Meltable Stannaborate Salts

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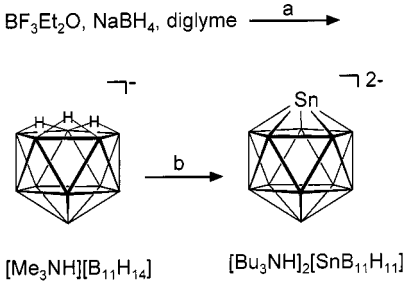
In a one-pot procedure, four imidazolium salts of alkylated stanna-*closo*-dodecaborate anions were synthesized. Alkyl substituents at the stannaborate anion and imidazolium cation were varied between ethyl and butyl, resulting in a range of melting points from 55 to 105 °C. The structures in the solids were determined in the case of [EMIM][Et–$SnB_{11}H_{11}$] (**1**) and [EMIM][Bu–$SnB_{11}H_{11}$] (**2**).

Introduction

Salts with a melting point under 100 °C are named ionic liquids, and are currently of growing interest.[1,2] This might be due to the expected high potential of these salts as an alternative reaction media in processes of technical relevance. The almost undetectable volatility of these compounds is one reason they might substitute conventional solvents. Obviously, the cation in these salts plays an important role for the low melting point and so far work is concentrated on *N*,*N*′-dialkylimidazolium and *N*-alkylpyridinium ions. A variety of classical, weak coordinating anions ($AlCl_4^-$, BF_4^-, PF_6^-, $CF_3SO_3^-$, NO_3^-, etc.) with these imidazolium or pyridinium cations exhibit the interesting properties of ionic liquids. Recently, C. A. Reed has presented the first studies on ionic liquids based on carborate salts of imidazolium and pyridinium cations.[3] Melting points down to 45 °C were determined for [*N*-ethyl-*N*′-methylimidazolium][propylcarba-*closo*-dodecaborate(12)]. Since the heteroborate anions are prominent for their very weak coordinating abilities, and they show resistance towards moisture and air, it is worthwhile to study these salts. We are currently investigating the chemistry of the easily accessible *closo*-heteroborate $[SnB_{11}H_{11}]^{2-}$. In this publication, we present imidazolium salts of the alkylated stanna-*closo*-dodecaborate with low melting points.

Results and Discussion

The synthesis of the nearly icosahedral stannaborate cluster was discovered by Todd in 1992,[4] and recently we have shown that this dianion can be used as a ligand in transition metal chemistry.[5] The air-stable stanna-*closo*-dodecaborate salt can be synthesized with a variety of counter-cations, offering the possibility of further modifying the solubility of the cluster salt. A key compound in this context is the tributylammonium salt $[Bu_3NH]_2[SnB_{11}H_{11}]$, since it drops out of water and the cations can be easily replaced by interaction with a base like KH. The ionic liquids of the alkylstannaborate anion are straightforwardly synthesized in to a two-step procedure. Starting from $[Me_3NH][B_{11}H_{14}]$ the stannaborate $[Bu_3NH]_2[SnB_{11}H_{11}]$ was synthesized in amounts of five grams and a yield of ca. 85% (Scheme 1).



Scheme 1. a) 1. 106 °C, 2. H_2O, $[Me_3NH]Cl$; b) 1. 4 equiv. BuLi, 2. $SnCl_2$, 3. H_2O, $[Bu_3NH]Cl$

The air-stable stannaborate was treated with 1 equiv. of the respective alkyl iodide. After this quantitative alkylation, 2 equiv. of super-hydride $KHBEt_3$ were added in order to substitute the ammonium against the potassium cation. The solvent was changed to water and the ionic liquid was precipitated in high yield after addition of the respective imidazolium iodide (Scheme 2).

