

Synthesis and Structural Characterisation of a Hexanuclear Ti^{IV} Compound $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OOCCHCl}_2)_8$

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Titanium tetra-butoxide was reacted with dichloroacetic acid in 1:1 and 1:2 molar ratio in toluene at ambient temperature to give, respectively, the mono- and bis-substituted products $\text{Ti}(\text{OBu}^t)_3(\text{OOCCHCl}_2)$ and $\text{Ti}(\text{OBu}^t)_2(\text{OOCCHCl}_2)_2$ (**1**) in quantitative yields. However, when a toluene solution of compound **1** was kept at -20°C for crystallisation, colourless crystals of a hexanuclear complex $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OOCCHCl}_2)_8$ (**2**) were obtained. The basic skeletal arrangement of compound **2**, as revealed by X-ray diffraction, can be described as corner-removed, inversion-related $[\text{Ti-O}]_4$ cubes with face-linked oxide bridges.

Key words: Titanium, Butoxy, Oxo, Dichloroacetate, Crystal Structure

Introduction

Although TiO_2 has a rather large band gap (3.2 eV), it is an attractive material for many technological fields like photoluminescence, solar energy conversion, photocatalysis *etc.* because it is cheap, non-toxic and highly insoluble in water. Titanium alkoxides have been the chief precursors in the sol-gel process for producing titania materials. Unfortunately, due to the fast kinetics of the hydrolysis and condensation reactions, relatively little information is available concerning progressive structural evolution in transition metal oxide systems in general [1–3]. Klemperer and coworkers [4, 5] have extended the concept of the molecular building block approach from silica to titania. The metal oxide core of low-nuclearity titanium oxo-alkoxides such as $\text{Ti}_7\text{O}_4(\text{OC}_2\text{H}_5)_{20}$ was found to be too kinetically labile, while that of the high-nuclearity $\text{Ti}_{16}\text{O}_{16}(\text{OC}_2\text{H}_5)_{32}$ is sufficiently inert to serve as a building block for the sol-gel processing of new forms of titania. Carboxylic acids, especially acetic acid, have been most extensively used to generate new molecular precursors by reacting then with $\text{Ti}(\text{OR})_4$, and compounds with metal oxygen cores having different skeletal arrangements

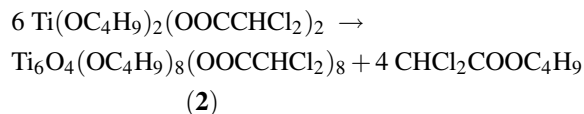
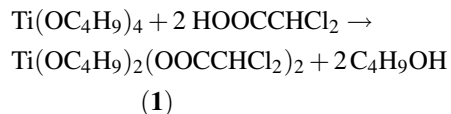
have been isolated. The generation of oxo ligands in these compounds was accompanied with either ester or ether elimination reactions. For example, reactions of $\text{Ti}(\text{OR})_4$ with n HOOCCH_3 have generated compounds of the general formula $\text{Ti}_6\text{O}_4(\text{OOCCH}_3)_{4n}(\text{OR})_{16-4n}$ ($R = \text{C}_2\text{H}_5$, $n = 2$ [6], $R = \text{Pr}^i$, $n = 1$ [7], $n = 2$ [8], $R = \text{C}_4\text{H}_9$, $n = 2$ [9]) out of ester elimination reactions. Notably all these reactions were performed as “neat” reactions (no solvents). Even when the steric bulk of the alkoxide and/or carboxylic acid was increased, the same core [10] was obtained. Boyle *et al.* [11] have recently reported the products $\text{Ti}_4(\mu_4\text{-O})_2(\mu\text{-O})_2(\mu\text{-OOCH})_2(\mu\text{-OPr}^i)_4(\text{OPr}^i)_6$ and $\text{Ti}_6(\mu_3\text{-O})_6(\mu\text{-OOCH})_6(\mu\text{-OPr}^i)_4(\text{OPr}^i)_6$ which were obtained in a medium with a small amount of solvent. Another product of the composition $\text{Ti}_6(\mu_3\text{-O})_6(\mu\text{-OOCCH}_2\text{C}_6\text{H}_4\text{OPh})_6(\text{OEt})_6$ has also been reported [12] which was produced in refluxing toluene out of the ester elimination pathway. Very recently, similar X-ray structures of mono-, di-, tetra-, and hexa-nuclear complexes of Ti^{IV} have been published [13]. The generation of oxo ligands in all the above products has been attributed to ester elimination which is facilitated under these conditions. Fehlner and coworkers have reported [10] compounds of the general

