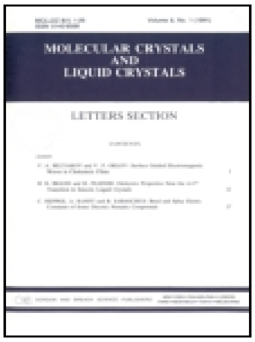

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Hexaaquamanganese(II) bis[hydrotris(3-methyl-2-thioxo-1-imidazolyl) borate] Tetrahydrate: A Non-coordinating Borate Ligand with Manganese(II) Metal Ion

S. Jayakumar, M. Nizam Mohideen & A. Kalilur Rahiman

To cite this article: S. Jayakumar, M. Nizam Mohideen & A. Kalilur Rahiman (2015) Hexaaquamanganese(II) bis[hydrotris(3-methyl-2-thioxo-1-imidazolyl) borate] Tetrahydrate: A Non-coordinating Borate Ligand with Manganese(II) Metal Ion, Molecular Crystals and Liquid Crystals, 608:1, 190-197, DOI: 10.1080/15421406.2014.949844

To link to this article: http://dx.doi.org/10.1080/15421406.2014.949844

Mol. Cryst. Liq. Cryst., Vol. 608: pp. 190–197, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.949844

Hexaaquamanganese(II) bis[hydrotris(3-methyl-2-thioxo-1-imidazolyl) borate] Tetrahydrate: A Non-coordinating Borate Ligand with Manganese(II) Metal Ion

S. JAYAKUMAR,[1] M. NIZAM MOHIDEEN,[2]
AND A. KALILUR RAHIMAN[1,*]

[1]Post-Graduate and Research Department of Chemistry, The New College (Autonomous), Chennai, India
[2]Department of Physics, The New College (Autonomous), Chennai, India

The metallation of a tripodal ligand, hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate with manganese(II) salt gave an unusual title compound, $[Mn(H_2O)_6](C_{12}H_{16}N_6BS_3)_2.4H_2O$. *The presence of soft donor atom in the borate moiety may be the cause of non-coordinating interaction with metal ion. The manganese(II) ion is coordinated with six water molecules leads to distorted octahedral geometry. In the crystal, the cations, anions and uncoordinated water molecules are linked by intermolecular* $O—H\cdots O$ *hydrogen bonds and week intermolecular* $O—H\cdots S$ *and* $C—H\cdots S$ *interaction, generating a three-dimensional network. The thermal behavior of the title compound was also investigated.*

Keywords Borate ligand; crystal structure; non-coordinating complex; thermal studies

1. Introduction

Since its first reported synthesis, Trofimenko's versatile N_3-donor poly(pyrazolyl)borates, also known as scorpionate ligands, has continued to be an active area of research, especially in borate-based chelating chemistry [1]. An analogous tripodal ligand hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate with softer donor atoms was first reported by Reglinski et al. [2, 3]. Unlike the analogous scorpionate ligands containing hard pyrazolyl donor nitrogen atoms, this ligand contains softer donor sulfur atoms. The donor properties of these types of anionic ligands have been extensively investigated and the coordination chemistry is of considerable interest for building inorganic models. These type of soft ligands have found application in the preparation of model compounds for sulfur-rich metalloenzymes such as

---

[*]Address correspondence to A. Kalilur Rahiman, Post-Graduate and Research Department of Chemistry, The New College (Autonomous), Chennai 600 014, India. E-mail: akrahmanjkr@gmail.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

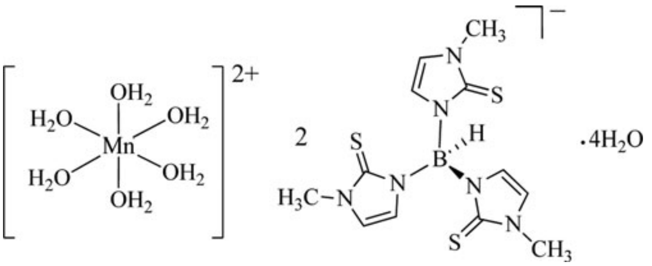

Figure 1. Hexaaquamanganese(II) bis[hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate] tetrahydrate.

liver alcohol dehydrogenase (LADH) and [NiFe] hydrogenases and in the preparation of radiopharamaceuticals incorporating ^{99m}Tc or $^{186/188}$Re isotopes [4–7].

