PAPER

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Amine adducts of titanium tetraalkoxides

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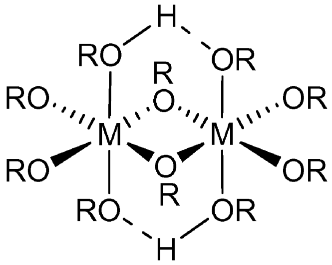
The crystalline compounds $Ti_2(O^iPr)_8(NH_2Pr)_2$, $Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(O^iPr)_3]_2$ and $Ti_2(O^iPr)_8[NH_2(CH_2)_6NH_2]$ were obtained by reaction of $Ti(O^iPr)_4$ with the corresponding amines. The molecular structures of the amine adducts are centrosymmetric dimers in which the titanium atoms are bridged by two OR groups. The amines are coordinated axially to the $Ti_2(\mu\text{-}OR)_2$ ring and hydrogen-bonded to a neighboring propoxy ligand. In the case of the 1,6-diaminohexane derivative, this results in coordination polymers where the $Ti_2(O^iPr)_8$ units are interconnected by the diamine.

Introduction

The Lewis acidic properties of metal alkoxides are well-known, which *inter alia* lead to phenomena called "coordination expansions", such as formation of oligomers by OR bridges or addition of solvent molecules. For example, $Ti(OMe)_4$ or $Ti(OEt)_4$ are tetramers in which the titanium atoms reach their optimal coordination number of 6 by formation of two μ_3-OEt and four μ_2-OEt bridges.[1] Some alkoxides of Ti, Zr and Hf crystallize from their parent alcohols as the alcohol adducts $M_2(OR)_8(ROH)_2$ (M = Ti,[2] Zr,[3] Hf[3,4]) where each metal atom is six-coordinate owing to both the formation of alkoxide bridges and coordination of alcohol molecules (Scheme 1).



Scheme 1 Schematic structure of $M_2(OR)_8(ROH)_2$ (M = Ti, Zr, Hf).

Despite the known Lewis acidity of metal alkoxides it is common practice in sol-gel chemistry to use metal alkoxides in combination with strongly Lewis basic compounds, such as ammonia (as a catalyst) or aminopropyltrialkoxysilanes (as co-reagents). Little is known of the extent of interaction between amines and metal alkoxides and on the structural chemistry of the resulting adducts. In this article, we report structural investigations on some amine adducts of $Ti(O^iPr)_4$.

Results and discussion

The crystalline compounds $Ti_2(O^iPr)_8(NH_2Pr)_2$ (**1**), $Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(O^iPr)_3]_2$ (**2**) and $Ti_2(O^iPr)_8[NH_2(CH_2)_6NH_2]$ (**3**) were obtained when $Ti(O^iPr)_4$ was reacted with propylamine, aminopropyltriethoxysilane or 1,6-diaminohexane, respectively. A slight excess of $Ti(O^iPr)_4$ facilitated crystallization of the compounds from the reaction mixtures. The chemical composition of **2** indicates that a partial alkoxy group exchange between aminopropyltriethoxysilane and titanium isopropoxide has occurred during the reaction.

The compounds **1**–**3** are not too stable under reduced pressure, which implies that the bonding of the amine ligands is not strong and that they can dissociate quite easily. The molecular structures of the amine adducts **1**–**3** are centrosymmetric dimers with octahedral titanium atoms (Figs. 1–3). The titanium coordination octahedra share an edge, that is, the two titanium atoms are bridged by two OR groups. In **2**, the bridges are formed by the smaller ethoxy groups. This is in line with the general rule that bridging OR groups are more basic than terminal ones and are preferentially substituted.[5] The low quality of the structure of **2** is due to a partial disorder of the OR groups due to alkoxide exchange; it is included here for the general structural implications in $Ti(OR)_4$-amine adducts.

