TiCl₄-Complexation by Mandelic Acid Methyleneester

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The complexes of trinuclear TiCl₃-O-TiCl₃/TiCl₂(O-(*R*)-mandelic acid methylester)₂ I, C₁₈H₁₈Cl₈O₇Ti₃, and dimeric TiCl₃O-*rac*-mandelic acid methylester II, C₁₈H₁₈Cl₆O₆Ti₂, were determined unambiguously by X-ray diffraction. Both crystal structures contain one solvent molecule toluene per complex. In structure I there are five independent complexes in the asymmetric unit cell. The formation of both the crystal structure as well as the coordination sphere of titanium is controlled sensitively by the chirality of mandelic acid methylesters.

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In order to interpret the results of regio- as well as stereoselectivity of direct aldol additions studies of structures of complexes used are ongoing. Knowledge of the molecular structure of metal complexes is very important to understand the catalytic mechanism of metal-catalyzed organic reactions. In contrast to the great number of X-ray structure analyses in the titanium(IV) alkoxide series, only little is known about titanium complexes of α -hydroxy acids. Especially X-ray structure results of titanium complexes of mandelic acid are rare.¹ That's why, such complexes have been further studied.

The TiCl₄-complexes were synthesized to act as catalysts in enantioselective direct aldol additions. At first, optically active (*R*)-mandelic acid methylester was dissolved with equimolar amounts of TiCl₄ at 0°C in toluene. A trinuclear TiCl₄-complex I, C₁₈H₁₈Cl₈O₇Ti₃, was obtained. After four days, dark-brown crystals were collected, washed with toluene and dried in a high vacuo at room temperature. Interestingly, under the same conditions racemic mandelic acid methylester reacts to a dinuclear complex II, C₁₈H₁₈Cl₆O₆Ti₂. Here, already after two days red-brown crystals were formed. They were also washed and dried as just mentioned.

X-ray data were collected using graphite-monochromated Mo-*K*_α radiation ($\lambda = 0.71073$ Å) at low temperatures on a Stoe 4-circle diffractometer for compound I and on a Stoe image plate diffractometer for compound II, respectively. Data reduction was carried out with the Stoe Program Package.² The structures were solved by direct methods using SHELXS97.³ All non-hydrogen atoms were refined anisotropically with SHELXL97^{3a} using blocked-matrix (for I) or full-matrix (for II) least-squares

on *F*². The positions of the hydrogen atoms were calculated and included in the refinement applying the riding model. Crystal and experimental data are listed in Table 1. The final positional parameters for non-hydrogen atoms in I and II (without solvent atoms) are given in Table 2. ORTEP⁴ plots of I and II are depicted in Figs. 2 and 3, respectively. For saving space in Table 2 and Fig. 2, only one of the five independent complexes I is given, because all are chemically equal.

During the complexation reactions, the tetrahedral titanium increases its coordination number (c.n.) considerably and forms rather different polyhedra. One pentagonal bipyramid (c.n. = 7) and two tetragonal pyramids (c.n. = 5) are observed in I,

Table 1 Crystal and experimental data of the complexes

	I	II
Formula	C ₂₅ H ₂₆ Cl ₈ O ₇ Ti ₃	C ₂₅ H ₂₆ Cl ₆ O ₆ Ti ₂
Formula weight	865.76	730.96
Crystal habit	brown block	red block
Crystal size/mm	0.72 × 0.70 × 0.64	0.52 × 0.48 × 0.36
Crystal system	triclinic	triclinic
Space group	<i>P</i> 1(1)	<i>P</i> $\bar{1}$ (2)
Temperature/K	150(2)	180(2)
<i>Z</i>	5	2
<i>a</i> /Å	10.923(1)	10.704(3)
<i>b</i> /Å	20.028(2)	12.125(4)
<i>c</i> /Å	22.273(2)	13.028(4)
α /°	65.72(2)	64.96(3)
β /°	76.87(2)	86.14(3)
γ /°	88.03(2)	84.91(4)
<i>V</i> /Å ³	4316.1(7)	1525.1(8)
<i>D</i> _{calc} /g cm ⁻³	1.665	1.592
μ _A (Mo- <i>K</i> _α)/mm ⁻¹	1.336	1.087
<i>T</i> _{min/max} (Abs.cor.)	0.415/0.482 (ψ -scan)	0.602/0.696 (refdelf)
No. of reflections	19324	17041
Refl., unique (<i>R</i> _{int})	19316(0.067)	5193(0.029)
Refl. [<i>I</i> > 2 σ (<i>I</i>)]	14092	4179
2 θ _{max} /° (complete)	25.97 (99.2%)	25.25(93.6%)
Data/restraints/param.	19316/46/1939	5193/0/355
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0469	0.0247
<i>wR</i> ₂ [all data]	0.1267	0.0677
($\Delta\rho$) _{max/min} /eÅ ⁻³	0.681/−0.417	0.310/−0.252
CCDC	684925	684926