formula $\text{Ti}_4\text{O}_4(\text{OR})_4\{\text{OOC}(\mu_3\text{-C})[\text{Co}_3(\text{CO})_9]\}_4$ ($R = \text{Pr}^i, \text{C}_4\text{H}_9, \text{C}_6\text{H}_5$) and $\text{Ti}_6\text{O}_4(\text{OC}_2\text{H}_5)_{12}\{\text{OOC}(\mu_3\text{-C})[\text{Co}_3(\text{CO})_9]\}_4$ by the reactions of titanium alkoxides with the cluster-substituted acid $(\text{CO})_9\text{Co}_3(\mu_3\text{-C})(\text{COOH})$ in sufficient amounts of solvents at ambient temperature. In these products an oxo group was found to be generated out of elimination of ether molecules. We have also reported the synthesis and structure of isopropoxy carboxylate clusters [14] of Ti^{IV} and a hexanuclear Gd^{III} compound [15] $\text{Gd}_6(\mu_3\text{-OH})_6(\text{acac})_{12} \cdot 1.25 \text{CHCl}_3$ which were formed by elimination of ether molecules from the corresponding alkoxy compounds. We present here the synthesis and single-crystal X-ray structure determination of a hexanuclear Ti^{IV} compound $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OOCCHCl}_2)_8$ showing interesting structural features.

Results and Discussion

Titanium tetra-butoxide was reacted with dichloroacetic acid in 1:1 molar ratio at ambient temperature in toluene, and the reaction mixture was stirred for eight hours. After evaporation of the solvent, a light-orange viscous liquid with analytically and spectroscopically confirmed composition $\text{Ti}(\text{OC}_4\text{H}_9)_3(\text{OOCCHCl}_2)$ was obtained in quantitative yield. In order to obtain the bis-substituted product, another reaction of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was carried out with dichloroacetic acid in 1:2 molar ratio under the same conditions. After removal of the solvent under vacuum a light-yellow powder corresponding analytically to $\text{Ti}(\text{OC}_4\text{H}_9)_2(\text{OOCCHCl}_2)_2$ (**1**) was obtained. Compound **1** was re-dissolved in toluene and left for crystallization at -30°C to give colourless crystals (67% yield) after 48 h.

One of the crystals was proven to be $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OOCCHCl}_2)_8$ (**2**) by X-ray analysis. The formation of the product **2** can be schematised by the following reactions:



The formation of product **2** out of an ester elimination reaction has been proven by the examination of the IR

spectrum of the volatiles of the solution, from which it was obtained. In the ambient-temperature ^1H NMR spectrum of **2** the characteristic peaks corresponding to both butoxy and dichloroacetate groups are visible and indicate that these groups are present in different environments. It is noteworthy that in all of the above mentioned titanium complexes [6–13], wherein the presence of oxo ligands is an outcome of ester elimination, have been made either with neat reactants, very small amounts of solvents, or in refluxing solvents, in single-step reactions. However, in the present work we have first isolated a bis-substituted product **1** which upon aging in a sufficient amount of solvent has led to the formation of the complex **2**. Compound **2** also possesses a Ti_6O_4 core which has been previously reported with other carboxylic acids [6–9] which are fairly less acidic than dichloroacetic acid used in the present work. This points towards the extra stability possessed by the Ti_6O_4 core as an important structural building block, *e. g.* in the sol-gel polymerisation. It is encountered irrespective of the steric bulk of the alkoxide and/or carboxylic acid, as well as of the acidity of the carboxylic acid and the reaction conditions.

