B	1841	–1976	2361	59	1
H11C	1580	–1008	2872	59	1
H12A	3603	–1426	2472	59	1
H12B	3046	–2170	2081	59	1
H12C	3209	–2419	2867	59	1
H15A	1078	4408	3041	31	1
H15B	903	3903	2309	31	1
H16A	1313	5716	2160	32	1
H16B	1964	5458	2615	32	1
H17A	2592	2625	3145	32	1
H17B	2456	3969	3160	32	1
H18A	3280	3276	2318	36	1
H18B	2650	2795	1901	36	1
H19A	2913	5153	2148	36	1
H19B	3012	4524	1432	36	1
H20A	1670	–500	535	30	1
H20B	2259	38	82	30	1
H21A	1229	674	–313	32	1
H21B	1020	1115	426	32	1
H22A	3165	733	573	34	1
H22B	3140	1396	1284	34	1
H23A	3216	2679	391	36	1
H23B	2532	2868	804	36	1
H24A	2474	2996	–439	33	1
H24B	2527	1636	–442	33	1

H25	342	1895	−500	34	1
H26A	1354	2002	−1073	32	1
H26B	1461	3315	−868	32	1
H28A	39	1830	−1711	68	1
H28B	650	2629	−1951	68	1
H28C	−112	2966	−2136	68	1
H29A	−664	3809	−502	62	1
H29B	−773	2563	−816	62	1
H29C	−883	3667	−1283	62	1
H30A	77	4912	−1548	66	1
H30B	837	4492	−1424	66	1
H30C	388	4920	−795	66	1
H31	2688	5084	481	29	1
H32A	2396	6374	1334	36	1
H32B	1608	6195	1180	36	1
H34A	2839	5432	−746	60	1
H34B	2419	6413	−1124	60	1
H34C	2049	5264	−891	60	1
H35A	1190	6347	−181	61	1
H35B	1531	7438	−532	61	1
H35C	1454	7382	280	61	1
H36A	2655	7666	500	51	1
H36B	2826	7783	−295	51	1
H36C	3214	6859	161	51	1
H13A	214	−413	2243	55	0.70
H13B	368	−1215	1592	55	0.70
H14A	−289	987	1522	92	0.70
H14B	−660	−200	1374	92	0.70
H14C	−95	261	859	92	0.70
H13C	−83	215	1379	55	0.30
H13D	83	−130	2156	55	0.30
H14D	485	−1512	1007	92	0.30
H14E	−160	−1806	1467	92	0.30
H14F	583	−1867	1788	92	0.30
H37A	−318	5115	768	122	0.48
H37B	−143	5652	1499	122	0.48
H38A	−411	3259	1344	101	0.48
H38B	−997	4142	1538	101	0.48
H38C	−379	3939	2050	101	0.48
H37C	−394	4304	1293	122	0.52
H37D	−234	4729	533	122	0.52
H38D	−517	6072	1679	101	0.52
H38E	−627	6393	894	101	0.52
H38F	102	6544	1236	101	0.52

4. Details of the crystal structure of $L^2Ti(O^iPr)_2$

Table 4/1 Crystal data and structure refinement.

Empirical formula	$C_{22}H_{48}N_2O_4Ti$	
Formula weight	452.52	
Temperature	120(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 8.830(5) Å	α = 93.801(5)°
	b = 9.726(5) Å	β = 98.098(5)°
	c = 17.047(5) Å	γ = 112.844(5)°
Volume	1323.9(11) Å^3	
Z	2	
Density (calculated)	1.135 Mg / m^3	
Absorption coefficient	0.349 mm^{-1}	
F(000)	496	
Crystal	Colourless plate	
Crystal size	0.30 × 0.20 × 0.02 mm^3	
θ range for data collection	2.98 – 25.03°	
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-20 \le l \le 20$	
Reflections collected	13694	
Independent reflections	4583 [R_{int} = 0.0501]	
Completeness to θ = 25.03°	97.8 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9930 and 0.9025	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4583 / 0 / 275	
Goodness-of-fit on F^2	1.030	
Final R indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0416, *wR2* = 0.0881	
R indices (all data)	*R1* = 0.0538, *wR2* = 0.0932	
Extinction coefficient	0.0073(15)	
Largest diff. peak and hole	0.209 and –0.366 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model.

Table 4/2 Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors.

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
N1	6552(2)	1007(2)	2697(1)	21(1)	1
N2	8831(2)	3588(2)	2138(1)	20(1)	1
O1	5101(2)	1909(1)	1546(1)	18(1)	1
O2	7941(2)	4334(2)	3416(1)	19(1)	1
O3	4628(2)	2768(2)	3097(1)	23(1)	1
O4	6300(2)	4872(2)	2002(1)	22(1)	1
Ti1	6296(1)	3256(1)	2500(1)	17(1)	1
C1	4493(2)	329(2)	1455(1)	18(1)	1
C2	4911(3)	−130(2)	2275(1)	21(1)	1
C3	7926(3)	914(2)	2310(1)	25(1)	1
C4	9379(3)	2434(2)	2455(1)	26(1)	1
C5	9948(3)	5102(2)	2561(1)	21(1)	1
C6	9637(2)	5213(2)	3421(1)	19(1)	1
C7	2622(2)	−410(2)	1078(1)	19(1)	1
C8	2419(3)	141(2)	264(1)	25(1)	1
C9	1555(3)	33(3)	1596(1)	28(1)	1
C10	2043(3)	−2127(2)	954(1)	29(1)	1
C11	6811(3)	787(3)	3547(1)	29(1)	1
C12	8803(3)	3556(3)	1268(1)	30(1)	1
C13	10186(3)	6848(2)	3821(1)	22(1)	1
C14	12056(3)	7717(3)	3830(2)	35(1)	1
C15	9187(3)	7647(2)	3388(1)	31(1)	1
C16	9880(3)	6798(2)	4681(1)	30(1)	1
C17	5482(3)	5058(2)	1267(1)	24(1)	1
C18	6458(3)	6613(3)	1064(2)	36(1)	1
C19	3701(3)	4806(3)	1322(2)	39(1)	1
C20	4551(3)	3382(2)	3865(1)	24(1)	1
C21	4150(3)	4750(3)	3786(1)	32(1)	1
C22	3244(3)	2183(3)	4219(2)	43(1)	1

Table 4/3 Bond lengths [Å] and angles [°].

