SHORT COMMUNICATION

Novel Ferrocene-Based Mono- and Bifunctional Tri-1-pyrazolylborate Ligands

Frieder Jäkle[a], **Kurt Polborn**[b], and **Matthias Wagner***[a]

Anorganisch-chemisches Institut, Technische Universität München[a],
Lichtenbergstraße 4, D-85747 Garching, Germany
Telefax: (internat.) +49(0)89-32093473
E-mail: (internat.) wagner@zaphod.anorg.chemie.tu-muenchen.de

Institut für Organische Chemie der Ludwig-Maximilians-Universität München[b],
Karlstraße 23, D-80333 München, Germany

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The reaction of (dibromoboryl)ferrocene (**1a**) with pyrazole/NEt$_3$ gave the ferrocenyltri-1-pyrazolylborate ligand **2**. Its thallium(I) derivative **2-Tl** provides the first example of a polymeric structure with bridging tri-1-pyrazolylborate units in the solid state. The trinuclear iron complex **2-Fe**, which is related to 1,1′-terferrocene, was obtained by reaction of **2** with FeCl$_2$. The bis(polydentate) ligand 1,1′-ferrocenediylbis(tri-1-pyrazolylborate) (**3-Li**) was prepared from 1,1′-bis[bis(dimethylamino)boryl]ferrocene (**1c**) and a mixture of lithium pyrazolide/pyrazole in refluxing toluene/THF. **3-Li** reacts with TlNO$_3$ to give the thallium(I) complex **3-Tl**.

Metallocenes are attracting increasing attention as components of oligomeric materials with interesting physical properties[1]. However, only few efficient routes to these macromolecular species have been developed up to now. One strategy that proved particularly successful is the thermal ring-opening polymerization (TROP) of strained, ring-tilted metallocenophanes[2].

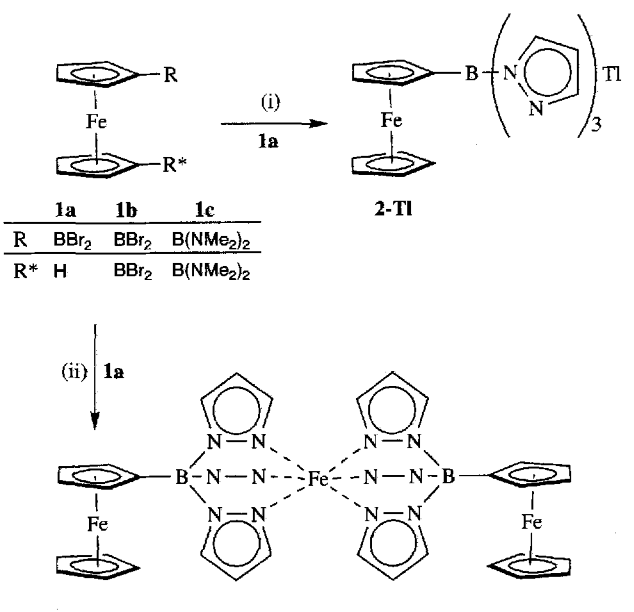
We recently reported on a novel approach to oligometallic compounds that benefits from the facile formation of boron-nitrogen bonds, which are employed to link the individual mononuclear specimens[3]. A shortcoming of these particular organometallic polymers is that they are readily hydrolyzed when exposed to air and therefore have to be kept strictly under inert gas. In this paper we describe how the stability can be improved by utilizing the tri-1-pyrazolylborate moiety[4] for the formation of oligonuclear organometallic compounds with stable B–N backbones. The aim was to form linear strains, which are composed of an appropriate transition metal fragment and a bifunctional tri-1-pyrazolylborate linker ($[\mathrm{pz_3B{-}E{-}Bpz_3}]^{2-}$; pz = 1-pyrazolyl). Only one ligand containing more than one $\mathrm{RBpz_3^-}$ donor site has been described so far[5]. For our purposes, an organometallic bridge –E– was best suited to connect both Bpz$_3$ units. We chose the 1,1′-ferrocenediyl fragment for the following reasons: (1) It shows a reversible one-electron oxidation. (2) The rigid molecule possesses a well-defined geometry. Nevertheless, some flexibility is maintained, because the ferrocene fragment can act as a hinge, which allows bending of the aimed for oligomeric strains.