Crystal structure

Compound **2** crystallises in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure (Fig. 1) consists of a hexanuclear unit of the formula $\text{Ti}_6\text{O}_4(\text{OC}_4\text{H}_9)_8(\text{OOCCHCl}_2)_8$. Each molecule possesses crystallographic inversion symmetry in the crystal and contains six titanium atoms each being hexa-coordinated. In the structure of this hexanuclear complex, there are two Ti_2O_{10} units (made by two edge-sharing octahedra) linked to two corner-sharing

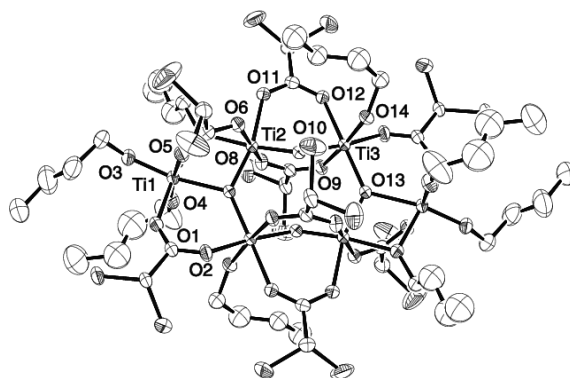


Fig. 1. ORTEP representation of the molecular structure of **2** in the crystal (displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths (Å) for **2**.

Ti1–O4	1.747(2)	Ti2–O6	2.015(2)
Ti2–O11	2.075(2)	Ti2–O7	2.029(2)
Ti2–Ti3	3.3800(7)	Ti2–O8	2.034(2)
Ti1–O3	1.775(2)	Ti3–O14	1.749(2)
Ti1–O7	1.973(2)	Ti3–O10	1.856(2)
Ti1–O1	2.065(2)	Ti3–O13	1.912(2)
Ti1–O13	2.113(2)	Ti3–O2	2.076(2)
Ti1–O5	2.200(2)		
Ti1–Ti2	3.0781(7)	Ti3–O12	2.116(2)
Ti2–O10	1.765(2)	Ti3–O9	2.121(2)
Ti2–O13	1.866(2)		

Table 2. Selected bond angles (deg) for **2**.

O4–Ti1–O3	101.56(12)	O10–Ti2–O8	92.13(9)
O10–Ti2–O11	90.38(9)	O13–Ti2–O8	91.41(9)
O6–Ti2–O8	172.39(9)	O7–Ti2–O8	89.02(9)
O4–Ti1–O7	98.99(10)	O13–Ti2–O11	164.09(9)
O3–Ti1–O7	97.46(10)	O7–Ti2–O11	83.63(8)
O3–Ti1–O1	92.30(10)	O14–Ti3–O10	100.41(10)
O7–Ti1–O1	161.81(9)	O14–Ti3–O13	100.31(10)
O4–Ti1–O13	94.79(10)	O10–Ti3–O13	97.85(8)
O4–Ti1–O5	172.31(10)	O14–Ti3–O2	90.84(10)
O3–Ti1–O5	85.30(10)	O10–Ti3–O2	163.97(9)
O7–Ti1–O5	83.39(9)	O13–Ti3–O2	91.24(9)
O1–Ti1–O5	82.15(9)	O14–Ti3–O12	89.28(10)
O13–Ti1–O5	78.60(8)	O13–Ti3–O12	167.30(9)
O10–Ti2–O13	105.15(9)	O2–Ti3–O12	80.22(9)
O10–Ti2–O6	93.33(9)	O14–Ti3–O9	166.77(10)
O13–Ti2–O6	92.28(9)	O10–Ti3–O9	87.50(8)
O10–Ti2–O7	173.76(9)	Ti1–O7–Ti2	100.52(9)
O13–Ti2–O7	80.94(8)	O6–Ti2–O7	84.99(9)