N1–C11	1.477(3)
N1–C2	1.482(3)
N1–C3	1.489(3)
N1–Ti1	2.325(2)
N2–C12	1.477(3)
N2–C5	1.481(3)
N2–C4	1.488(3)
N2–Ti1	2.313(2)
O1–C1	1.407(2)
O1–Ti1	1.9056(15)
O2–C6	1.405(2)
O2–Ti1	1.9006(15)
O3–C20	1.425(2)
O3–Ti1	1.8363(15)
O4–C17	1.415(2)
O4–Ti1	1.8342(16)
C1–C2	1.534(3)
C1–C7	1.542(3)
C3–C4	1.510(3)
C5–C6	1.534(3)
C6–C13	1.547(3)
C7–C8	1.531(3)
C7–C9	1.535(3)
C7–C10	1.535(3)
C13–C16	1.529(3)
C13–C14	1.532(3)
C13–C15	1.533(3)
C17–C19	1.513(3)
C17–C18	1.514(3)
C20–C21	1.512(3)
C20–C22	1.517(3)
C11–N1–C2	109.82(16)
C11–N1–C3	110.64(17)
C2–N1–C3	110.65(16)
C11–N1–Ti1	113.65(12)
C2–N1–Ti1	102.21(12)
C3–N1–Ti1	109.58(12)
C12–N2–C5	110.27(16)
C12–N2–C4	111.10(16)
C5–N2–C4	110.06(17)
C12–N2–Ti1	113.71(13)
C5–N2–Ti1	102.45(11)
C4–N2–Ti1	108.92(12)
C1–O1–Ti1	126.75(12)

C6–O2–Ti1	126.10(12)
C20–O3–Ti1	132.32(13)
C17–O4–Ti1	135.18(13)
O4–Ti1–O3	107.70(7)
O4–Ti1–O2	98.10(7)
O3–Ti1–O2	91.41(7)
O4–Ti1–O1	91.10(7)
O3–Ti1–O1	99.38(7)
O2–Ti1–O1	163.03(6)
O4–Ti1–N2	89.70(6)
O3–Ti1–N2	159.17(7)
O2–Ti1–N2	74.47(7)
O1–Ti1–N2	91.43(6)
O4–Ti1–N1	159.25(6)
O3–Ti1–N1	89.56(6)
O2–Ti1–N1	92.78(7)
O1–Ti1–N1	74.37(6)
N2–Ti1–N1	76.20(6)
O1–C1–C2	107.55(16)
O1–C1–C7	111.60(16)
C2–C1–C7	114.11(16)
N1–C2–C1	108.83(16)
N1–C3–C4	109.50(17)
N2–C4–C3	110.12(17)
N2–C5–C6	108.92(16)
O2–C6–C5	108.10(16)
O2–C6–C13	112.19(16)
C5–C6–C13	113.65(17)
C8–C7–C9	108.72(17)
C8–C7–C10	109.19(17)
C9–C7–C10	110.08(17)
C8–C7–C1	107.66(16)
C9–C7–C1	111.62(17)
C10–C7–C1	109.51(17)
C16–C13–C14	109.06(19)
C16–C13–C15	108.45(18)
C14–C13–C15	110.08(18)
C16–C13–C6	108.20(17)
C14–C13–C6	109.13(17)
C15–C13–C6	111.86(18)
O4–C17–C19	109.80(18)
O4–C17–C18	108.95(18)
C19–C17–C18	111.91(19)
O3–C20–C21	109.33(18)
O3–C20–C22	109.03(18)
C21–C20–C22	111.61(19)

Table 4/4 Anisotropic displacement parameters [$Å^2 \times 10^3$].

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N1	20(1)	23(1)	19(1)	0(1)	1(1)	10(1)
N2	18(1)	22(1)	20(1)	−2(1)	4(1)	7(1)
O1	19(1)	14(1)	21(1)	1(1)	4(1)	5(1)
O2	16(1)	17(1)	20(1)	−1(1)	4(1)	3(1)
O3	19(1)	22(1)	25(1)	−2(1)	8(1)	6(1)
O4	23(1)	19(1)	23(1)	2(1)	1(1)	9(1)
Ti1	15(1)	16(1)	20(1)	0(1)	4(1)	6(1)
C1	18(1)	16(1)	20(1)	0(1)	5(1)	7(1)
C2	20(1)	18(1)	24(1)	0(1)	3(1)	7(1)
C3	23(1)	26(1)	31(1)	−3(1)	1(1)	16(1)
C4	21(1)	29(1)	30(1)	−3(1)	2(1)	14(1)
C5	16(1)	23(1)	22(1)	1(1)	5(1)	5(1)
C6	16(1)	18(1)	21(1)	2(1)	3(1)	6(1)
C7	18(1)	18(1)	20(1)	1(1)	3(1)	6(1)
C8	22(1)	26(1)	24(1)	1(1)	2(1)	6(1)
C9	21(1)	32(1)	32(1)	3(1)	9(1)	11(1)
C10	24(1)	21(1)	34(1)	0(1)	0(1)	2(1)
C11	36(1)	27(1)	24(1)	5(1)	0(1)	13(1)
C12	24(1)	40(1)	24(1)	−2(1)	8(1)	12(1)
C13	20(1)	16(1)	26(1)	2(1)	2(1)	4(1)
C14	26(1)	20(1)	51(2)	0(1)	3(1)	2(1)
C15	35(1)	21(1)	36(1)	3(1)	4(1)	13(1)
C16	39(1)	21(1)	25(1)	−7(1)	1(1)	9(1)
C17	24(1)	22(1)	25(1)	3(1)	1(1)	10(1)
C18	40(2)	29(1)	35(1)	13(1)	6(1)	8(1)
C19	25(1)	36(1)	58(2)	17(1)	3(1)	14(1)
C20	23(1)	26(1)	22(1)	−1(1)	9(1)	9(1)
C21	32(1)	32(1)	34(1)	−2(1)	8(1)	17(1)
C22	51(2)	35(2)	47(2)	7(1)	32(1)	13(1)