Starting from the readily available ferrocene derivatives **1a**, **b**, **c**[6], this work describes the synthesis and structure of the building blocks **2** and **3** (Schemes 1, 2). Both ligands were characterized as their thallium(I) salts, which offer the possibility of carrying out further reactions in hydrocarbon solvents. However, for the general synthesis of transition metal complexes, both the free acid FcBpz$_3$H (Fc: ferrocenyl) and the lithium salt **3-Li** are perfectly suitable starting materials.

Results and Discussion

(Dibromoboryl)ferrocene (**1a**) was allowed to react with 3 equiv. of pyrazole (Hpz) and 2 equiv. of NEt$_3$ in toluene at 0°C (Scheme 1). Reaction of the resulting free acid FcBpz$_3$H with one equiv. of TlOEt gave **2-Tl**. X-ray quality crystals were grown by layering a CH$_2$Cl$_2$ solution of **2-Tl** with hexane. For the generation of the homotrinuclear complex **2-Fe**, two equiv. of FcBpz$_3$H were deprotonated with NEt$_3$ and stirred with a suspension of FeCl$_2$ in THF.

Scheme 1. Reagents: (i) 3 Hpz, 2 NEt$_3$, 0°C (pz, N–N: 1-pyrazolyl); 1 TlOEt, −78°C. – (ii) 2 **1a**, 6 Hpz, 4 NEt$_3$, 0°C; 2 NEt$_3$, 1 FeCl$_2$, ambient temp.



The bifunctional ligand **3-Li** could be obtained by slowly adding a toluene solution of 1,1′-bis(dibromoboryl)ferrocene[6] (**1b**) to an ethereal solution of 6 equiv. of lithium pyrazolide, Lipz, at −78°C (Method A). While the yield of **2-Tl** is about 80%, the synthesis of **3-Li** according to Method A is severely hampered by the formation of side product **4**, which is inert toward further attack of Lipz

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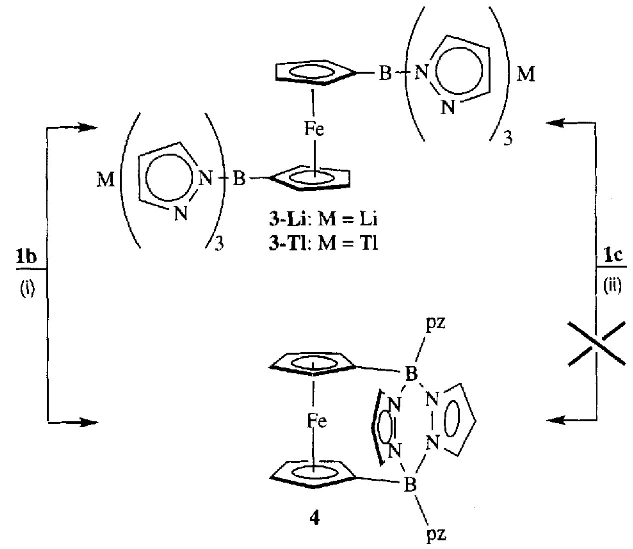
(Scheme 2). We already described the synthesis, structure and chemical properties of various derivatives of **4**[7]. It is important to note that **3-Li** is perfectly stable once it has been formed and does not show any tendency to generate **4** by eliminating Lipz. The formation of **4** as byproduct of the synthesis of **3-Li** can be completely suppressed by employing 1,1′-bis[bis(dimethylamino)boryl]ferrocene (**1c**)[6] rather than **1b** as starting material. Compound **1c** possesses boron centers of low Lewis acidity, which bear poor leaving groups. The reaction of **1c** with 2 equiv. of Lipz and 4 equiv. of Hpz in refluxing THF/toluene gave **3-Li** in 80% yield (Method B). Upon treatment of **3-Li** with 2 equiv. of $TlNO_3$ in THF/water the thallium compound **3-Tl** was formed almost quantitatively.