The metal coordination properties of the ligand reveals that it reacts with Group 2 metals in which the borate acts as non-coordinating species [8] whereas with transition metals such as mercury it forms a 1:1 metal complex [9] or metal cluster complex [10]. Reglinski et al. [11] have reported a wide variety of complexes with both transition and main group metal with soft donor ligands. However, in this paper, we report synthesis, FT-IR and thermal analysis of the non-coordinated manganese(II) complex of a tripodal ligand hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate, $[Mn(H_2O)_6](C_{12}H_{16}N_6BS_3)_2.4H_2O$. In the crystal structure of a water-rich manganese(II) borate(1-) complex, the soft binding borate ligand acts as a non-coordinating species with transition metal ion (Fig. 1). The manganese cation is coordinated by six aqua molecules and associated with the anionic ligand through hydrogen bonds.

2. Experimental

2.1. Materials and Methods

2-Mercapto-1-methyl-imidazole (methimazole) and manganese(II) acetate were purchased from Aldrich (USA), and all other reagents were purchased as analytical grade and used without further purification. Solvents were dried and purified before being used according to the standard procedure and stored over molecular sieves. The elemental analysis (% C, H and N) was measured with a Carlo Erba elemental analyzer Model 1106. Infrared spectra were recorded on ABB instruments, MB-3000 spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}. Thermogravimetric analysis was carried out using SSI Nanotechnologies TGA/DTA 6300 thermal analyzer to record simultaneously TGA/DTA curves under a nitrogen atmosphere with a heating rate of 20°C/min in the temperature range 30—180°C.

2.2. Synthesis of Hexaaquamanganese(II) bis[hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate] tetrahydrate

The ligand hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate was synthesized according to the literature method [12]. The title compound was synthesized by adding the methanolic solution (10 mL) of $Mn(OAc)_2.4H_2O$ (1 mmol, 0.245 g) dropwise to the methanolic solution (10 mL) of ligand (1 mmol, 0.374 g) with constant stirring at room temperature for 1 h followed by refluxing for 2 h. The resulting compound was kept at room temperature for several days which gave crystals suitable for X-ray diffraction.

Analytical data for [$C_{24}H_{52}B_2N_{12}O_{10}S_6Mn$] (FW: 937.70 g/mol): Calculated (%) C, 30.74; H, 5.59; N, 17.92. Found (%): C, 31.40; H, 5.45; N, 18.21.

2.3. Crystal Structure Determination

Suitable single crystals were obtained for XRD measurements by the slow evaporation of the manganese(II) complex in methanol at room temperature. Dark green crystals obtained was sorted using polarizing microscope (Leica DMLSP). Crystals having good morphology were chosen for three-dimensional intensity data collection. A crystal with dimensions of 0.35 × 0.35 × 0.30 mm was mounted on a glass fiber for diffraction experiment. X-ray single crystal data were collected on a Kappa Apex2 CCD diffractometer equipped with a fine-focus sealed tube X-ray source and graphite monochromated Mo $K\alpha$ radiation in the wavelength (λ) of 0.71073 Å at room temperature (293 ± 2 K). The intensity data were collected using ω and φ scans with frame width of 0.5°. The frame integration and data reduction were performed using Bruker SAINT-plus (Version 7.06a) software. Empirical absorption corrections were applied for the complex, using SADABS program [13]. The structure was solved by using SIR92 [14] and the full-matrix least-squares refinement on F^2 was performed using SHELXL-97 program [15]. The scattering factors incorporated in SHELXL-97 were used. After several cycles of refinement, the positions of the hydrogen atoms were calculated and added to the refinement process. Molecular graphics, hydrogen bonding and packing figures were generated by using the softwares ORTEP 3.0 [16] and Mercury 3.0 [17]. The final R-value of the complex was 0.0281, and the final electrodensity map contains maximum and minimum peak heights of 0.421 and -0.411 e Å^{-3}, respectively.