Table 4/5 Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H1	5121	18	1085	22	1
H2A	4036	–191	2593	25	1
H2B	4954	–1132	2206	25	1
H3A	7523	597	1729	30	1
H3B	8291	156	2535	30	1
H4A	9822	2722	3036	31	1
H4B	10284	2380	2188	31	1
H5A	9722	5883	2283	25	1
H5B	11129	5269	2565	25	1
H6	10306	4751	3744	22	1
H8A	3169	–58	–56	38	1
H8B	2697	1225	343	38	1
H8C	1260	–392	–15	38	1
H9A	414	–297	1297	42	1
H9B	2038	1128	1740	42	1
H9C	1530	–450	2084	42	1
H1A	885	–2592	667	43	1
H1B	2111	–2491	1475	43	1
H1C	2762	–2396	642	43	1
H1D	5924	898	3797	44	1
H1E	7898	1540	3822	44	1
H1F	6781	–224	3585	44	1
H1G	8429	4319	1074	45	1
H1H	8032	2559	994	45	1
H1I	9928	3770	1160	45	1
H1J	12439	8714	4140	53	1
H1K	12248	7829	3281	53	1
H1L	12676	7162	4076	53	1
H1M	7989	7042	3346	46	1
H1N	9451	7773	2850	46	1
H1O	9483	8637	3689	46	1
H1P	10590	6375	4980	45	1
H1Q	8704	6167	4681	45	1
H1R	10151	7820	4934	45	1
H17	5464	4293	839	29	1
H1S	6537	7373	1493	54	1
H1T	5884	6761	561	54	1
H1U	7583	6714	1005	54	1
H1V	3107	3784	1444	58	1
H1W	3141	4935	811	58	1
H1X	3703	5537	1747	58	1
H20	5663	3695	4220	29	1
H2A	5021	5503	3559	47	1
H2B	4103	5178	4314	47	1
H2C	3068	4455	3433	47	1

H2D	2155	1849	3866	65	1
H2E	3178	2600	4746	65	1
H2F	3554	1325	4273	65	1

5. Details of the crystal structure of $(L^2)_2Zr$

Table 5/1 Crystal data and structure refinement.

Empirical formula	C32 H68 N4 O4 Zr
Formula weight	664.12
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 10.762(2) A alpha = 76.68(3) deg. b = 12.115(2) A beta = 72.59(3) deg. c = 15.963(3) A gamma = 68.58(3) deg.
Volume	1831.5(6) A^3
Z, Calculated density	2, 1.204 Mg/m^3
Absorption coefficient	0.337 mm^-1
F(000)	720
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	2.92 to 27.45 deg.
Limiting indices	-13<=h<=13, -15<=k<=15, -20<=l<=20
Reflections collected / unique	36431 / 8322 [R(int) = 0.0562]
Completeness to theta = 27.45	99.4 %
Max. and min. transmission	Sortav 0.9356 and 0.8956
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8322 / 0 / 407
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0851
R indices (all data)	R1 = 0.0458, wR2 = 0.0886
Extinction coefficient	0.0057(8)
Largest diff. peak and hole	1.117 and -0.520 e.A^-3

Table 5/2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zr(1)	2351(1)	7887(1)	2459(1)	17(1)
O(1)	3762(1)	6396(1)	2952(1)	23(1)
O(2)	2009(2)	6822(1)	1774(1)	25(1)
O(3)	2744(1)	9484(1)	2302(1)	21(1)
O(4)	293(1)	8850(1)	2723(1)	24(1)
N(1)	4815(2)	7525(2)	1408(1)	25(1)
N(2)	2298(2)	8862(2)	819(1)	28(1)
N(3)	2310(2)	8381(1)	3967(1)	21(1)
N(4)	947(2)	6798(2)	3804(1)	26(1)
C(1)	5164(2)	5859(2)	2605(1)	27(1)
C(2)	5464(2)	6222(2)	1604(1)	28(1)
C(3)	4807(3)	7868(2)	460(1)	33(1)
C(4)	3640(3)	9004(2)	330(1)	33(1)
C(5)	1972(3)	8052(2)	402(2)	40(1)
C(6)	1307(3)	7238(2)	1097(2)	38(1)
C(7)	5655(2)	4482(2)	2870(2)	34(1)
C(8)	5034(3)	3867(2)	2438(2)	42(1)
C(9)	5210(3)	4207(2)	3876(2)	52(1)
C(10)	7230(3)	4000(2)	2591(2)	56(1)
C(11)	5588(2)	8170(2)	1617(2)	34(1)
C(12)	1245(3)	10041(2)	787(2)	39(1)
C(13)	1170(3)	6215(2)	738(2)	36(1)
C(14)	467(5)	6706(3)	-30(2)	77(1)
C(15)	2557(4)	5304(3)	446(2)	64(1)
C(16)	304(4)	5565(3)	1490(2)	64(1)
C(17)	2721(2)	10115(2)	2941(1)	23(1)
C(18)	1863(2)	9702(2)	3827(1)	23(1)
C(19)	1359(2)	7941(2)	4736(1)	28(1)
C(20)	1350(2)	6739(2)	4623(1)	27(1)
C(21)	-529(2)	7483(2)	3871(2)	39(1)
C(22)	-763(3)	8352(3)	3039(2)	27(1)
C(23)	2227(2)	11491(2)	2679(1)	28(1)
C(24)	2390(3)	12105(2)	3362(2)	42(1)
C(25)	722(3)	11958(2)	2619(2)	38(1)
C(26)	3138(3)	11789(2)	1773(2)	39(1)
C(27)	3698(2)	7895(2)	4138(2)	28(1)
C(28)	1213(3)	5565(2)	3660(2)	37(1)
C(29)	-2206(2)	9338(2)	3189(2)	37(1)
C(30)	-2305(4)	10274(3)	3679(3)	44(1)
C(31)	-3326(4)	8764(4)	3605(3)	54(1)
C(32)	-2404(4)	9961(4)	2229(3)	53(1)
C(32A)	-2392(10)	8947(8)	2524(6)	39(2)
C(30A)	-2398(10)	10679(8)	3097(7)	39(2)
C(31A)	-3339(10)	9099(9)	4153(7)	42(2)
C(22A)	-777(7)	8663(6)	3515(5)	23(2)

Table 5/3 Bond lengths [A] and angles [deg].