Scheme 2. Reagents: (i) 6 Lipz, −78 °C. − (ii) 2 Lipz, 4 Hpz, toluene/THF, reflux; exc. $TlNO_3$



The ^{11}B-NMR spectrum of **2-Tl** shows one signal in the typical range for tetracoordinated boron nuclei[8] (δ = 0.9). The positions 3, 4 and 5 of the pyrazole rings give rise to three resonances in the ^{1}H- and in the ^{13}C-NMR spectrum. All three pyrazole moieties are magnetically equivalent at ambient temperature. No spin coupling of ^{205}Tl with the rest of the molecule is resolved, which indicates rather weak Tl−N bonding. The same general features as observed for **2-Tl** are found in the NMR spectra of **2-Fe**. However, the ^{1}H- and ^{13}C-NMR resonances of this compound are extremely broadened, which was already reported for other octahedral low-spin Fe(II) poly(1-pyrazolyl)borate complexes[9]. In the case of **3-Li** and **3-Tl** the positions 3, 4 and 5 of the pyrazole fragments are again magnetically non-equivalent, which clearly distinguishes these compounds from the more symmetrical **4**.

The molecular structure of **2-Tl** in the solid state shows the following particularities (Figure 1): The tri-1-pyrazolylborate moiety does not act as a tridentate ligand, but coordinates to two different thallium atoms, thereby generating a polymeric structure (Figure 2). Dinuclear complexes with bridging tri-1-pyrazolylborate ligands are rare[10], and polynuclear complexes have previously not been known. The Tl−N distances are significantly longer [i.e. 2.638(5), 2.676(5), 2.780(5) Å] than those found in tridentate thallium poly(1-pyrazolyl)borate complexes (average value: 2.59 Å)[11]. These findings further support the assumption of unusually weak Tl−N bonding in **2-Tl**. One of the three pyrazole substituents of every Bpz_3 unit is placed in a position almost orthogonal to the planes of the cyclopentadienyl rings [angle between the best planes C(10)−C(14)//N(1)−C(3): 82.8(2)°].

Figure 1. View of two molecules of **2-Tl**. Elements are represented by thermal ellipsoids at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths/interatomic distances [Å], angles and angles between best planes (deg). N(6A) indicates that this atom belongs to a neighboring molecule **2-Tl** [i.e. Tl(1)−N(6A) is an *inter*molecular bond]: B(1)−C(10) 1.579(7), B(1)−N(1) 1.567(7), B(1)−N(3) 1.552(7), B(1)−N(5) 1.578(7), N(1)−N(2) 1.357(6), N(3)−N(4) 1.354(6), N(5)−N(6) 1.371(6), Tl(1)−N(2) 2.638(5), Tl(1)−N(4) 2.676(5), Tl(1)−N(6A) 2.780(5), Tl(1)···Tl(1A) 5.27(2); N(1)−B(1)−N(3) 110.0(4), N(1)−B(1)−N(5) 107.1(4), N(3)−B(1)−N(5) 104.8(4), C(10)−B(1)−N(1) 106.8(4), C(10)−B(1)−N(3) 115.8(4), C(10)−B(1)−N(5) 112.1(4), N(2)−Tl(1)−N(4) 70.9(2), N(2)−Tl(1)−N(6A) 83.2(1), N(4)−Tl(1)−N(6A) 92.4(1); C(10)−C(14)//C(15)−C(19) 4.2(2), N(1)−C(3)//N(3)−C(6) 57.4(2), N(1)−C(3)//N(5)−C(9) 64.5(2), N(3)−C(6)//N(5)−C(9) 72.8(2), C(10)−C(14)//N(1)−C(3) 82.8(2)