3. Results and Discussion

The title compound was obtained by the metallation of the ligand, hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate with $Mn(OAc)_2.4H_2O$ in methanol. The compound was stable at room temperature and possessed good keeping qualities. It was non-hygroscopic solid, insoluble in n-hexane, petroleum ether, and diethyl ether, and soluble in dichloromethane and chloroform. IR spectrum of the compound show bands at 3783 and 3691 cm^{-1} due to symmetric and asymmetric υ(O—H) stretching vibrations of the water molecules coordinated to Mn(II) ion. The broad band at 2936 cm^{-1} assigned to υ(C—H) stretching of heterocyclic nitrogen atom with alkyl group in the ligand. The strong band at 2347 cm^{-1} is due to υ(B—H) stretching, whereas the bands at 1451 and 1293 cm^{-1} are assigned to υ(B—N) and υ(C=S) stretching, respectively.

Figure 2 displays the TG and DTA curves of the crystal obtained in flowing N_2 atmosphere in the temperature range 30–180°C with a heating rate of 20°C min^{-1}. The complex undergo decomposition (or) weight loss between 34–180°C attributed to the loss of water molecules, both coordinated and lattice water molecules present in complex structure. The first weight loss of 16.7% (calc.15.3%) from 34–98°C with an endotherm at 83°C corresponds to the release of eight water molecules, both coordinated and lattice water molecules. The second weight loss of 18.2% (calc.19.1%) from 98–180°C with an endotherm at 144°C, corresponds to the release of two lattice water molecules. The third stage presumably involve further decomposition leading to the formation manganese(II) sulfide.

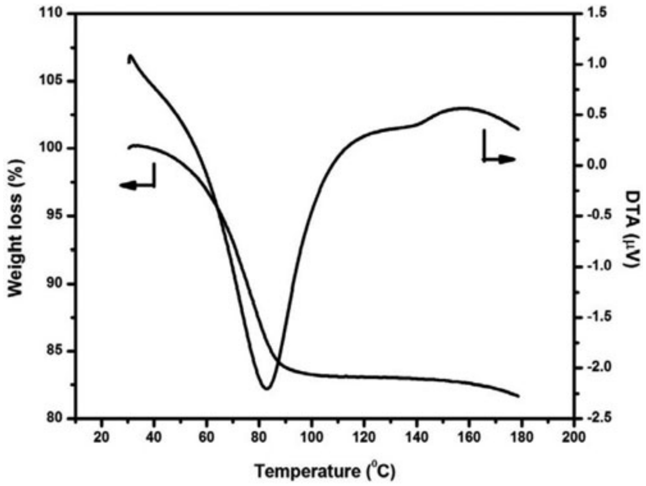

Figure 2. TG/DTA curves of the non-coordinating manganese(II) complex.

The single crystal structure of $[Mn(H_2O)_6](C_{12}H_{16}N_6BS_3)_2.4H_2O$ has been solved and the crystal data and structure refinement details are given in Table 1. The ORTEP diagram of the complex, along with atom numbering scheme is shown in Figure 3, and the selected bond distances and bond angles are given in Table 2. The molecular structure consists of metal atom in the hexaaqua-coordinated cations lie on center of inversion in octahedral coordination geometry with Mn–O bond lengths in the range of 2.139 (2)–2.212 (2) Å, but the anion has no coordinative interaction with the manganese cation. This rare transition metal compound is placed in the context of previously reported similar Group 2 metal compounds that emphasizes its peculiarity [8]. The molecular structure has not a planar conformation. Imidazole rings A (N1/N2/C1–C3), B (N3/N4/C4–C6) and C