Zr(1)-O(4)	2.0559(16)
Zr(1)-O(2)	2.0574(14)
Zr(1)-O(1)	2.0602(15)
Zr(1)-O(3)	2.0727(14)
Zr(1)-N(3)	2.5953(17)
Zr(1)-N(4)	2.616(2)
Zr(1)-N(1)	2.620(2)
Zr(1)-N(2)	2.6207(19)
O(1)-C(1)	1.398(3)
O(2)-C(6)	1.397(3)
O(3)-C(17)	1.399(2)
O(4)-C(22)	1.388(3)
O(4)-C(22A)	1.470(8)
N(1)-C(2)	1.475(3)
N(1)-C(11)	1.476(3)
N(1)-C(3)	1.476(3)
N(2)-C(12)	1.465(3)
N(2)-C(4)	1.474(3)
N(2)-C(5)	1.491(3)
N(3)-C(27)	1.476(3)
N(3)-C(18)	1.476(2)
N(3)-C(19)	1.478(3)
N(4)-C(28)	1.474(3)
N(4)-C(20)	1.475(3)
N(4)-C(21)	1.483(3)
C(1)-C(2)	1.524(3)
C(1)-C(7)	1.551(3)
C(3)-C(4)	1.509(3)
C(5)-C(6)	1.501(3)
C(6)-C(13)	1.549(3)
C(7)-C(9)	1.527(4)
C(7)-C(8)	1.534(4)
C(7)-C(10)	1.535(4)
C(13)-C(15)	1.510(4)
C(13)-C(14)	1.523(4)
C(13)-C(16)	1.537(4)
C(17)-C(18)	1.527(3)
C(17)-C(23)	1.551(3)
C(19)-C(20)	1.511(3)
C(21)-C(22A)	1.369(7)
C(21)-C(22)	1.516(4)
C(22)-C(29)	1.566(4)
C(23)-C(25)	1.533(3)
C(23)-C(26)	1.533(3)
C(23)-C(24)	1.536(3)
C(29)-C(32A)	1.348(9)
C(29)-C(30)	1.476(4)
C(29)-C(31)	1.515(4)
C(29)-C(30A)	1.539(9)
C(29)-C(32)	1.584(5)
C(29)-C(22A)	1.634(8)
C(29)-C(31A)	1.693(10)
O(4)-Zr(1)-O(2)	90.08(6)
O(4)-Zr(1)-O(1)	141.74(6)
O(2)-Zr(1)-O(1)	88.99(6)
O(4)-Zr(1)-O(3)	87.69(6)
O(2)-Zr(1)-O(3)	141.97(6)

O(1)-Zr(1)-O(3)	115.17(6)
O(4)-Zr(1)-N(3)	85.54(6)
O(2)-Zr(1)-N(3)	148.77(6)
O(1)-Zr(1)-N(3)	75.98(6)
O(3)-Zr(1)-N(3)	68.82(6)
O(4)-Zr(1)-N(4)	68.49(6)
O(2)-Zr(1)-N(4)	82.00(6)
O(1)-Zr(1)-N(4)	73.52(6)
O(3)-Zr(1)-N(4)	131.36(6)
N(3)-Zr(1)-N(4)	67.62(6)
O(4)-Zr(1)-N(1)	149.78(6)
O(2)-Zr(1)-N(1)	88.28(6)
O(1)-Zr(1)-N(1)	68.41(6)
O(3)-Zr(1)-N(1)	75.44(6)
N(3)-Zr(1)-N(1)	110.46(6)
N(4)-Zr(1)-N(1)	140.81(6)
O(4)-Zr(1)-N(2)	84.02(7)
O(2)-Zr(1)-N(2)	68.05(6)
O(1)-Zr(1)-N(2)	130.24(6)
O(3)-Zr(1)-N(2)	73.97(6)
N(3)-Zr(1)-N(2)	141.65(5)
N(4)-Zr(1)-N(2)	139.22(6)
N(1)-Zr(1)-N(2)	67.43(6)
C(1)-O(1)-Zr(1)	131.01(12)
C(6)-O(2)-Zr(1)	125.24(13)
C(17)-O(3)-Zr(1)	129.74(12)
C(22)-O(4)-C(22A)	37.2(3)
C(22)-O(4)-Zr(1)	124.79(15)
C(22A)-O(4)-Zr(1)	127.6(3)
C(2)-N(1)-C(11)	109.98(17)
C(2)-N(1)-C(3)	110.53(17)
C(11)-N(1)-C(3)	108.21(18)
C(2)-N(1)-Zr(1)	102.78(12)
C(11)-N(1)-Zr(1)	111.85(13)
C(3)-N(1)-Zr(1)	113.41(14)
C(12)-N(2)-C(4)	108.52(18)
C(12)-N(2)-C(5)	109.40(19)
C(4)-N(2)-C(5)	109.94(19)
C(12)-N(2)-Zr(1)	111.07(14)
C(4)-N(2)-Zr(1)	110.48(13)
C(5)-N(2)-Zr(1)	107.43(12)
C(27)-N(3)-C(18)	110.21(16)
C(27)-N(3)-C(19)	108.29(16)
C(18)-N(3)-C(19)	110.64(16)
C(27)-N(3)-Zr(1)	110.73(12)
C(18)-N(3)-Zr(1)	102.44(11)
C(19)-N(3)-Zr(1)	114.43(12)
C(28)-N(4)-C(20)	108.20(17)
C(28)-N(4)-C(21)	109.45(19)
C(20)-N(4)-C(21)	111.35(18)
C(28)-N(4)-Zr(1)	110.44(13)
C(20)-N(4)-Zr(1)	110.18(12)
C(21)-N(4)-Zr(1)	107.23(13)
O(1)-C(1)-C(2)	108.04(17)
O(1)-C(1)-C(7)	113.24(18)
C(2)-C(1)-C(7)	112.50(18)
N(1)-C(2)-C(1)	109.08(17)
N(1)-C(3)-C(4)	110.28(18)
N(2)-C(4)-C(3)	111.68(18)
N(2)-C(5)-C(6)	110.61(19)
O(2)-C(6)-C(5)	108.3(2)

