HETEROCYCLES, Vol. 97, No. 1, 2018, pp. 211 - 217. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 30th October, 2017, Accepted, 15th November, 2017, Published online, 17th November, 2017
DOI: 10.3987/COM-17-S(T)3

POLYMERIC SILVER(I) COMPLEXES BASED ON BIDENTATE IMIDAZOLINE-2-THIONES. SYNTHESIS AND CRYSTAL STRUCTURES

Barbara Rietzler,[1] Gerhard Laus,[1] Klaus Wurst,[1] Thomas Gelbrich,[1] Sven Nerdinger,[2]* Erwin Schreiner,[2] and Herwig Schottenberger[1]

[1]Faculty of Chemistry and Pharmacy, Leopold-Franzens University, Innrain 80, 6020 Innsbruck, Austria. [2]Sandoz GmbH, Biochemiestrasse 10, 6250 Kundl, Austria

Abstract – The bidentate ligand 1,6-bis(1-methylimidazol-2-ylthio)hexane or its hexafluoride salt reacted with silver(I) triflate, nitrate or oxide, respectively, to give the corresponding polymeric silver(I) complexes. Three crystal structures have been determined and showed linear and cyclic motifs.

INTRODUCTION

The outstanding ease with which 2-mercaptoimidazoles, such as the commercial anti-thyroid drug methimazole, [CARN 60-56-0], undergo *S*-alkylation[1] or oxidative dimerization[2] (disulfide formation) offers high potential for the construction of flexible bidentate ligands. In particular, polymethylene-bridged bis-methimazoles allow for straightforward synthetic access to a huge variety of sulfur-functionalized ligands. The diversity can be increased by ion metathesis. In this work, bidentate ligands have been employed for the preparation of silver(I) coordination polymers.[3,4] In recent years their potential electrical conductivity has received attention in material sciences.