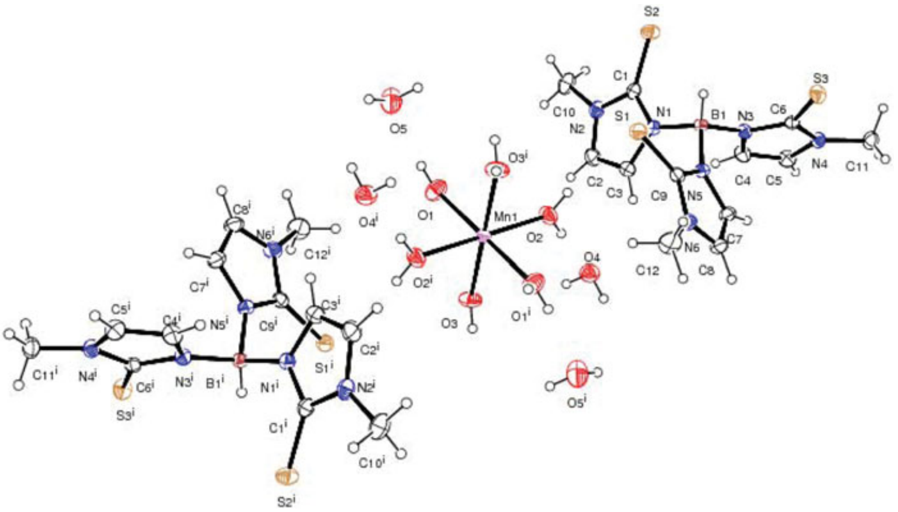

Figure 3. ORTEP diagram of the complex showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Crystal data and structure refinement for complex

Empirical formula	$C_{24}H_{52}B_2N_{12}O_{10}S_6Mn$
Formula weight	937.70
Temperature	293 ± 2 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a [Å]	8.7953(5)
b [Å]	9.4361(5)
c [Å]	13.0663(6)
α [°]	90.732(2)
β [°]	92.8670(10)
γ [°]	90.820(2)
Volume [$Å^3$]	1,082.85(10)
Z	1
Calculated density [Mg/m^3]	1.438
Adsorption coefficient [mm^{-1}]	0.655
$F(000)$	491
Crystal size (mm)	0.35 × 0.35 × 0.30
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 10$, $-11 \le l \le 15$
Reflections collected	18,690
Independent reflections	3817 [R(int) = 0.0230]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3817/0/291
GOF on F^2	1.063
Final R indices [$I < 2\sigma(l)$]	$R1 = 0.0281$, $wR2 = 0.0753$
R indexes (all data)	$R1 = 0.0302$, $wR2 = 0.0775$
Largest diff. peak and hole	0.421 and −0.411 e.$Å^{-3}$

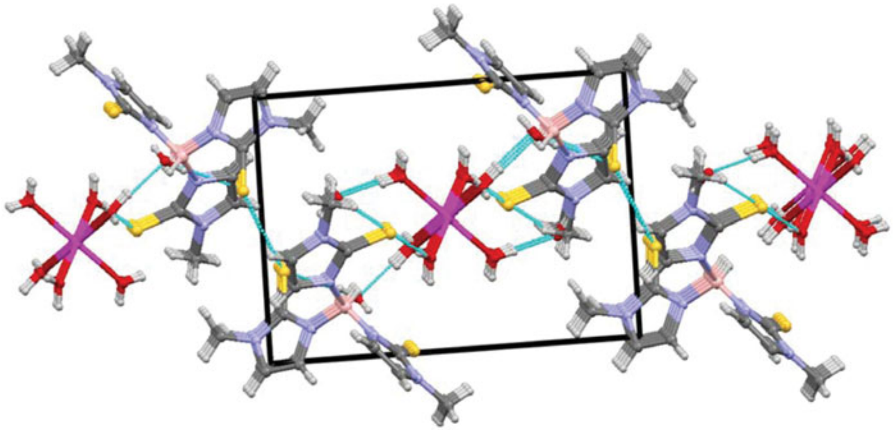

Figure 4. Packing diagram showing the stacking of the borate and the connection through the hexaaquamanganese(II) complex cations.