O(2)-C(6)-C(13)	112.86(18)
C(5)-C(6)-C(13)	114.2(2)
C(9)-C(7)-C(8)	109.2(2)
C(9)-C(7)-C(10)	108.4(2)
C(8)-C(7)-C(10)	109.9(2)
C(9)-C(7)-C(1)	108.53(19)
C(8)-C(7)-C(1)	111.22(18)
C(10)-C(7)-C(1)	109.5(2)
C(15)-C(13)-C(14)	109.8(3)
C(15)-C(13)-C(16)	107.3(2)
C(14)-C(13)-C(16)	109.0(3)
C(15)-C(13)-C(6)	111.1(2)
C(14)-C(13)-C(6)	110.9(2)
C(16)-C(13)-C(6)	108.5(2)
O(3)-C(17)-C(18)	108.29(16)
O(3)-C(17)-C(23)	113.20(16)
C(18)-C(17)-C(23)	112.84(17)
N(3)-C(18)-C(17)	108.58(16)
N(3)-C(19)-C(20)	110.27(17)
N(4)-C(20)-C(19)	111.83(17)
C(22A)-C(21)-N(4)	114.1(4)
C(22A)-C(21)-C(22)	36.6(3)
N(4)-C(21)-C(22)	112.0(2)
O(4)-C(22)-C(21)	108.8(2)
O(4)-C(22)-C(29)	111.7(2)
C(21)-C(22)-C(29)	112.7(2)
C(25)-C(23)-C(26)	109.4(2)
C(25)-C(23)-C(24)	109.3(2)
C(26)-C(23)-C(24)	108.85(19)
C(25)-C(23)-C(17)	111.61(18)
C(26)-C(23)-C(17)	107.89(18)
C(24)-C(23)-C(17)	109.70(18)
C(32A)-C(29)-C(30)	153.7(5)
C(32A)-C(29)-C(31)	74.0(5)
C(30)-C(29)-C(31)	112.8(3)
C(32A)-C(29)-C(30A)	117.6(6)
C(30)-C(29)-C(30A)	37.1(4)
C(31)-C(29)-C(30A)	125.6(4)
C(32A)-C(29)-C(22)	85.4(4)
C(30)-C(29)-C(22)	113.6(2)
C(31)-C(29)-C(22)	110.2(3)
C(30A)-C(29)-C(22)	123.1(4)
C(32A)-C(29)-C(32)	47.8(4)
C(30)-C(29)-C(32)	107.5(3)
C(31)-C(29)-C(32)	106.8(3)
C(30A)-C(29)-C(32)	70.4(4)
C(22)-C(29)-C(32)	105.4(2)
C(32A)-C(29)-C(22A)	118.6(5)
C(30)-C(29)-C(22A)	82.5(3)
C(31)-C(29)-C(22A)	115.4(3)
C(30A)-C(29)-C(22A)	104.4(5)
C(22)-C(29)-C(22A)	33.2(3)
C(32)-C(29)-C(22A)	128.5(3)
C(32A)-C(29)-C(31A)	111.1(6)
C(30)-C(29)-C(31A)	77.8(4)
C(31)-C(29)-C(31A)	37.3(4)
C(30A)-C(29)-C(31A)	103.3(5)
C(22)-C(29)-C(31A)	115.9(4)
C(32)-C(29)-C(31A)	132.1(4)
C(22A)-C(29)-C(31A)	99.3(5)
C(21)-C(22A)-O(4)	112.6(5)

C(21)-C(22A)-C(29)	117.0(5)
O(4)-C(22A)-C(29)	103.9(4)

Symmetry transformations used to generate equivalent atoms:

Table 5/4 Anisotropic displacement parameters (A^2 x 10^3).