octahedra with the help of four bridging oxygen atoms: two triply bridging (μ_3 -oxo) O13 and O*13 and two doubly bridging O10 and O*10. In the structure all the dichloroacetate groups are bridging bidendately while the butoxy groups are of two types. Out of the eight butoxy groups six are present at terminal positions and two (O8 and O*8) are occupying bridging positions. Although all six titanium atoms are bonded to triply bridging oxygen atoms, they have non-equivalent environments. Ti1 is attached to two oxygen atoms of terminal butoxy groups, one oxygen atom of the bridging butoxy group shared with Ti2 and two oxygen atoms in *cis* positions of the bridging acetate groups. Ti2 is connected to one oxygen atom of the bridging butoxy group (shared with Ti1), three oxygen atoms of the dichloroacetate groups at equatorial positions, and one μ_2 -oxo ligand, while Ti3 has three oxygen atoms of the acetate groups in facial positions, one oxygen atom of the terminal butoxy group, and one doubly bridging oxygen atom (with Ti2). The important bond lengths and angles for complex **2** are listed in Tables

1 and 2, respectively. In general, the titanium-oxygen bond lengths range from 1.747 to 2.200 Å (average bond lengths 1.972 Å). The Ti–O bonds of the terminal butoxy groups are short (average 1.747 Å), and the corresponding Ti–O–C angles are rather large (144.1 – 175.1°).

Longer Ti–O bonds (Ti1–O13 = 2.113 Å and Ti1–O5 = 2.200 Å) are due to the *trans* influence of the opposite bonds. The Ti–O bond lengths of the bridging butoxy groups are comparatively longer (Ti1–O7 = 1.973(2) and Ti2–O7 = 1.973(2) Å) with corresponding smaller angles (C13–O7–Ti1 = 124.1(3) and C13–O7–Ti2 = 135.3(3)°). The sum of the angles around μ_3 -O is 360° making the perfectly planar configuration which is a common observation in titanium oxide chemistry. A similar tricoordinate oxygen atom has been reported in the trinuclear complex $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-OC}_3\text{H}_7)_2(\text{OC}_3\text{H}_7)_5(\mu_2\text{-OOCCHCl}_2)_3$ [14].

Experimental Section

All reactions were carried out under stringently anhydrous conditions using glove box and Schlenk techniques under dry argon. $\text{Ti}(\text{OBu}^n)_4$ (Aldrich Chemicals) was used as supplied for carrying out the reactions. Toluene and CDCl_3 were dried by standard procedures. A Jasco FT-IR-5300 spectrometer was used for recording the infrared spectra of the compounds as Nujol mulls between NaCl plates. ^1H NMR spectra were recorded in CDCl_3 on a Bruker Biospin ARX 300 spectrometer with tetramethylsilane as internal reference. Titanium was gravimetrically determined as TiO_2 .

Syntheses

Synthesis of $\text{Ti}(\text{OC}_4\text{H}_9)_3(\text{OOCCHCl}_2)$

A solution of CHCl_2COOH (0.748 g, 5.80 mmol) in toluene (20 mL) was added dropwise to a stirred solution of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (1.973 g, 5.80 mmol) in toluene (30 mL) over 30 min at r.t. (25 °C). After complete addition, stirring of the reaction mixture was continued for 8 h. Then all the solvent was removed *in vacuo* to give a light-orange viscous liquid. (2.269 g, 98.9 %). – $\text{TiC}_{14}\text{H}_{28}\text{Cl}_2\text{O}_5$ (394.83): calcd. Ti 12.12, C 42.54, H 7.09; found Ti 12.09, C 44.59, H 7.05. – ^1H NMR (25 °C): δ = 4.11, 4.33, 4.64 (t, OCH_2 of OBu^n); 1.55, 1.63 (m, CH_2 of OBu^n); 1.11 (t, CH_3 of OBu^n); 5.95, 6.11, 6.21 (s, CHCl_2 of acid). – FT-IR (Nujol): ν = 2900 $\nu(\text{C-H})$, ~ 1000 $\nu(\text{C-O})$, 1773 $\nu_{\text{as}}(\text{CO}_2)$, 1365 $\nu_{\text{s}}(\text{CO}_2)$, 1580 $\nu_{\text{as}}(\text{CO}_2)$, 1440 $\nu_{\text{s}}(\text{CO}_2)$ cm^{-1} .