Table 2. Selected bond lengths (Å) and bond angles (°)

Bond lengths (Å)			
O(1)-Mn(1)	2.2121(17)	O(3)-Mn(1)	2.1913(15)
O(2)-Mn(1)	2.1386(14)	N(1) –B(1)	1.549(2)
N(3) –B(1)	1.552(2)	C(2)–N(2)	1.371(3)
C(2)–C(3)	1.339(3)	C(10)–N(2)	1.460(3)
Bond angles (°)			
Mn(1)–O(1)–H(1B)	123(2)	O(3)–Mn(1)–O(3)#1	180.0
Mn(1)–O(1)–H(1A)	126(3)	O(2)#1–Mn(1)–O(1)	91.32(7)
Mn(1)–O(2)–H(2B)	120(2)	O(2)–Mn(1)–O(1)	88.69(7)
Mn(1)–O(2)–H(2A)	125.9(18)	O(3)–Mn(1)–O(1)	86.38(7)
Mn(1)–O(3)–H(3A)	125(3)	O(3)#1–Mn(1)–O(1)	93.63(7)
Mn(1)–O(3)–H(3B)	125(2)	O(2)–Mn(1)–O(1)#1	91.31(7)
O(2)#1–Mn(1)–O(2)	180.0	O(3)–Mn(1)–O(1)#1	93.62(7)
O(2)#1–Mn(1)–O(3)	91.34(6)	O(3)#1–Mn(1)–O(1)#1	86.37(7)
O(2)–Mn(1)–O(3)	88.66(6)	O(1)–Mn(1)–O(1)#1	180.0

(N5/N6/C7–C9) are, of course, planar [maximum deviation of 0.003 (1) A for N1, 0.004 (1) A for N4 and 0.003 (2) A for C8, respectively] and they are oriented at a dihedral angle of A/B = 81.05 (2), A/C = 88.74 (2) and B/C = 85.25 (2)°, respectively. The thio-imidazole rings of the molecule display typical geometrical parameters, with the C—S bond lengths significantly longer than that of an isolated C—S double bond (1.60 Å), which can be

Table 3. Hydrogen bonding parameters [Å and°]

D—H... A	d(D—H)	d(H... A)	d(D... A)	<(DHA)
O(1)-H(1B)... O(5)	0.78(3)	1.94(4)	2.719(3)	173(3)
O(2)-H(2A)... O(4)	0.87(3)	1.83(3)	2.701(2)	176(3)
O(1)-H(1A)... S(2)#5	0.71(3)	2.78(3)	3.4761(19)	168(3)
O(2)-H(2B)... S(1)	0.81(3)	2.45(3)	3.2392(16)	164(3)
O(3)-H(3A)... S(1)#4	0.79(4)	2.49(4)	3.2672(18)	171(3)
O(3)-H(3B)... S(2)#4	0.84(3)	2.53(3)	3.3585(18)	168(3)
O(4)-H(4A)... S(2)#4	0.80(3)	2.53(3)	3.326(2)	170(3)
O(4)-H(4B)... S(3)#4	0.83(4)	2.44(4)	3.269(2)	172(3)
O(5)-H(5A)... S(1)#6	0.80(4)	2.52(4)	3.310(2)	176(4)
O(5)-H(5B)... S(3)#6	0.87(5)	2.46(5)	3.332(2)	175(4)
C(11)-H(11A)... O(4)#2	0.96	2.64	3.576(3)	163.9
C(12)-H(12A)... S(3)#3	0.96	2.77	3.723(3)	173.1
C10-H10C... Cg1	0.96	2.70	3.437(2)	134
C11-H11C... Cg2	0.96	2.74	3.355(2)	122

Symmetry transformations used to generate equivalent atoms:
#1: $-x + 1, -y, -z + 1$; #2: $x-1, y, z$; #3: $-x + 1, -y + 1, -z + 1$; #4: $-x + 1, -y, -z + 2$; #5: $-x + 1, -y + 1, -z + 2$; #6: $-x + 2, -y, -z + 2$.

correlated with the contribution of resonance structures involving the lone pair electrons of the adjacent N atoms [18].