The new salts **1**–**4** were characterized by elemental analysis, DSC, NMR, and IR spectroscopy, and in the case of **1** and **2** also by single-crystal X-ray structure analysis. In contrast to the ionic liquids based on the classical anions like $[AlCl_4]^-$ or $[BF_4]^-$, the synthesized stannaborate salts were not hygroscopic, and showed no tendency to react with water and air even at higher temperatures. After melt-

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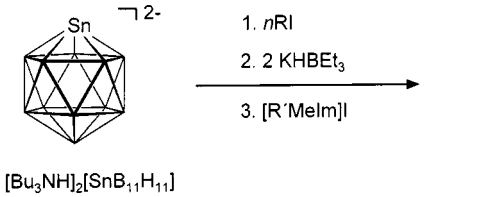

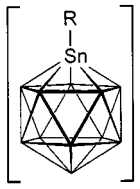

[R´MeIm]

	1	2	3	4
R	Et	Bu	Et	Bu
R´	Et	Et	Bu	Bu
yield (%)	73	62	61	60
MP(°C)	106	80	64	55

Scheme 2

ing the borates **1**−**4** at 200 °C for several hours, repeated elemental analyses confirmed the correct composition. In the series of the imidazolium salts **1**−**4**, the lowest melting point of 55 °C was achieved for the derivative with the butyl substituents at the imidazolium cation and the tin atom in the cluster. According to this concept, we tried to synthesize the octyl-substituted salt, but were not able to purify this waxy solid for satisfactory elemental analysis.

The imidazolium salts **1** and **2** crystallized in the monoclinic space group $P2_1/c$ and showed no disorder in the solid state. For both compounds, we did not find any indications for cation−anion contacts. In Figures 1 and 2, an ORTEP plot of the salts is shown. The interatomic distances in **1** and **2** are not unusual, and selected values and angles are listed in the captions of Figures 1 and 2.

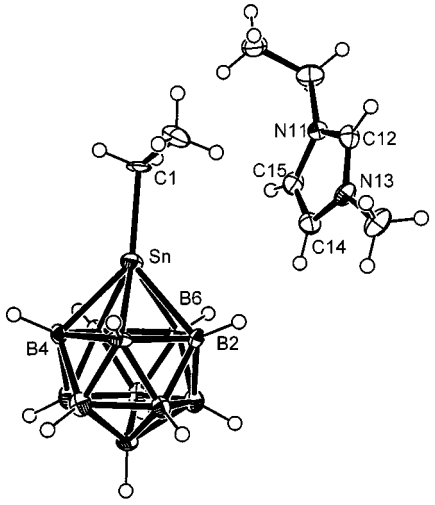

Figure 1. ORTEP drawing of the salt **1**; thermal ellipsoids are drawn at the 50% probability level; selected interatomic distances [Å]: Sn−C1 2.148(4), Sn−B2 2.308(5), Sn−B3 2.323(5), Sn−B4 2.311(6), Sn−B5 2.299(5), Sn−B6 2.298(6), N11−C12 1.332(7), C12−N13 1.332(7), N13−C14 1.380(7), C14−C15 1.353(8), C15−N11 1.380(8)

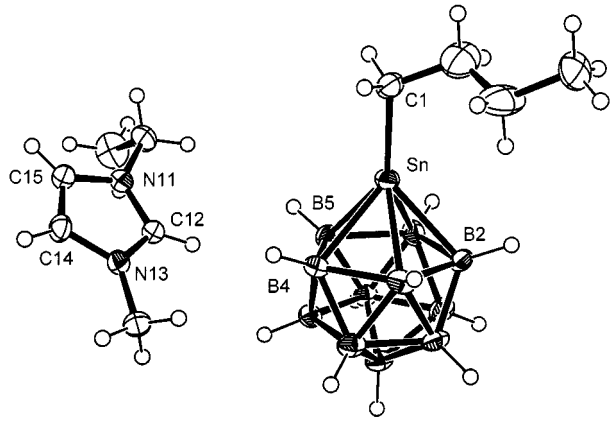

Figure 2. ORTEP drawing of the salt **2**; thermal ellipsoids are drawn at the 50% probability level; selected interatomic distances [Å]: Sn−C1 2.122(5), Sn−B2 2.307(6), Sn−B3 2.314(5), Sn−B4 2.312(5), Sn−B5 2.303(6), Sn−B6 2.312(5), N11−C12 1.335(6), C12−N13 1.329(6), N13−C14 1.386(6), C14−C15 1.355(7), C15−N11 1.376(6)

Conclusion

The quantitative alkylation of the stannaborate dianion offers the possibility of introducing this heteroborate into imidazolium salts exhibiting a low melting point. Positional disorder in the solid state is not an indicator for the relative low melting point of **1** and **2**.