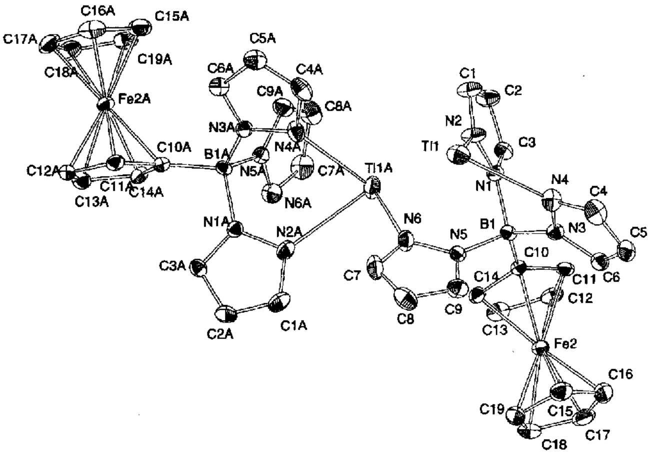
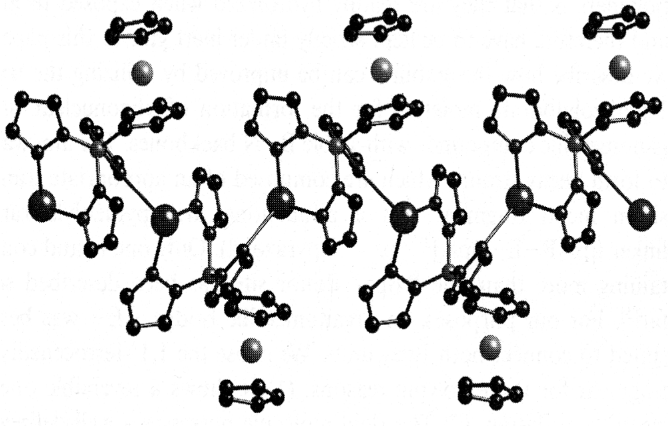


Figure 2. Polymeric structure of **2-Tl** in the solid state



2-Fe is related to 1,1′-terferrocene[12], given that the tri-1-pyrazolylborate moiety is known to possess many similarities to the cyclopentadienyl ligand[4]. We have demonstrated that Fe(II) ions can be used to establish bonding between two different ferrocenyltri-1-pyrazolylborate units, that is to initiate chain formation, when **3** instead of **2** is employed. Both **2-Fe** and the material obtained from the reaction of **3-Li** with $FeCl_2$ exhibit a rather complex electrochemical behavior, which is currently the object of further studies in our laboratory.

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Experimental

All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon by using standard Schlenk equipment or in an argon-filled drybox. Solvents were freshly distilled under N_2 from Na/K alloy/benzophenone (toluene, hexane, THF, Et_2O) or from CaH_2 (CH_2Cl_2) prior to use. – NMR: Jeol JMN-GX 400 and Bruker DPX 400 (abbreviations: vt virtual triplet, br broad). ^{11}B-NMR spectra were referenced to external $BF_3 \cdot Et_2O$. The assignment of NMR resonances follows the common numbering scheme for pyrazoles. – MS (FAB/CI mode): Finnigan MAT 90. – Elemental analyses: Microanalytical laboratory of the Technische Universität München.

The compounds **1a**, **b**, **c**[6] were synthesized according to literature procedures. Lithium pyrazolide (Lipz) was obtained from pyrazole (Hpz) and *n*-butyllithium in toluene or ether.

1. *Preparation of* **2-Tl**: A toluene solution of **1a** (1.02 g, 2.87 mmol) was allowed to react with a toluene solution of Hpz (0.58 g, 8.52 mmol) at 0 °C. After the addition of neat NEt_3 (0.58 g, 5.73 mmol), the reaction mixture was stirred at ambient temp. for 12 h. Insoluble $[HNEt_3]Br$ was removed by filtration and the filtrate treated with a toluene solution of TlOEt (0.72 g, 2.89 mmol) at −78 °C. The mixture was allowed to warm to ambient temp. and stirred for 12 h. The solvent was removed in vacuo and the crude solid residue crystallized from CH_2Cl_2/hexane (1:1). Yield 1.36 g (79%). – ^{11}B NMR (128.3 MHz, $CDCl_3$): $\delta = 0.9$ ($h_{1/2} = 120$ Hz). – ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.21$ (s, 5H, C_5H_5), 4.27, 4.48 (vt, vt, 2H, $J_{HH} = 2$ Hz, C_5H_4), 6.22 (vt, 3H, $J_{HH} = 2$ Hz, pz-H4), 7.55, 8.13 (d, d, 3H, 3H, $J_{HH} = 2$ Hz, pz-H3,5). – ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 69.0$ (C_5H_5), 70.0, 75.1 (C_5H_4), n.o. (C_5H_4-*ipso*), 103.9 (pz-C4), 135.7, 139.1 (pz-C3,5). – CI-MS, *m/z* (%): 602 (100) $[M^+]$, 417 (25) $[(M^+ - C_{10}H_9Fe)]$, 330 (90) $[(M^+ - Tlpz)]$. – $C_{19}H_{18}BFeN_6Tl$ (601.4): calcd. C 37.95, H 2.99, N 13.97; found C 38.00, H 3.09, N 14.21.