The general structure type of **1**–**3** is that of the parent compounds $M_2(OR)_8(ROH)_2$ (Scheme 1), where the coordinated alcohol molecules are replaced by the amines. An interesting structural aspect is that 1,6-diaminohexane bridges two different $Ti_2(O^iPr)_8$ units rather than chelating one titanium atom [as in the titanium isopropoxide complex with a 1,1-bis(phenolate)-substituted ethylene diamine ligand[6]] or bridging the two titanium atoms within the same $Ti_2(O^iPr)_8$ unit. The formation of a coordination polymer is not restricted to the long-chained diaminohexane, since the same structures were found for $Ti_2(O^iPr)_6(OMe)_2(NH_2CH_2CH_2NH_2)$ and $Ti_2(O^iPr)_8[NH_2CH_2CHMe(CH_2)_3NH_2]$.[7]

The overall structural parameters of **1**–**3** are very similar (Table 1). The central $Ti_2(\mu\text{-}OR)_2$ ring is slightly asymmetric, with the two Ti–O distances differing by 3–4 pm. This is also reflected in slightly different Ti–O distances of the terminal OR groups *trans* to the μ-O^iPr groups (**2** is not comparable because bridging and terminal groups are different). The longest Ti–O distance of the terminal OR ligands is that *trans* to the nitrogen atom because of the *trans* effect of the amine.

The bonding of the amine ligand to the titanium atom is supported by a hydrogen bridge between one of the N–H groups and the oxygen atom of the axial O^iPr ligand of the neighboring titanium atom. The Ti–O and Ti–N vectors of these ligands are parallel because of geometrical restrictions imposed by the edge-sharing octahedra, and the O···N distance would already be rather short for the same geometrical reason. To enable hydrogen bonding, an even closer distance between the two atoms is necessary. This is achieved by

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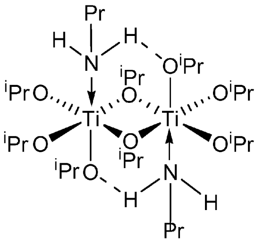

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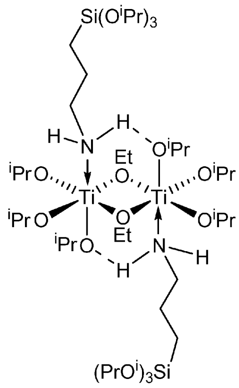

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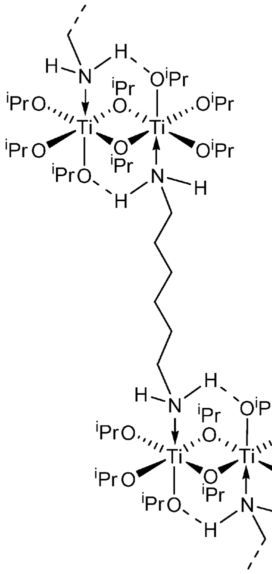

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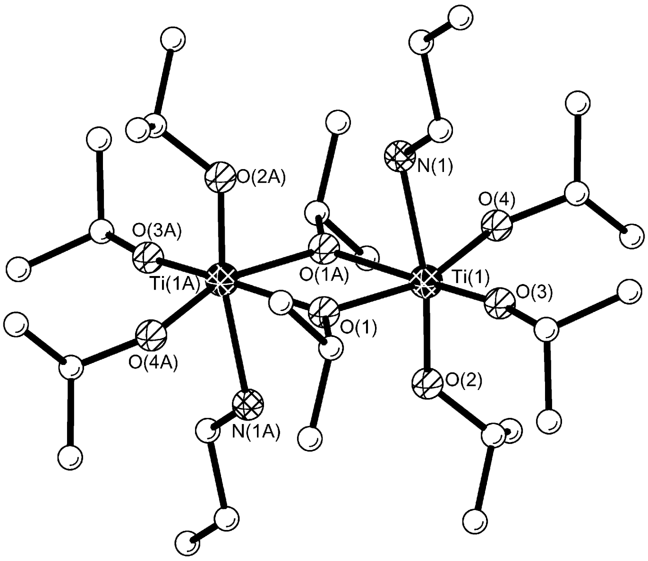


Fig. 1 Molecular structure of $Ti_2(O^iPr)_8(NH_2Pr)_2$ (**1**).