Experimental Section

General: All experiments were carried out under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under an inert gas from appropriate drying agents. All imidazolium iodides were prepared according to procedures known from the literature.[6] NMR spectroscopy was performed with a Bruker AC 200 spectrometer (^{1}H: 200 MHz, int. TMS; ^{13}C{^{1}H}: 50 MHz, int. TMS; ^{11}B and ^{11}B{^{1}H}: 64 MHz, ext. $BF_3{\cdot}OEt_2$). IR spectrometer: IFS66v/s Bruker. Elemental analyses were carried out in the Institut für Anorganische Chemie der Universität zu Köln with a Heraeus C,H,N,O-Rapid analyser. DSC measurements were performed with a Netzsch STA 409-Skimmer thermal analyser.

[EMIM][1-Et−SnB$_{11}$H$_{11}$] (1): 1-Iodoethane (0.08 mL, 0.99 mmol) was added to a solution of $[Bu_3NH]_2[SnB_{11}H_{11}]$ (510 mg, 0.82 mmol) in 40 mL of THF at room temperature. The mixture was heated under reflux for 3 h. Afterwards, the solvent was evaporated in vacuum and the residue dried for another 24 h. This was then dissolved in 20 mL of THF and treated with $LiHBEt_3$ (1.95 mL, 1 M solution in THF, 1.95 mmol). The solution was stirred for another 2 h and volatiles were removed in vacuum. The remaining white solid was dissolved in 50 mL of H_2O and [EMIM]I (0.40 g, 1.68 mmol) was added. The white precipitate was filtered off and dried in vacuum. Single crystals were obtained by slow evaporation of methanol from the product. Yield: 234 mg, 0.60 mmol, 73.3%. ^{1}H NMR (CD_2Cl_2): δ = 1.58 (t, ^3J = 7.3 Hz, 3 H, $SnCH_2CH_3$), 1.69 (t, ^3J = 7.8 Hz, 3 H, NCH_2CH_3), 2.62 (q, ^3J = 7.8 Hz, 2

H, SnCH_2CH$_3$), 3.97 (s, 3 H, NCH_3), 4.27 (q, ^3J = 7.3 Hz, 2 H, NCH_2CH$_3$), 0.99 (t, ^3J = 7.1 Hz, 3 H, CH$_2$CH$_2$CH_3), 7.30 (s, 2 H, NC*H*C*H*N), 8.69 (s, 1 H, NC*H*N). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): δ = −12.5 (s, B12), −17.0 (s, B2−6 and B7−11). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 9.0 (SnCH$_2$*C*H$_3$), 13.7 (Sn*C*H$_2$CH$_3$), 15.5 (NCH$_2$*C*H$_3$), 37.1 (N*C*H$_3$), 46.0 (N*C*H$_2$CH$_3$), 122.3 (N*C*H$_2$CH$_2$N), 124.1 (NCH$_2$*C*H$_2$N), 135.8 (N*C*H$_2$N). $C_8H_{27}B_{11}N_2Sn$ (388.9): calcd. C 24.71, H 7.00, N 7.20; found C 25.41, H 7.02, N 7.43. DSC: M.p. 105.7 °C. IR (KBr): ṽ = 2490 (vs), 2866 (vw), 2926 (w), 2958 (w), 3095 (s), 3097 (s), 3109 (s), 3140 (s), 3159 cm^{-1} (w).