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zr(1)	17(1)	17(1)	15(1)	-2(1)	-3(1)	-4(1)
O(1)	19(1)	22(1)	21(1)	-2(1)	-4(1)	-1(1)
O(2)	35(1)	21(1)	20(1)	-3(1)	-10(1)	-8(1)
O(3)	25(1)	19(1)	18(1)	-3(1)	-2(1)	-8(1)
O(4)	17(1)	24(1)	30(1)	-3(1)	-5(1)	-5(1)
N(1)	24(1)	26(1)	21(1)	-4(1)	-1(1)	-8(1)
N(2)	39(1)	23(1)	24(1)	1(1)	-13(1)	-10(1)
N(3)	22(1)	22(1)	18(1)	-3(1)	-2(1)	-7(1)
N(4)	25(1)	26(1)	25(1)	-2(1)	-3(1)	-10(1)
C(1)	20(1)	29(1)	27(1)	-6(1)	-5(1)	-3(1)
C(2)	21(1)	28(1)	28(1)	-8(1)	0(1)	-1(1)
C(3)	40(1)	36(1)	17(1)	-2(1)	3(1)	-12(1)
C(4)	48(2)	31(1)	20(1)	2(1)	-4(1)	-17(1)
C(5)	68(2)	39(1)	27(1)	5(1)	-25(1)	-27(1)
C(6)	57(2)	29(1)	34(1)	-6(1)	-22(1)	-13(1)
C(7)	27(1)	29(1)	38(1)	-3(1)	-10(1)	3(1)
C(8)	43(2)	28(1)	47(2)	-4(1)	-7(1)	-7(1)
C(9)	61(2)	36(1)	41(2)	7(1)	-20(1)	4(1)
C(10)	32(2)	40(2)	80(2)	-8(1)	-18(2)	10(1)
C(11)	26(1)	38(1)	36(1)	-8(1)	2(1)	-15(1)
C(12)	47(2)	32(1)	35(1)	4(1)	-21(1)	-6(1)
C(13)	58(2)	27(1)	33(1)	-8(1)	-20(1)	-13(1)
C(14)	146(4)	43(2)	78(2)	1(2)	-77(3)	-37(2)
C(15)	87(3)	39(2)	63(2)	-27(1)	-24(2)	0(2)
C(16)	97(3)	60(2)	59(2)	-12(2)	-21(2)	-46(2)
C(17)	24(1)	24(1)	22(1)	-6(1)	-3(1)	-9(1)
C(18)	27(1)	22(1)	19(1)	-5(1)	-3(1)	-8(1)
C(19)	34(1)	28(1)	18(1)	-3(1)	1(1)	-11(1)
C(20)	32(1)	27(1)	19(1)	1(1)	0(1)	-11(1)
C(21)	24(1)	49(2)	39(1)	3(1)	-2(1)	-14(1)
C(22)	20(2)	33(2)	28(2)	-9(1)	-4(1)	-9(1)
C(23)	33(1)	21(1)	27(1)	-5(1)	1(1)	-10(1)
C(24)	57(2)	31(1)	42(1)	-12(1)	0(1)	-21(1)
C(25)	40(1)	24(1)	37(1)	1(1)	-7(1)	-2(1)
C(26)	49(2)	27(1)	36(1)	-3(1)	6(1)	-19(1)
C(27)	30(1)	29(1)	26(1)	-5(1)	-11(1)	-7(1)
C(28)	49(2)	34(1)	32(1)	-3(1)	-2(1)	-27(1)
C(29)	19(1)	40(1)	50(2)	-13(1)	-9(1)	-5(1)
C(30)	29(2)	45(2)	56(3)	-28(2)	-8(2)	0(2)
C(31)	22(2)	72(3)	69(3)	-11(2)	-8(2)	-17(2)
C(32)	33(2)	73(3)	44(2)	-8(2)	-16(2)	-2(2)

Table 5/5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(1)	5680	6201	2848	32
H(2A)	6469	6007	1355	34
H(2B)	5096	5792	1330	34
H(3A)	4705	7216	236	40
H(3B)	5691	7991	118	40
H(4A)	3765	9659	535	40
H(4B)	3658	9229	-310	40
H(5A)	2828	7567	33	48
H(5B)	1346	8536	11	48
H(6)	354	7740	1359	45
H(8A)	5143	3046	2737	62
H(8B)	5507	3852	1810	62
H(8C)	4055	4311	2492	62
H(9A)	5507	3339	4053	77
H(9B)	4207	4530	4067	77
H(9C)	5630	4577	4154	77
H(10A)	7620	4405	2861	84
H(10B)	7532	4150	1944	84
H(10C)	7542	3137	2789	84
H(11A)	6539	7930	1266	50
H(11B)	5580	7973	2249	50
H(11C)	5160	9034	1475	50
H(12A)	1452	10572	1068	59
H(12B)	343	9960	1104	59
H(12C)	1236	10381	169	59
H(14A)	1054	7057	-533	115
H(14B)	-415	7322	156	115
H(14C)	308	6055	-207	115
H(15A)	2431	4594	333	95
H(15B)	3059	5076	912	95
H(15C)	3080	5651	-99	95
H(16A)	147	4956	1261	96
H(16B)	-580	6144	1728	96
H(16C)	794	5180	1963	96
H(17)	3684	9879	3005	28
H(18A)	1992	9998	4314	27
H(18B)	877	10026	3822	27
H(19A)	420	8522	4792	34
H(19B)	1651	7864	5285	34
H(20A)	2277	6148	4606	32
H(20B)	700	6462	5139	32
H(21A)	-885	7932	4384	47
H(21B)	-1049	6918	3975	47
H(22)	-712	7886	2581	32
H(24A)	3335	11763	3435	64
H(24B)	1752	11978	3932	64
H(24C)	2187	12965	3156	64
H(25A)	124	11937	3217	56
H(25B)	573	11453	2283	56
H(25C)	508	12784	2318	56
H(26A)	2872	12659	1604	59
H(26B)	3022	11419	1329	59
H(26C)	4102	11479	1808	59

H(27A)	3700	8225	4643	42
H(27B)	4358	8117	3612	42
H(27C)	3956	7021	4272	42
H(28A)	2197	5126	3580	55
H(28B)	922	5586	3129	55
H(28C)	696	5164	4174	55
H(30A)	-1546	10598	3392	65
H(30B)	-2254	9927	4291	65
H(30C)	-3182	10917	3678	65
H(31A)	-4224	9371	3596	81
H(31B)	-3285	8420	4219	81
H(31C)	-3191	8130	3269	81
H(32A)	-2290	9354	1875	79
H(32B)	-1717	10369	1943	79
H(32C)	-3327	10546	2275	79
H(32D)	-3330	9365	2451	59
H(32E)	-2244	8084	2665	59
H(32F)	-1735	9108	1973	59
H(30D)	-1710	10888	2585	58
H(30E)	-2286	10853	3635	58
H(30F)	-3321	11151	3012	58
H(31D)	-4273	9591	4102	63
H(31E)	-3125	9316	4635	63
H(31F)	-3276	8252	4279	63
H(22A)	-783	9108	3972	27