2. *Preparation of* **2-Fe**: A toluene solution of **1a** (1.07 g, 3.01 mmol) was allowed to react with a toluene solution of Hpz (0.61 g, 8.97 mmol) at 0 °C. After the addition of neat NEt_3 (0.61 g, 6.04 mmol), the reaction mixture was stirred at ambient temp. for 12 h. Insoluble $[HNEt_3]Br$ was removed by filtration and the filtrate again treated with neat NEt_3 (0.30 g, 2.97 mmol) at ambient temp. A suspension of $FeCl_2$ (0.19 g, 1.50 mmol) in THF was added with vigorous stirring, whereupon the color of the reaction mixture changed from orange to purple. After stirring for 1 h, insoluble material was removed by filtration and the filtrate cooled to 0 °C. A brown microcrystalline solid formed, which was collected on a frit, extracted with toluene and CH_2Cl_2 and dried in vacuo. Yield 1.87 g (73%). – ^{11}B NMR (128.3 MHz, $CDCl_3$): $\delta = -1.0$ ($h_{1/2} = 50$ Hz). – ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.39$ (s, 10H, C_5H_5), 4.68, 4.70 (br, br, 4H, 4H, C_5H_4), 6.1 (br, 6H, pz-H4), 6.5, 8.4 (br, br, 6H, 6H, pz-H3,5). – ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 69.0$ (C_5H_5), 70.5, 75.2 (br, C_5H_4), n.o. (C_5H_4-*ipso*), 104 (br, pz-C4), 138, 145 (br, pz-C3,5). – FAB-MS, *m/z*: 850 $[M^+]$. – $C_{38}H_{36}B_2Fe_3N_{12}$ (849.7): calcd. C 53.72, H 4.24, N 19.77; found C 53.10, H 4.49, N 20.08.

3. *Preparation of* **3-Li**. – *Method A:* An ethereal solution of Hpz (0.68 g, 10.0 mmol) was treated with *n*-butyllithium (1.6 M solution in hexane, 6.3 ml) at −78 °C. The mixture was allowed to warm to ambient temp., stirred for 3 h and again cooled to −78 °C. A toluene solution of **1b** (0.87 g, 1.66 mmol) was added dropwise with vigorous stirring to the colorless solution of Lipz. The reaction mixture was slowly warmed to ambient temp. and stirred for 12 h. After filtration from a small amount of insoluble material, the filtrate was concentrated in vacuo. The resulting yellow solid was first extracted three times with 15 ml of toluene each and afterwards twice with 10 ml of water each. The remaining solid exhibited the same resonances in the ^{11}B-, ^1H- and ^{13}C-NMR spectra as the material obtained according to Method B. Yield: 15% of **3-Li**.