In the crystal, the cations, anions and uncoordinated water molecules are linked by intermolecular O—H···O hydrogen bonds and weak intermolecular O—H···S and C—H···S interaction, generating a three-dimensional network (Fig. 4). In addition, C—H···π interaction is observed between the (C10—H10C and C11—H11C) methyl H atom and the imidazole ring A and B, respectively, of the adjacent molecule (Table 3).

4. Conclusions

The non-coordinating manganese(II) complex with formula $[Mn(H_2O)_6](C_{12}H_{16}N_6BS_3)_2 \cdot 4H_2O$ has been synthesized and characterized. The structure consists of isolated manganese(II) ion octahedrally coordinated by six water molecules, cations and anions are linked by intermolecular hydrogen bond interaction, generating a three-dimensional network. The presence of soft donor atom in the borate moiety may be the cause of non-coordinating interaction with metal ion. The thermal behavior of the synthesized complex was investigated using TG/DTA techniques with two substantial consecutive water releasing steps for manganese(II) complex. The first step is ascribed to release of eight water molecules both coordinated and lattice water molecules, followed by the loss of two lattice water molecules.

Acknowledgments

The authors thank Sophisticated Analytical Instruments Facility (SAIF), Indian Institute Technology Madras (IIT-M), Chennai 600 025, for solving the crystal structure of the compound.

Supplementary Data

CCDC 936554 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 0330).

References

[1] Trofimenko, S. (1967). *J. Am. Chem. Soc.*, *89*, 3170.
[2] Garner, M., Reglinski, J., Cassidy, I., Spicer, M. D., & Kennedy, A. R. (1996). *Chem. Commun.*, 1975.
[3] Reglinski, J., Spicer, M. D., Garner, M., & Kennedy, A. R. (1999). *J. Am. Chem. Soc.*, *121*, 2317.
[4] Garcia, R., Paulo, A., Domingos, A., Santos, I., Ortner, K., & Alberto, R. (2000). *J. Am. Chem. Soc.*, *122*, 11240.
[5] Kimblin, C., Bridgewater, B. M., Churchill, D. G., & Parkin, G. (1999). *Chem. Commun.*, 2301.
[6] Alvarez, H. M., Krawiec, M., Donovan-Merket, B. T., Fouzi, M., & Rabinovich, D. (2001). *Inorg. Chem.*, *40*, 5736.
[7] Garcia, R., Paulo, A., Domingos, A., & Santos, I. (2001). *J. Organomet. Chem.*, *632*, 41.
[8] Soares, L. F., Silva, R. M., Doriguetto, A. C., Ellena, J., Mascarenhas, Y. P., & Castellano, E. E. (2004). *J. Braz. Chem. Soc.*, *15*, 695.

[9] Cassidy, I., Garner, M., Kennedy, A. R., Potts, G. B. S., Reglinski, J., Slavin, P. A., & Spicer, M. D. (2002). *Eur. J. Inorg. Chem.*, 1235.

[10] Cetin, A., & Ziegler, C. J. (2005). *Dalton Trans.*, 1006.

[11] Dodds, C. A., Kennedy, A. R., Reglinski, J., & Spicer, M. D. (2004). *Inorg. Chem.*, *43*, 394.

[12] Hill, A. F., Owen, G. R., White, A. J. P., & William, D. J. (1999). *Angew. Chem., Int. Ed. 38*, 2759.

[13] Bruker-Nonius. (2004). *APEX-II and SAINT-plus (Version 7.06a), Bruker AXS Inc*. Madison, Wisconsin, USA.

[14] Altomare, A., Cascarano, G., Giacovazzo, C., & Guagliardi, A. (1993). *J Appl. Crystallogr.*, *26*, 343.

[15] Sheldrick, G. M. (2008). *Acta Crystallogr., Sec A.*, *64*, 112.

[16] Farrugia, L. J. (1997). *J. Appl. Crystallogr.*, *30*, 565.

[17] Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M., & Van de Streek, J. (2006). *J. Appl. Crystallogr.*, *39*, 453.

[18] Williamson, C., Storey, J. M. D., & Harrison, W. T. A. (2006). *J. Chem. Crystallogr.*, *36*, 277.