X-ray Crystallographic Analysis of 1: $C_8H_{27}B_{11}N_2Sn$, formula mass 388.92 g/mol; monoclinic, space group $P2_1/c$ (no.14); a = 7.451(1), b = 17.564(2), c = 14.081(2) Å, β = 99.09(2)°, V = 1819.7(4) Å^3, Z = 4, $d_{calcd.}$ = 1.420 g·cm^{-3}, μ(Mo-K_α) = 1.392 mm^{-1}. Image Plate STOE (IPDS) diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 170 K on a crystal of dimensions 0.2 × 0.2 × 0.1 mm, using ω scans in the range 2.3° ≤ θ ≤ 27.0°, yielded 15956 reflections. The data were corrected for Lorentz and polarization effects. Numerical absorption corrections with programs X-RED (Stoe, Darmstadt, **2001**) and X-SHAPE (Stoe, Darmstadt, **1999**): T_{min}/T_{max} = 0.7474/0.8849. 3925 unique reflections with $I > 2\,\sigma(I)$ remained for structure solution by direct methods.[7] The structure model was completed by Fourier difference synthesis, F^2 refinement;[8−10] anisotropic parameters for non-hydrogen atoms and hydrogen atoms placed in calculated positions (C−H = 0.98 Å; B−H = 1.1 Å). Convergence obtained for 200 variables, 3925 data, and R_1(all) = 0.094, wR_2(all) = 0.087, GooF = 0.826. A final difference Fourier map showed the highest peak with 0.56 e·Å^{-3} 1.22 Å from B2 and the deepest hole with −1.40 e·Å^{-3} 0.02 Å from the Sn.

[EMIM][1-Bu−SnB$_{11}$H$_{11}$] (2): 1-Iodobutane (0.05 mL, 0.44 mmol) was added to a solution of [Bu$_3$NH]$_2$[SnB$_{11}$H$_{11}$] (235 mg, 0.38 mmol) in 40 mL of THF at room temperature. The mixture was heated under reflux for 3 h. Afterwards, the solvent was evaporated in vacuum and the residue dried for another 24 h. This was then dissolved in 20 mL of THF and treated with LiHBEt$_3$ (0.83 mL, 1 M solution in THF, 0.83 mmol). The solution was stirred for another 2 h and volatiles were removed in vacuum. The remaining white solid was dissolved in 50 mL of H$_2$O and [EMIM]I (0.18 g, 0.76 mmol) was added. The white precipitate was filtered off and dried in vacuum. Single crystals were obtained by slow evaporation of methanol from the product. Yield: 113 mg, 0.27 mmol, 62%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.99 (t, ^3J = 7.1 Hz, 3 H, CH$_2$CH$_2$CH_3), 1.57 (m, 5 H, CH$_2$CH_2CH$_3$ and NCH$_2$CH_3), 1.99 (m, 2 H, SnCH$_2$CH_2CH$_2$), 2.70 (t, ^3J = 7.1 Hz, 2 H, SnCH_2), 3.97 (s, 3 H, NCH_3), 4.27 (q, ^3J = 7.3 Hz, 2 H, NCH_2CH$_3$), 7.30 (s, 2 H, NC*H*C*H*N), 8.69 (s, 1 H, NC*H*N). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): δ = −12.3 (s, B12), −16.9 (s, B2−6 and B7−11). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 13.5 (CH$_2$CH$_2$*C*H$_3$), 15.5 (NCH$_2$*C*H$_3$), 16.9 (SnCH$_2$*C*H$_2$), 26.8 (SnCH$_2$*C*H$_2$), 30.3 (Sn*C*H$_2$), 37.1 (N*C*H$_3$), 46.1 (N*C*H$_2$CH$_3$), 122.3 (N*C*H$_2$CH$_2$N), 124.1 (NCH$_2$*C*H$_2$N), 136.0 (N*C*H$_2$N). $C_{10}H_{31}B_{11}N_2Sn$ (417.0): calcd. C 28.80, H 7.42, N 6.72; found C 29.02, H 7.21, N 6.76. DSC: M.p. 80.3 °C. IR (KBr): ṽ = 2496 (vs), 2849 (vw), 2866 (vw), 2922 (w), 2957 (w), 3093 (s), 3113 (s), 3146 cm^{-1} (s)