reduction of the N–Ti–O_{bridge} angles to about 80° by bending the amino ligand towards the center of the $Ti_2(\mu\text{-}O^iPr)_2$ ring. The N···O distances in **1**–**3** are thus reduced to 295.2(2), 296.6(8) and 295.1(2) pm, and the NHO angles to 160.0°, 160.8° and 161.7°, respectively. This is in good agreement with literature values.[8]

The compounds **1**–**3** are amine derivatives of the general composition $M_2(OR)_8L_2$, where M is Ti, Zr or Hf, and L a neutral ligand. Apart from the alcohol adducts (L = ROH) mentioned above, the other structurally characterized derivative of this type with a monodentate ligand L is $Hf_2(O^iPr)_8(^iPrOH)(py)$.[4] Several compounds with chelating or bridging bidentate ligands are also variations of this structural motive (Scheme 2). From spectroscopic data, a dimeric structure with bridging OR ligands was deduced for the acetate derivative;[9] since carboxylate ligands in oligomeric titanium oxo/alkoxo compounds are always bridging,[10] it must be assumed that $[Ti(OR)_3(acetate)]_2$ has the structure depicted in Scheme 2. In this compound, the coordinated alcohol and its neighboring OR ligand in the $M_2(OR)_8(ROH)_2$ structure (at the origin of the RO···HOR bridge) are formally replaced by a bridging acetate ligand. Several structures with anionic chelating bidentate ligands $X\cap Y$, $[Ti(OR)_3(X\cap Y)]_2$, were structurally characterized (such as $X\cap Y$ = β-diketonates,[11] glycinate,[12] isoeugenolate,[13] aminoethanolate,[13] or the dianion of dihydroxypyrimidine[14]). In the latter derivatives, the neutral ligand is in the X position (Scheme 2), that is, in the same position as the neutral donor ligand in $M_2(OR)_8L_2$.

Conclusions

We have shown in this article that several primary amines, RNH_2, form coordination compounds of the type $Ti_2(O^iPr)_8(NH_2R)_2$ when reacted with $Ti(O^iPr)_4$. The structures

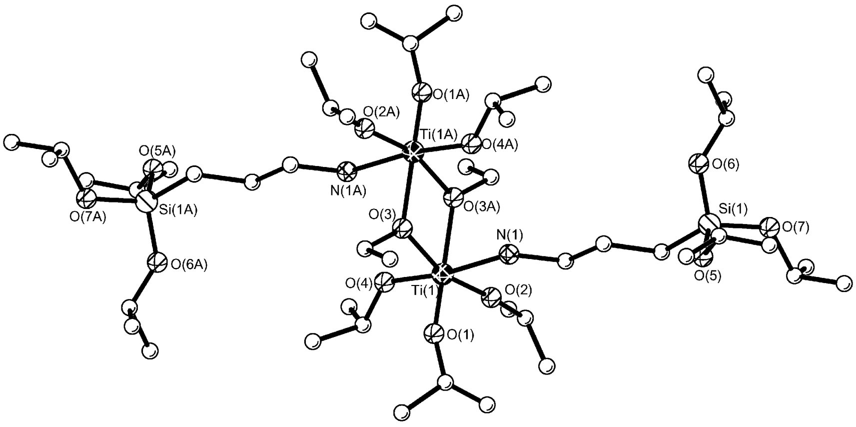


Fig. 2 Molecular structure of $Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(OPr^i)_3]_2$ (**2**).