Fig. 1 Chemical structure of the studied complexes.

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Fig. 2 Molecular structure I showing 50% probability atomic displacement ellipsoids. H atoms not bounded at stereocenters are omitted.

Fig. 3 Molecular structure II showing 50% probability atomic displacement ellipsoids. H atoms not bounded at stereocenters are omitted.

whereas two octahedra (c.n. = 6) are found in II. All observed polyhedra are distorted, obviously caused by a chelating effect of the ester ligand. Among these polyhedra, the pentagonal bipyramid has the least distorted form. Here, the oxygen and chlorine atoms are strictly separated for the basal plane on one side and apexes on the other side. This type of a seven-coordinated titanium with five oxygen atoms in the basal plane and two chlorine atoms at the apexes of a pentagonal bipyramid is to the best of our knowledge unknown up to now for multinuclear titanium-complexes. The biggest deviation from the equatorial plane is even 0.11(1) Å for O4. For the characteristic angles within the pentagonal-bipyramidal coordination polyhedron see Table 3. As expected, all Cl-Ti-O angles are about 90°, while the Cl-Ti-Cl angle is near 180°. This also holds within the limits of error for the other four corresponding, but symmetry-independent polyhedra in the unit cell of compound I.

While all five trinuclear complexes in I are without symmetry, the unique complex in II (Fig. 3) is nearly centrosymmetric. Thus, a comparison of the two related, but stereochemically different compounds permit the conclusion that the formation of both the crystal structure as well as the coordination sphere of titanium seems to be controlled sensitively by the chirality of the mandelic acid methylesters.