X-ray Crystallographic Analysis of 2: $C_{10}H_{31}B_{11}N_2Sn$: formula mass 416.97 g/mol; monoclinic, space group $P2_1/c$ (no.14); a = 11.378 (1), b = 11.030 (1), c = 16.911 (2) Å, β = 100.81(2)°, V = 2084.6 (4) Å^3, Z = 4, $d_{calcd.}$ = 1.329 g·cm^{-3}, μ(Mo-K_α) = 1.220 mm^{-1}. Image Plate STOE (IPDS) diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 170 K on a crystal of dimensions 0.3 × 0.25 × 0.1 mm using ω scans in the range 1.8° ≤ θ ≤ 24.1° yielded 12909 reflections. The data were corrected for Lorentz and polarization effects. Numerical absorption corrections with programs X-RED (Stoe, Darmstadt, **2001**) and X-SHAPE (Stoe, Darmstadt, **1999**): $T_{min.}/T_{max}$ = 0.7218/0.8928. 3287 unique reflections with $I > 2\,\sigma(I)$ remained for structure solution by direct methods.[7] The structure model was completed by Fourier difference synthesis, F^2 refinement;[8−10] anisotropic parameters for non-hydrogen atoms, and hydrogen atoms placed in calculated positions (C−H = 0.98 Å; B−H = 1.1 Å). Convergence obtained for 219 variables, 3287 data, and R_1(all) = 0.072, wR_2(all) = 0.069, GooF = 0.878. A final difference Fourier map showed the highest peak with 0.92 e·Å^{-3} 1.03 Å from C3 and the deepest hole with −0.50 e·Å^{-3} 0.38 Å from H2a.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-169179 (**1**) and -169180 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[BMIM][1-Et−SnB$_{11}$H$_{11}$] (3): Salt **3** was synthesised according to the procedure outlined for the synthesis of **1**, starting from [Bu$_3$NH]$_2$[SnB$_{11}$H$_{11}$] (413 mg, 0.67 mmol) with 1-iodoethane (0.06 mL, 0.74 mmol) and LiHBEt$_3$ (1.44 mL, 1 M solution in THF, 1.44 mmol). The salt was precipitated by adding [BMIM]I (0.36 g, 1.35 mmol). The white solid was dried in vacuum. Yield: 170 mg, 0.41 mmol, 61.2%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.97 (t, ^3J = 7.3 Hz, 3 H, CH$_2$CH$_2$CH_3), 1.39 (m, 2 H, CH$_2$CH_2CH$_3$), 1.69 (t, ^3J = 7.8 Hz, 3 H, SnCH$_2$CH_3),), 1.89 (m, 2 H, NCH$_2$CH_2CH$_2$),), 2.62 (q, ^3J = 7.8 Hz, 2 H, SnCH_2), 3.98 (s, 3 H, NCH_3), 4.21 (q, ^3J = 7.3 Hz, 2 H, NCH_2CH$_3$), 7.30 (s, 2 H, NC*H*C*H*N), 8.70 (s, 1 H, NC*H*N). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): δ = −11.9 (s, B12), −17.1 (s, B2−6 and B7−11). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 9.0 (CH$_2$CH$_2$*C*H$_3$), 13.6 (SnCH$_2$*C*H$_3$), 13.7 (CH$_2$*C*H$_2$CH$_3$), 19.7 (NCH$_2$CH$_2$*C*H$_2$), 32.3 (Sn*C*H$_2$), 37.2 (N*C*H$_3$), 50.7 (N*C*H$_2$CH$_3$), 122.6 (N*C*H$_2$CH$_2$N), 124.0 (NCH$_2$*C*H$_2$N), 136.2 (N*C*H$_2$N). $C_{10}H_{31}B_{11}N_2Sn$ (417.0): calcd. C 28.80, H 7.42, N 6.72; found C 29.25, H 7.48, N 6.87. DSC: M.p. 64.0 °C. IR (KBr): ṽ = 2501 (vs), 2868 (w), 2930 (w), 2958 (s), 3093 (s), 3115 (s), 3109 (s), 3142 (w), 3157 cm^{-1} (w).