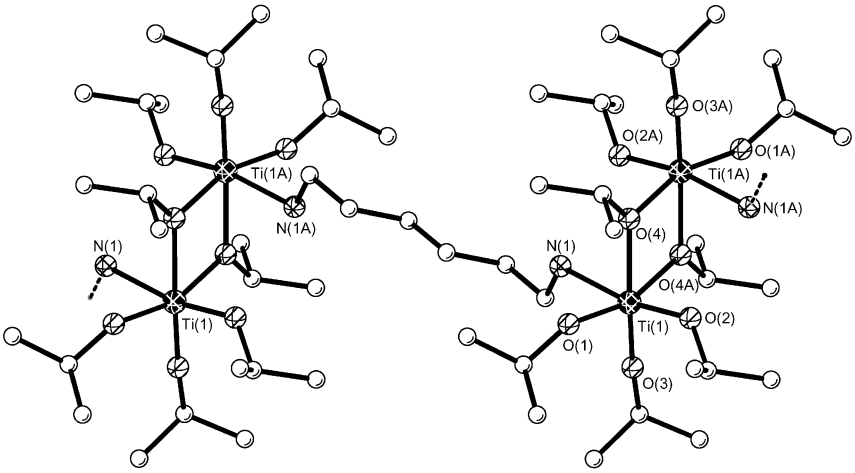


Fig. 3 Molecular structure of $Ti_2(O^iPr)_8[NH_2(CH_2)_6NH_2]$ (**3**).

of all adducts obtained are of the same type: OR-bridged dimers where the amine ligands are coordinated axially to the four-membered $Ti_2(\mu\text{-}O^iPr)_2$ ring and *trans* to each other. It must be assumed that similar structures are also formed with other amines.

The formation of Lewis base–Lewis acid adducts must be taken into account when Lewis basic nitrogen compounds are co-reacted with titanium alkoxides (and metal alkoxides in general), especially in sol-gel processes. This is demonstrated by compound **2**, where two commonly used precursors, $Ti(O^iPr)_4$ and $(EtO)_3SiCH_2CH_2CH_2NH_2$, were reacted. The adduct formation has two consequences: (i) the amino group is blocked and may therefore not serve the intended purpose (catalysis, subsequent coupling reactions, coordination of metals, *etc.*) and (ii) the hydrolysis and condensation rates of the metal alkoxide will be influenced because a coordination site is blocked.

Experimental

All operations were carried out in an atmosphere of dry argon using the Schlenk technique. $Ti(O^iPr)_4$ (Aldrich, 97%) was used as received. All other chemicals were purified before use; solvents were dried by standard techniques.

Syntheses

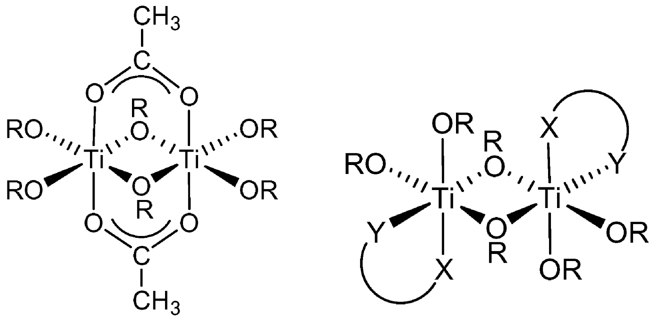
$Ti_2(OPr^i)_8(PrNH_2)_2$ (1). $Ti(O^iPr)_4$ (875 mg, 3.08 mmol) was dissolved at room temperature in 2 ml of isopropanol in a Schlenk tube under Ar. Then 174 mg (2.94 mmol) of 1-propylamine (Fluka >99%, distilled from CaH_2) was added dropwise under stirring. After reflux for 5 min the closed vessel was stored at 4 °C. Colorless crystals were obtained after 12 h. The supernatant solvent was decanted off to afford 642 mg of a colorless solid. The compound was re-crystallized from isopropanol. The product could not be dried because of the low thermal stability of the obtained crystals. ^1H NMR (CD_2Cl_2, 21 °C) δ: 4.51 [sept, J = 6.1 Hz, $OCH(CH_3)_2$], 2.63 (t, J = 6.9 Hz, H_2NCH_2), 1.44 (m, $H_2NCH_2CH_2$), 1.26 [d, J = 6.1 Hz, $OCH(CH_3)_2$], 1.00 (b, NH_2), 0.92 [t, J = 7.4 Hz, $H_2N(CH_2)_2CH_3$]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C) δ: 76.42 [$OCH(CH_3)_2$], 44.39 (H_2NCH_2), 27.10 ($H_2NCH_2CH_2$), 26.42 [$OCH(CH_3)_2$], 11.28 [$H_2N(CH_2)_2CH_3$].

$Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(O^iPr)_3]_2$ (2). $Ti(O^iPr)_4$ (1.003 g, 3.53 mmol) was mixed with 706 mg (3.19 mmol) of 3-aminopropyltriethoxysilane (Wacker, used as received) in a Schlenk tube under Ar. Storing of the closed vessel at ambient temperature for 2 days afforded a colorless solid quantitatively. This solid was liquified by gentle heating and addition of 0.01 ml of toluene. The vessel was then stored at 4 °C and colorless elongated crystals were obtained after 3 days. Yield 1.257 g (74%). The product could not be dried because of the low thermal stability of the obtained crystals. ^1H NMR (CD_2Cl_2, 21 °C) δ: 4.51, 4.33 [br, $TiOCH(CH_3)_2$], 4.22 [sept, J = 6.1 Hz, $SiOCH(CH_3)_2$], 4.00 [br, $HOCH(CH_3)_2$], 3.82 (q, J = 7.0 Hz, $SiOCH_2CH_3$), 3.80 (q, J = 7.0 Hz, $SiOCH_2CH_3$), 2.65 (t, J =

Table 1 Selected bond distances (in pm) and angles (in deg) in **1**–**3**. Corresponding values are given on the same line

1		**2**		**3**	
Ti(1)–O(3)	180.5(1)	Ti(1)–O(1)	178.3(5)	Ti(1)–O(3)	180.6(1)
Ti(1)–O(4)	184.0(1)	Ti(1)–O(2)	177.8(6)	Ti(1)–O(1)	184.1(1)
Ti(1)–O(2)	186.9(1)	Ti(1)–O(4)	183.0(6)	Ti(1)–O(2)	186.6(1)
Ti(1)–O(1)	204.9(1)	Ti(1)–O(3)	201.5(4)	Ti(1)–O(4)	204.9(1)
Ti(1)–O(1)[a]	208.1(1)	Ti(1)–O(3)[a]	205.0(5)	Ti(1)–O(4)[a]	209.1(1)
Ti(1)–N(1)	231.1(2)	Ti(1)–N(1)	229.8(6)	Ti(1)–N(1)	229.8(1)
O(3)–Ti(1)-O(4)	95.92(6)	O(2)–Ti(1)–O(1)	98.4(3)	O(1)–Ti(1)–O(3)	96.73(6)
O(3)–Ti(1)–O(1)	165.37(5)	O(1)–Ti(1)–O(3)	162.6(2)	O(3)–Ti(1)–O(4)	164.88(5)
O(4)–Ti(1)–O(1)[a]	161.97(5)	O(2)–Ti(1)–O(3)[a]	163.1(2)	O(1)–Ti(1)–O(4)[a]	161.21(5)
O(2)–Ti(1)–O(1)	90.61(5)	O(4)–Ti(1)–O(3)	93.9(2)	O(2)–Ti(1)–O(4)	89.57(5)
O(2)–Ti(1)–O(1)[a]	92.78(5)	O(4)–Ti(1)–O(3)[a]	92.5(2)	O(2)–Ti(1)–O(4)[a]	93.40(5)
O(2)–Ti(1)–N(1)	170.18(5)	O(4)–Ti(1)–N(1)	171.3(3)	O(2)–Ti(1)–N(1)	169.59(5)
O(1)–Ti(1)–N(1)	80.61(5)	O(3)–Ti(1)–N(1)	81.8(2)	O(4)–Ti(1)–N(1)	81.08(5)
O(1)[a]–Ti(1)–N(1)	80.45(5)	O(3)[a]–Ti(1)–N(1)	79.0(2)	O(4)[a]–Ti(1)–N(1)	79.42(5)
O(1)–Ti(1)–O(1)[a]	72.64(5)	O(3)–Ti(1)–O(3)[a]	72.3(2)	O(4)–Ti(1)–O(4)[a]	72.11(5)
Ti(1)–O(1)–Ti(1)[a]	107.36(5)	Ti(1)–O(3)–Ti(1)[a]	107.7(2)	Ti(1)–O(4)–Ti(1)[a]	107.89(5)

[a] Inversion related atoms.



Scheme 2 Schematic structures of $[Ti(OR)_3(acetate)]_2$ and $[Ti(OR)_3(X\cap Y)]_2$ ($X\cap Y$ = anionic chelating bidentate ligand).