Synthesis of $\text{Ti}(\text{OC}_4\text{H}_9)_2(\text{OOCCHCl}_2)_2$ (**1**)

A solution of CHCl_2COOH (0.924 g, 10.14 mmol) in toluene (30 mL) was added dropwise to a stirred solution

Table 3. Crystallographic data for complex **2**.

Formula	C ₄₈ H ₈₀ Cl ₁₆ O ₂₈ Ti ₆
<i>M_r</i>	1959.577
Crystal size, mm ³	0.23 × 0.10 × 0.07
<i>T</i> , K	200(2)
Radiation; wavelength, Å	MoK _α ; 0.71073
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.8165(2)
<i>b</i> , Å	12.2826(2)
<i>c</i> , Å	15.2306(3)
α , deg	95.0076(8)
β , deg	102.4856(9)
γ , deg	107.2994(9)
<i>V</i> , Å ³	2033.19(6)
<i>Z</i>	1
<i>D</i> _{calcd} , g cm ^{−3}	1.60
μ (MoK _α), mm ^{−1}	1.2
Absorption correction	none
θ range, deg	3.33–26.03
Refls. measured / unique / <i>R</i> _{int}	14184 / 7856 / 0.0186
mean $\sigma(I)/I$	0.0360
Observed refls. [<i>I</i> ≥ 2σ(<i>I</i>)]	6657
Refined parameters	436
<i>R</i> 1(<i>F</i>) ^a [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0472
<i>wR</i> 2(<i>F</i> ²) ^a (all reflections)	0.1241
<i>x</i> , <i>y</i> (weighting scheme) ^a	0.0521, 3.6084
<i>S</i> (GOF) ^a	1.039
shift/error _{max}	0.001
$\Delta\rho_{\text{fin}}$ (max / min), e Å ^{−3}	1.02 / −0.76

^a *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, *wR*2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, *w* = $[\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where *P* = (Max(*F*_o², 0) + 2*F*_c²)/3; *S* = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where *n*_{obs} is the number of data and *n*_{param} the number of refined parameters.

of Ti(OC₄H₉)₄ (1.725 g, 5.07 mmol) in toluene (30 mL) over 30 min at r. t. (25 °C). After complete addition, stirring of the reaction mixture was continued for 8 h. Then all the solvent was removed *in vacuo* to give a light-yellow powder (2.279 g, 99.8 %). – TiC₁₂H₂₀O₆Cl₄ (449.82): calcd. Ti 10.64, C 42.54, H 4.44; found Ti 12.09, C 32.01, H 4.49. – ¹H NMR (25 °C): δ = 4.11, 4.43, 4.54 (t, OCH₂ of OBUⁿ); 1.33, 1.55 (m, CH₂ of OBUⁿ); 1.10 (t, CH₃ of OBUⁿ); 5.85, 6.10, 6.19 (s, CHCl₂ of acid). – FT-IR (Nujol): ν = 2906 ν (C–H), \sim 1000 ν (C–O), 1769 ν_{as} (CO₂), 1360 ν_{s} (CO₂), 1595 ν_{as} (CO₂), 1440 ν_{s} (CO₂) cm^{−1}.