[BMIM][1-Bu−SnB$_{11}$H$_{11}$] (4): Salt **4** was synthesised according to the procedure outlined for the synthesis of **1**, starting from [Bu$_3$NH]$_2$[SnB$_{11}$H$_{11}$] (302 mg, 0.49 mmol) with 1-iodobutane (0.07 mL, 0.61 mmol) and LiHBEt$_3$ (1.00 mL, 1 M solution in THF, 1.00 mmol). The salt was precipitated by adding [BMIM]I (0.275 g, 1.16 mmol). The light yellow-brown solid was dried in vacuum. The residue was dissolved in 5 mL of acetone, and precipitated by adding 20 mL of water. The light brown salt was filtered and dried in vacuum. Yield: 130 mg, 0.29 mmol, 60%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.97 (m, 6 H, CH$_2$CH_3 and CH$_2$CH_3), 1.37 (m, 4 H, SnCH$_2$CH$_2$CH_2 and NCH$_2$CH$_2$CH_2), 1.63 (m, 4 H, SnCH$_2$CH_2CH$_2$ and NCH$_2$CH$_2$CH_2), 1.88 (m, 2 H, NCH$_2$CH_2), 2.66 (m, 2 H, SnCH_2CH$_2$), 3.98 (s, 3 H, NCH_3), 4.20 (t, ^3J = 7.3 Hz, 2 H, NCH_2CH$_3$), 7.28 (s, 2 H, NC*H*C*H*N), 8.70 (s, 1 H, NC*H*N). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): δ = −12.1 (s, B12), −16.9 (s, B2−6 and B7−11). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 13.5 (CH$_2$CH$_2$*C*H$_3$), 15.5 (NCH$_2$*C*H$_3$) 16.9 (SnCH$_2$*C*H$_2$), 26.8 (SnCH$_2$*C*H$_2$), 30.3 (Sn*C*H$_2$), 37.1 (N*C*H$_3$), 46.1 (N*C*H$_2$CH$_3$), 122.3 (N*C*H$_2$CH$_2$N), 124.1 (NCH$_2$*C*H$_2$N), 136.0 (N*C*H$_2$N).

$C_{12}H_{35}B_{11}N_2Sn$ (445.1): calcd. C 32.39, H 7.93, N 6.29; found C 32.22, H 7.33, N 7.07. DSC: M.p. 54.9 °C. IR (KBr): $\tilde{\nu}$ = 2505 (vs), 2856 (w), 2870 (w), 2926 (s), 2957 (s), 3097 (s), 3111 (w), 3140 (s), 3159 cm^{-1} (w).

[1] K. R. Seddon, *J. Chem. Tech. Biotechnol.* **1997**, *68*, 351−356.
[2] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926−3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772−3789.
[3] A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7264−7272.
[4] R. W. Chapman, J. G. Kester, K. Folting, W. E. Streib, L. J. Todd, *Inorg. Chem.* **1992**, *31*, 979−983.
[5] T. Marx, L. Wesemann, S. Dehnen, I. Pantenburg, *Chem. Eur. J.* **2001**, *7*, 3025−3032, and references therein.
[6] J. D. Holbrey, K. R. Seddon, *J. Chem. Soc., Dalton Trans.* **1999**, 2133−2139.
[7] [7a] *X-RED 1.22, Data Reduction for STAD4 and IPDS*, Fa. Stoe & Cie, Darmstadt, **2001**.[7b] *X-SHAPE 1.06, Crystal Optimization for Numerical Absorption Correction*, Fa. Stoe & Cie, Darmstadt, **1999**.
[8] *WINGX 1.63*: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
[9] *SIR 92 − A program for crystal structure solution*: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343−350.
[10] G. M. Sheldrick, *SHELXL 93, Program for the Refinement of Crystal Structures*, Göttingen, **1993**.

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