Table 2 Crystallographic and structural parameters of **1**–**3**

	1	**2**	**3** · toluene
Empirical formula	$C_{30}H_{74}N_2O_8Ti_2$	$C_{46}H_{110}N_2O_{14}Si_2Ti_2$	$C_{37}H_{79}N_2O_8Ti_2$
Formula weight/g mol^{-1}	686.7	1067.3	775.8
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P{-}1$	$P{-}1$
a/pm	1006.86(7)	939.4(6)	964.8(1)
b/pm	1784.2(1)	1244.1(9)	987.9(1)
c/pm	1245.15(8)	1443.5(9)	1221.9(1)
α/°	—	100.63(1)	78.94(2)
β/°	113.427(1)	95.93(2)	82.49(2)
γ/°	—	111.95(1)	78.50(2)
U/pm^3	$2052.5(2)\cdot 10^6$	$1510.1(2)\cdot 10^6$	$1114.8(2)\cdot 10^6$
Z	2	1	1
ρ_{calcd}/g cm^{-3}	1.111	1.174	1.156
μ/mm^{-1}	0.430	0.360	0.403
Reflections collected	10890	7279	6084
Unique reflections	3585	5188	3871
R_{int}	0.0218	0.1631	0.0168
R_1 [$I > 2\sigma(I)$]	0.0383	0.1158	0.0368
wR_2	0.1128	0.2523	0.0986

7.0 Hz, H_2NCH_2), 1.57–1.44 (m, $H_2NCH_2CH_2$), 1.38–1.12 [m, $Ti/SiOCH(CH_3)_2$, $Ti/SiOCH_2CH_3$], 1.32 (br, NH_2), 0.66–0.53 [m, $H_2N(CH_2)_2CH_2$]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C) δ = 64.78 [$SiOCH(CH_3)_2$], 58.06 ($SiOCH_2CH_3$), 45.37 (H_2NCH_2), 27.57 ($H_2NCH_2CH_2$), 26.24, 25.48, 19.04, 18.19 [$Ti/SiOCH(CH_3)_2$, $Ti/SiOCH_2CH_3$], 8.63 [$H_2N(CH_2)_2CH_2$].

$Ti_2(OPr^i)_8[NH_2(CH_2)_6NH_2]$ (3). $Ti(O^iPr)_4$ (983 mg, 3.46 mmol) was dissolved at room temperature in 3 ml of toluene in a Schlenk tube under Ar. Then 393 mg (3.38 mmol) of 1,6-diaminohexane (Aldrich 98%, used as received) was added. The solution was heated to 110 °C with stirring until all of the amine was dissolved. The closed vessel was allowed to cool to ambient temperature to afford colorless crystals after 2 h. The solvent was decanted off and the crystals were dried *in vacuo*. Yield: 1.212 g of **3** · toluene (90%). ^1H NMR (d_8-toluene, 21 °C) δ: 4.51 [sept, J = 6.1 Hz, $OCH(CH_3)_2$], 4.00 [sept, J = 6.1 Hz, $HOCH(CH_3)_2$], 2.66 (t, J = 6.4 Hz, H_2NCH_2), 1.42 (m, $H_2NCH_2CH_2$), 1.35 (m, $H_2NCH_2CH_2CH_2$), 1.26 [d, J = 6.1 Hz, $OCH(CH_3)_2$], 1.19 [d, J = 6.1 Hz, $HOCH(CH_3)_2$], 0.94 (b, NH_2); $^{13}C\{^1H\}$ NMR (d_8-toluene, 21 °C) δ: 76.24 [$OCH(CH_3)_2$], 64.12 [$HOCH(CH_3)_2$], 42.32 (H_2NCH_2), 34.18 ($H_2NCH_2CH_2$), 26.78 ($H_2NCH_2CH_2CH_2$), 26.37 [$OCH(CH_3)_2$], 25.32 [$HOCH(CH_3)_2$].

X-Ray structure analyses

Selected crystals were mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated MoKα radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 5.0 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections (Table 2). The structure was solved by the Patterson method (SHELXS97). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.†

Acknowledgements

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