Synthesis of Ti₆(μ₂-O)₂(μ₃-O)₂(μ₂-OC₄H₉)₂(OC₄H₉)₆-(OOCCHCl₂)₈ (**2**)

1.548 g of the product **1** was dissolved in 10 mL of toluene and kept at −30 °C. After 48 h a colourless crystalline product was obtained (0.752 g, 67 %). – Ti₆C₄₈H₈₀O₂₈Cl₁₆ (1959.57): calcd. Ti 14.66, C 29.39, H 4.08; found Ti 14.76, C 29.24, H 4.11. – ¹H NMR (25 °C): δ = 4.12, 4.23, 4.44, 4.54 (t, OCH₂ of OBUⁿ); 1.33, 1.45, 1.51 (m, CH₂ of OBUⁿ); 1.10, 1.21 (t, CH₃ of OBUⁿ); 5.85, 5.94, 6.15 (s, CHCl₂ of acid). – FT-IR (Nujol): ν = 2913 ν (C–H), \sim 1000 ν (C–O), 1753 ν_{as} (CO₂), 1346 ν_{s} (CO₂), 1595 ν_{as} (CO₂), 1443 ν_{s} (CO₂) cm^{−1}.

Crystal structure determination and refinement of **2**

A single crystal suitable for X-ray crystallography was selected under a polarisation microscope, mounted on the tip of a glass fiber, and investigated on a Nonius Kappa CCD diffractometer using MoK_α radiation (graded multi-layer X-ray optics). Crystal data for compound **2** are given in Table 3. The measurement temperature was 200 K. The structure was solved by Direct Methods with the programme SIR97 [16] and refined by full-matrix least-squares calculations [17] on *F*² (SHELXL-97). Anisotropic displacement parameters were refined for all non-hydrogen atoms with the exception of atoms described by split models because of disorder (all together ten C atoms as part of *n*-butoxy groups (C8, C9, C13–C16 and C21–C24) and the less occupied site of a disordered Cl atom (Cl7)). The hydrogen atoms were positioned geometrically and treated as riding on their parent atoms.

CCDC 700833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] D. C. Bradley, *Chem. Rev.* **1989**, 89, 1317–1322.
- [2] K. G. Caulton, L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, 90, 969–995.
- [3] R. C. Mehrotra, A. Singh, S. Sogani, *Chem. Rev.* **1994**, 94, 1643–1660.
- [4] W. J. Klemperer, *Mats. Res. Soc. Proc.* **1990**, 180, 29–35.
- [5] Y. W. Chen, W. J. Klemperer, C. W. Park, *Matls. Res. Symp. Proc.* **1992**, 271, 57–60.

- [6] I. G. Luneau, A. Mosset, J. Galy, Z. *Kristallogr.* **1987**, 180, 83–85.
- [7] S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, C. R. Acad. Sci. Paris **1989**, 308, 1409–1412.
- [8] I. Laaziz, A. Larbot, C. Guizard, J. Durand, L. Cot, J. Joffre, *Acta Crystallogr.* **1990**, C46, 2332–2334.
- [9] S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, *Inorg. Chem.* **1989**, 28, 4439–4445.

- [10] X. Lei, M. Shang, T. P. Fehlner, *Organometallics* **1996**, *15*, 3779–3781.
- [11] T. J. Boyle, T. M. Alam, C. J. Tatoya, B. L. Scott, *Inorg. Chem.* **1998**, *37*, 5588–5594.
- [12] R. Papiernik, L. G. H. Pfalzgraf, J. Vaissermann, M. C. H. B. Goncalves, *J. Chem. Soc., Dalton Trans.* **1998**, 2285–2287.
- [13] M. Shavit, E. Y. Tshuva, *Eur. J. Inorg. Chem.* **2008**, *9*, 1467–1474.
- [14] A. Pandey, V. D. Gupta, H. Nöth, *Eur. J. Inorg. Chem.* **2000**, 1351–1357.
- [15] A. Pandey, A. Pandey, P. Mayer, W. J. Parak, A. B. Samaddar, *Z. Naturforsch.* **2009**, *64b*, 263–268.
- [16] A. Altomare, M. C. Burla, M. Camalli, G. L.ascarano, C. Giacovazzo, A. Guagliardi, A. G. C. Moliterni, G. Polidori, R. Spagna, SIR97, A Program for the Automatic Solution of Crystal Structures by Direct Methods; see: *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
- [17] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.