Method B: A freshly prepared toluene solution of **1c** (1.61 g, 4.22 mmol) was treated with a THF solution of Lipz (0.62 g, 8.38 mmol) at ambient temp. Neat Hpz (1.15 g, 16.90 mmol) was added, and the reaction mixture was kept at reflux for 12 h, whereupon a yellow precipitate formed. All volatile components were removed from the reaction mixture under reduced pressure. The yellow microcrystalline residue was extracted three times with toluene and dried in vacuo. NMR spectroscopy showed it to contain 0.7 equiv. of THF. Yield 2.10 g (80%). – ^{11}B NMR (128.3 MHz, $[D_8]$THF): $\delta = -0.4$ ($h_{1/2} = 250$ Hz). – ^1H NMR (400 MHz, $[D_8]$THF): $\delta = 4.17, 4.28$ (vt, vt, 4H, 4H, $J_{HH} = 2$ Hz, C_5H_4), 6.02 (vt, 6H, $J_{HH} = 2$ Hz, pz-H4), 7.44, 7.84 (d, d, 6H, 6H, $J_{HH} = 2$ Hz, pz-H3,5). – ^{13}C NMR (100.5 MHz, $[D_8]$THF): $\delta = 70.3, 73.7$ (C_5H_4), n.o. (C_5H_4-*ipso*), 100.9 (pz-C4), 133.1, 137.0 (pz-C3,5). – $C_{28}H_{26}B_2FeLi_2N_{12}$ (621.7) · 0.7 THF (72.1): calcd. C 55.04, H 4.70, Fe 8.31, Li 2.06, N 25.00; found C 55.03, H 4.93, Fe 8.22, Li 2.00, N 25.14.

4. *Preparation of* **3-Tl**: A solution of 0.22 g (0.33 mmol) of **3-Li** · 0.7 THF in THF was treated with an excess of $TlNO_3$ (0.25 g, 1.00 mmol) in water at ambient temp. The amount of solvents was reduced in vacuo until a yellow precipitate formed. Insoluble material was collected on a frit (G4), extracted with water and dried in vacuo. Crystallization of the crude material from toluene/hexane (1:1) gave 0.27 g (83%) of **3-Tl**. – ^{11}B NMR (128.3 MHz, $CDCl_3$): $\delta = 0.9$ ($h_{1/2} = 200$ Hz). – ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.37$ (s, 8H, C_5H_4), 6.24 (vtr, 6H, $J_{HH} = 2$ Hz, pz-H4), 7.57, 8.16 (d, d, 6H, 6H, $J_{HH} = 2$ Hz, pz-H3,5). – ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 72.0, 75.6$ (C_5H_4), n.o. (C_5H_4-*ipso*), 104.1 (pz-C4), 135.6, 139.2 (pz-C3,5). – FAB-MS, *m/z*: 1018 $[M^+]$. – $C_{28}H_{26}B_2FeN_{12}Tl_2$ (1016.6): calcd. C 33.08, H 2.58, N 16.53; found C 33.47, H 2.88, N 16.31.

5. *X-Ray Crystal Structure Analysis of* **2-Tl**[13]: An air-stable orange crystal of **2-Tl** ($C_{19}H_{18}BFeN_6Tl$, $M = 601.42$) was mounted on top of a glass filament on a goniometer head. An automatic four-circle diffractometer (CAD4, Enraf Nonius) was used to collect reflections. Final lattice parameters were obtained by least-squares refinement of 15 reflections (graphite monochromator, $\lambda = 0.71073$ Å – Mo-K_α). Monoclinic system, space group $P21/n$, $a = 10.006(1)$, $b = 10.072(1)$, $c = 19.928(2)$ Å, $\beta = 93.50°$, $V = 2004.5(3)$ Å^3, $D_{calcd} = 1.993$ g/cm^3, $\mu = 8.77$ mm^{-1}, $Z = 4$. Data were collected at 293(2) K and corrected for Lp and absorption ($t_{min} = 0.4125$; $t_{max} = 0.9937$). Range of measurement $2.87° < \Theta < 22.98°$, 3154 reflections collected, 2773 independent reflections, 199 with negative intensity, 2773 reflections with $I > 2 \cdot \sigma(I)$. The structure was solved by direct methods (SHELXS-86) and refined with difference Fourier techniques (SHELXL-93). All hydrogen positions were calculated in ideal geometry (riding model). Number of parameters refined: 253; data per parameter: 11; GOOF: 0.771; residual electron density: $+0.546$ eÅ^{-3}, -1.158 eÅ^{-3}; $R1 = 0.026$ [for $I > 2\sigma(I)$] $wR2 = 0.080$ (all data); minimized function was $\Sigma w(|F_o|^2 - |F_c|^2)^2$; $w = 1/[\sigma^2|F_o|^2 + (0.1\,P)^2]$ with $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

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[13] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405012, the names of the authors and the literature citation.

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