6. $^{13}C\{^{1}H\}$ NMR spectra for H_2L^2 and $L^2Ti(O^iPr)_2$

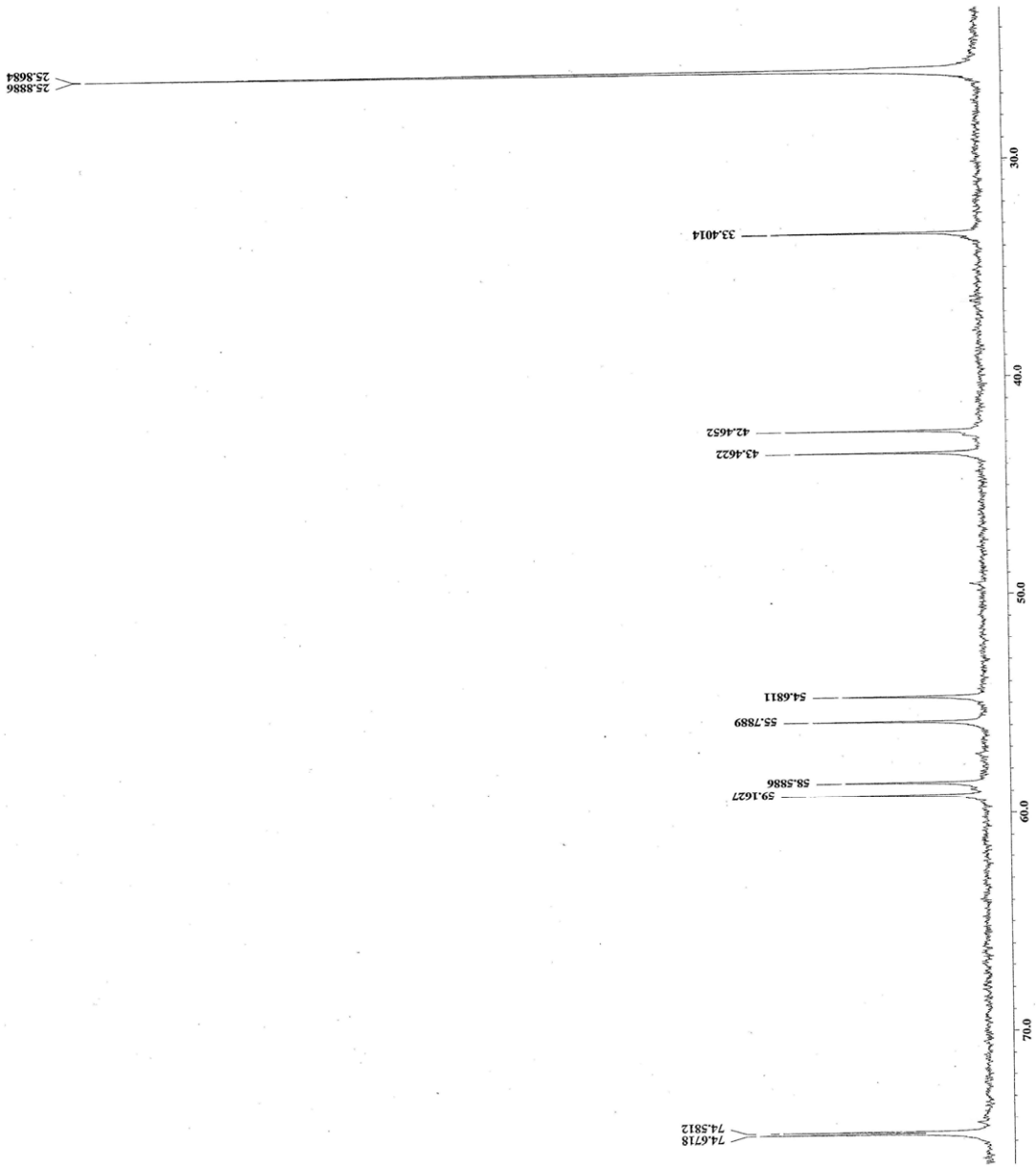


Figure 6/1

$^{13}C\{^{1}H\}$ NMR spectrum of $H_2\mathbf{L^2}$ isolated as a clear oil containing a mixture of rac (*R*,*R*/*S*,*S*) and meso (*R*,*S*) diastereoisomers at room temperature (waxy solid at -25°C).