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
I				
C1	403 (4)	2880 (2)	4574 (2)	20 (1)
C2	1818 (5)	2878 (2)	4458 (2)	23 (1)
C3	-132 (4)	3321 (3)	4977 (2)	30 (1)
C4	-274 (5)	3024 (4)	5664 (3)	43 (2)
C5	-740 (6)	3436 (4)	6041 (3)	56 (2)
C6	-1082 (6)	4130 (4)	5713 (3)	55 (2)
C7	-998 (5)	4451 (3)	5016 (3)	41 (2)
C8	-524 (5)	4031 (3)	4652 (3)	31 (1)
C9	3619 (5)	2502 (3)	4909 (3)	38 (2)
C10	3163 (4)	4561 (2)	1604 (2)	19 (1)
C11	4029 (4)	4154 (2)	2065 (2)	19 (1)
C12	3411 (4)	4453 (2)	961 (2)	20 (1)
C13	3882 (5)	5036 (3)	345 (2)	31 (1)
C14	4182 (5)	4945 (3)	-247 (3)	34 (1)
C15	4002 (4)	4250 (3)	-229 (3)	28 (1)
C16	3510 (6)	3670 (3)	369 (3)	37 (2)
C17	3211 (5)	3769 (3)	974 (3)	34 (1)
C18	6068 (5)	3886 (4)	2213 (3)	43 (2)
C19	1609 (1)	2547 (1)	2989 (1)	29 (1)
C20	1793 (1)	4748 (1)	3156 (1)	27 (1)
C21	-1259 (1)	1795 (1)	4276 (1)	32 (1)
C22	-1588 (1)	2681 (1)	2696 (1)	27 (1)
C23	-2712 (1)	3398 (1)	3849 (1)	31 (1)
C24	-190 (1)	4278 (1)	1206 (1)	45 (1)
C25	-1566 (1)	5050 (1)	2319 (1)	44 (1)
O1	1174 (1)	5765 (1)	1330 (1)	33 (1)
O2	201 (3)	3206 (2)	3904 (1)	17 (1)
O3	2500 (3)	3191 (2)	3882 (2)	24 (1)
O4	3595 (3)	3759 (2)	2665 (2)	24 (1)
O5	1929 (3)	4273 (2)	2028 (2)	18 (1)
O6	13 (3)	3813 (2)	2790 (2)	17 (1)
O7	2257 (3)	2551 (2)	4995 (2)	29 (1)
O8	5221 (3)	4254 (2)	1773 (2)	27 (1)
O9	1646 (1)	3671 (1)	3047 (1)	16 (1)
O10	-1016 (1)	2949 (1)	3479 (1)	17 (1)
O11	235 (1)	4639 (1)	1938 (1)	21 (1)
II				
C1	294 (2)	4870 (1)	3181 (1)	19 (1)
C2	581 (2)	5095 (1)	1952 (1)	18 (1)
C3	-1030 (2)	5301 (1)	3372 (1)	20 (1)
C4	-2047 (2)	4920 (2)	3021 (2)	27 (1)
C5	-3254 (2)	5336 (2)	3183 (2)	31 (1)
C6	-3462 (2)	6136 (2)	3701 (2)	31 (1)
C7	-2455 (2)	6515 (2)	4056 (2)	29 (1)
C8	-1241 (2)	6103 (2)	3889 (1)	23 (1)
C9	850 (2)	6510 (2)	38 (2)	35 (1)
C10	4992 (2)	29 (2)	1762 (1)	21 (1)
C11	4688 (2)	-177 (1)	2985 (1)	20 (1)
C12	6322 (2)	-408 (2)	1582 (1)	22 (1)
C13	6543 (2)	-1256 (2)	1119 (1)	26 (1)
C14	7766 (2)	-1644 (2)	941 (2)	32 (1)
C15	8763 (2)	-1183 (2)	1214 (2)	35 (1)
C16	8546 (2)	-343 (2)	1683 (2)	38 (1)
C17	7331 (2)	37 (2)	1872 (2)	32 (1)
C18	4418 (2)	-1548 (2)	4904 (2)	35 (1)
C19	2028 (2)	7858 (2)	3096 (2)	33 (1)
C20	2629 (2)	6706 (2)	3631 (2)	36 (1)
C21	3320 (2)	6154 (2)	3040 (2)	45 (1)
C22	3441 (2)	6735 (3)	1872 (2)	55 (1)
C23	2867 (3)	7893 (3)	1313 (2)	57 (1)
C24	2158 (2)	8447 (2)	1919 (2)	40 (1)
C25	1261 (2)	8439 (2)	3762 (2)	48 (1)
C26	-762 (1)	1937 (1)	2925 (1)	28 (1)
C27	1594 (1)	913 (1)	4820 (1)	31 (1)
C28	2045 (1)	1752 (1)	1850 (1)	21 (1)
C29	3234 (1)	3212 (1)	3008 (1)	23 (1)
C30	6057 (1)	2946 (1)	2025 (1)	30 (1)
C31	3771 (1)	3992 (1)	56 (1)	34 (1)
C32	514 (1)	3579 (1)	3795 (1)	21 (1)
C33	857 (1)	4222 (1)	1708 (1)	20 (1)
C34	521 (1)	6231 (1)	1231 (1)	26 (1)
C35	4785 (1)	1315 (1)	1128 (1)	22 (1)
C36	4403 (1)	709 (1)	3207 (1)	21 (1)
C37	4739 (1)	-1307 (1)	3719 (1)	27 (1)
C38	1069 (1)	2506 (1)	3223 (1)	18 (1)
C39	4227 (1)	2411 (1)	1677 (1)	19 (1)

Table 3 Central angles/° at Ti1 in a pentagonal bipyramid of I

O5-Ti1-Cl2	96.92(11)	O5-Ti1-Cl1	87.24(11)
O4-Ti1-Cl2	87.91(10)	O4-Ti1-Cl1	94.97(11)
O1-Ti1-Cl2	94.13(10)	O1-Ti1-Cl1	85.80(10)
O3-Ti1-Cl2	89.74(11)	O3-Ti1-Cl1	87.79(11)
O2-Ti1-Cl2	86.88(11)	O2-Ti1-Cl1	88.85(11)
Cl1-Ti1-Cl2	175.56(6)		

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