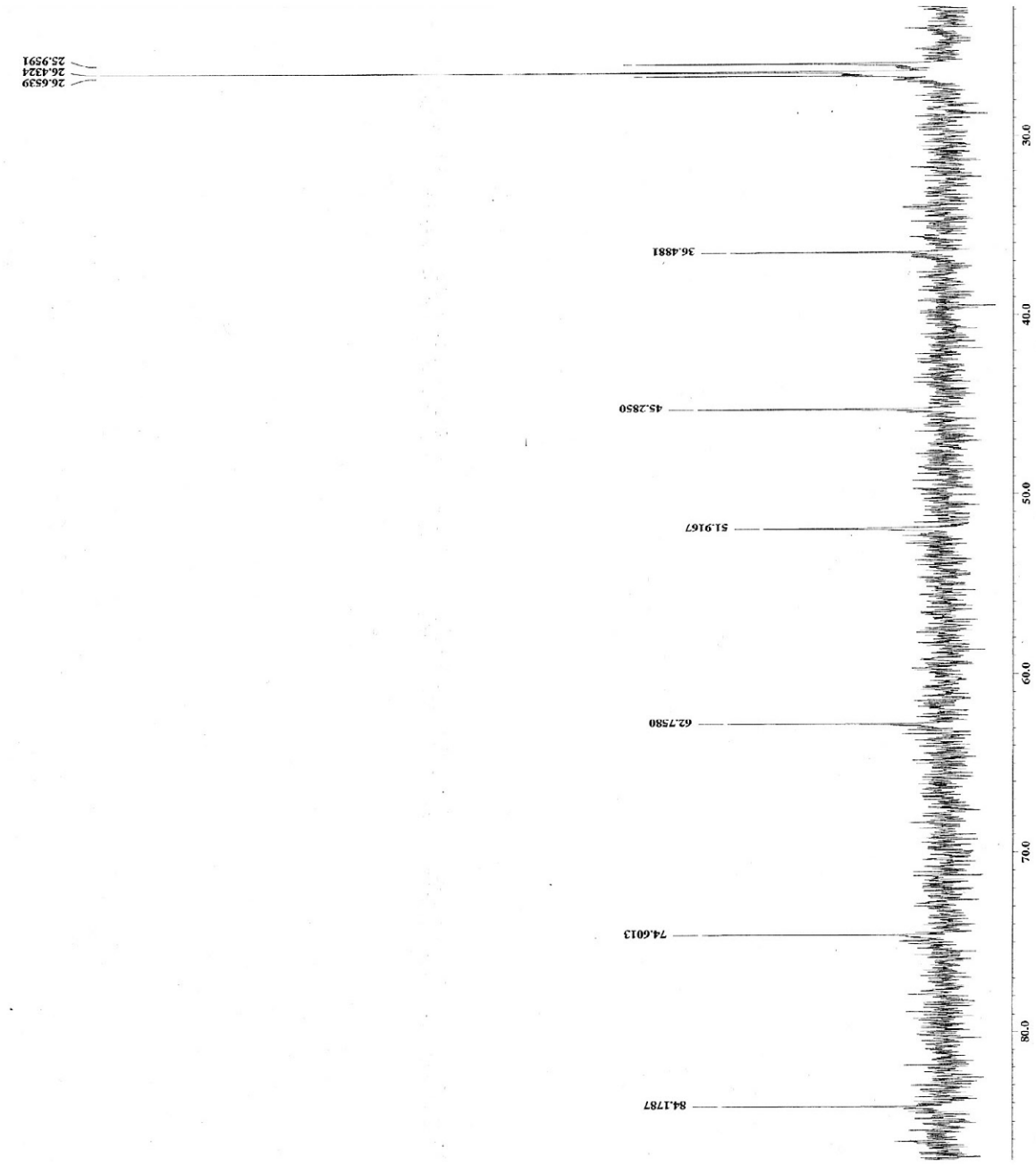
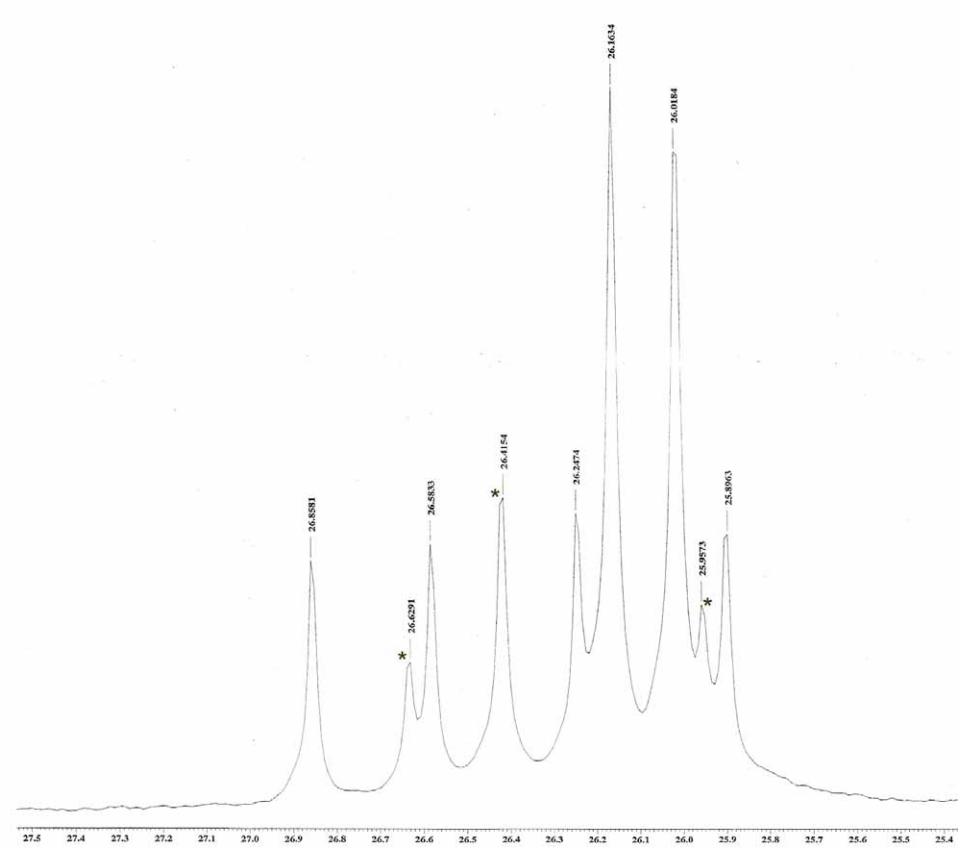


Figure 6/2

$^{13}C\{^{1}H\}$ NMR spectrum of the crystalline product obtained from the reaction of $Ti(O^{i}Pr)_4$ with $H_2\mathbf{L^2}$ after two recrystallizations. The nine peaks correspond to the expected signals for the crystallographically characterized C_2 symmetric [(*R*,*R*) and (*S*,*S*)] isomers of $\mathbf{L^2}Ti(O^{i}Pr)_2$.

26.0184
26.1634
26.2474
26.4154
34.6449
36.4542
45.2638
47.8976
50.1840
51.9131
56.7226
59.1807
59.3792
62.7229
65.9674
74.4488
74.6778
74.7847
84.1059
84.7701
85.0831
30.0
40.0
50.0
60.0
70.0
80.0



Figures 6/3a (previous page) and 6/3b

$^{13}C\{^{1}H\}$ NMR spectra (including expansion on the ^{i}Pr and ^{t}Bu methyl region, bottom) of the oil obtained from the supernatent hexane solution in the reaction of $Ti(O^{i}Pr)_4$ with $H_2\mathbf{L^2}$. The peaks marked with an asterix (*) correspond to the minor component of the mixture - *i.e.* the C_2 symmetric [(*R*,*R*) and (*S*,*S*)] isomers. The remaining peaks correspond to the major component [*i.e.* the C_1 symmetric (*R*,*S*)/(*S*,*R*) isomers of $\mathbf{L^2}Ti(O^{i}Pr)_2$].