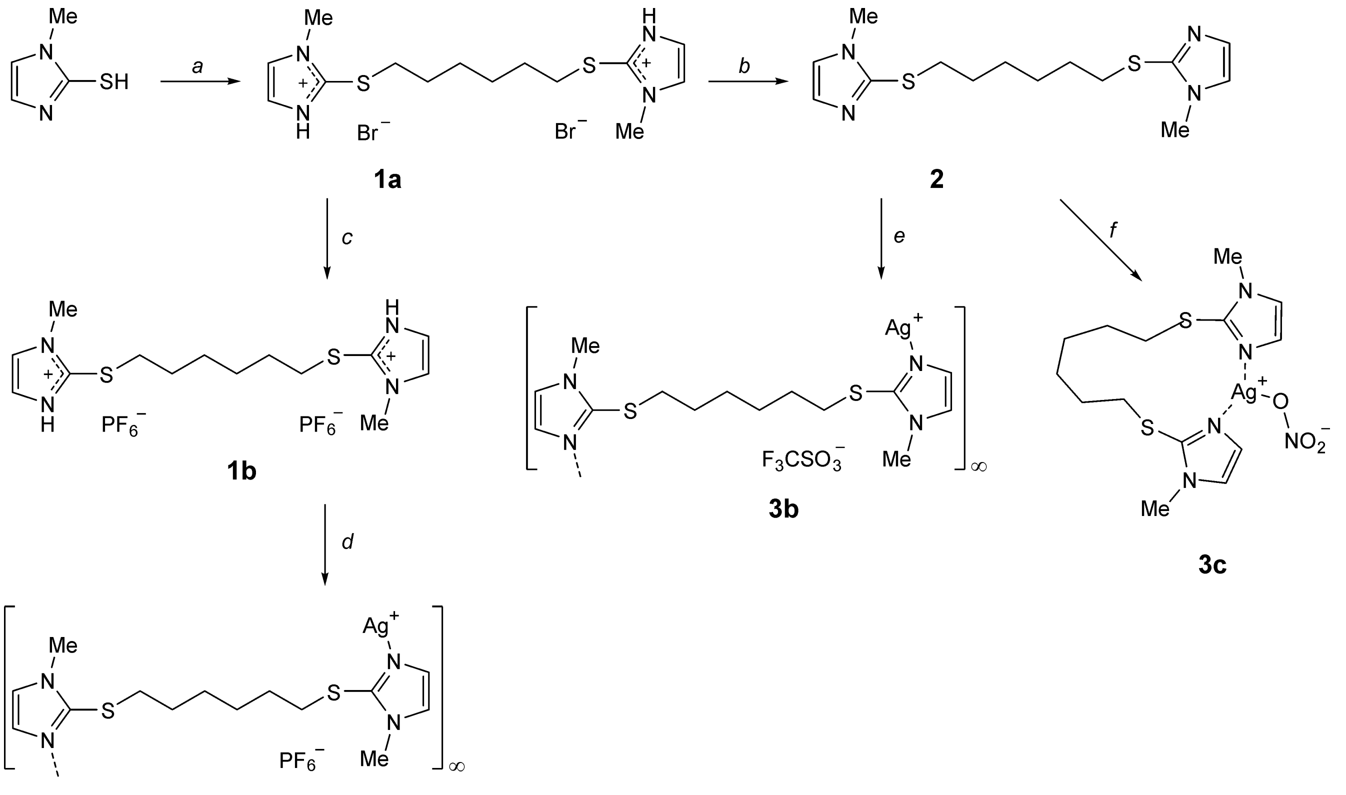
RESULTS AND DISCUSSION

S-Alkylation of methimazole with 1,6-dibromohexane resulted in dicationic bromide **1a** and ion metathesis gave hexafluoridophosphate **1b** (Scheme). The neutral ligand **2** was readily obtained by treatment with sodium hydrogen carbonate. The salt **1b** was directly converted to silver complex **3a**. Complexes **3b** and **3c** were obtained from the neutral ligand. The coordination polymers crystallized in the monoclinic space groups $P2_1/n$ and $P2_1/c$. Complexes **3a** and **3b** are isostructural. The geometrically flexible bidentate ligand

---

This paper is dedicated to Professor Kiyoshi Tomioka on the occasion of his 70th birthday.

serves either as a bridge between two metal centres (in **3a** and **3b**) or it alternatingly chelates a single metal centre (in **3c**). The anions can exist in coordinated or uncoordinated modes and can act as auxiliary ligands. In **3a** and **3b**, the silver(I) ions are two-coordinate, displaying nearly linear N–Ag–N angles of 178° and 174° in the presence of the noncoordinating hexafluoridophosphate ion (Figure 1) or the weakly coordinating triflate anion. In addition, the polymeric triflate complex **3b** (Figure 2) exhibits interionic Ag···O contacts (2.81 Å) with the weakly coordinating anion.



3a

Scheme. Reagents and conditions: (*a*) 1,6-dibromohexane, CH_2Cl_2; (*b*) $NaHCO_3$, H_2O; (*c*) NH_4PF_6, H_2O; (*d*) Ag_2O, MeOH; (*e*) AgO_3SCF_3, CH_2Cl_2; (*f*) $AgNO_3$, H_2O/EtOH

To the contrary, in the polymeric nitrate **3c**, short Ag···O contacts of 2.65 Å as well as N–Ag–N angles of 173° (cyclic motif containing three-coordinate silver(I) ions) and 178° (linear motif) are observed (Figure 3). In **3a** and **3b**, the polymers propagate parallel to the *b* axis; voids are occupied by anions (Figure 1 and 2). In **3c**, chelate complexes form centrosymmetric stacks along the *c* axis which alternate with 1-periodic coordination polymers; non-coordinating nitrate ions are accommodated in the remaining voids (Figure 3). Silver (I)–nitrate coordination in polymers has been reported previously.[5]

The structure of silver(I) complexes can be surprisingly varied even with similar ligands, due to supramolecular interactions such as hydrogen bonding, anion binding and ligand flexibilty. The crystal data and refinement details are summarized in Table 1.

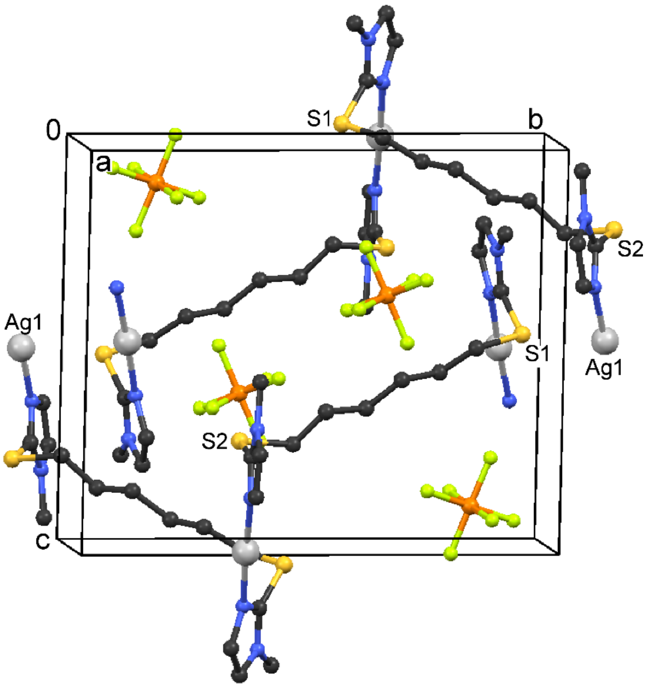


Figure 1. Coordination polymer in the crystal structure of poly[silver(I)-μ-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] hexafluoridophosphate] (**3a**)

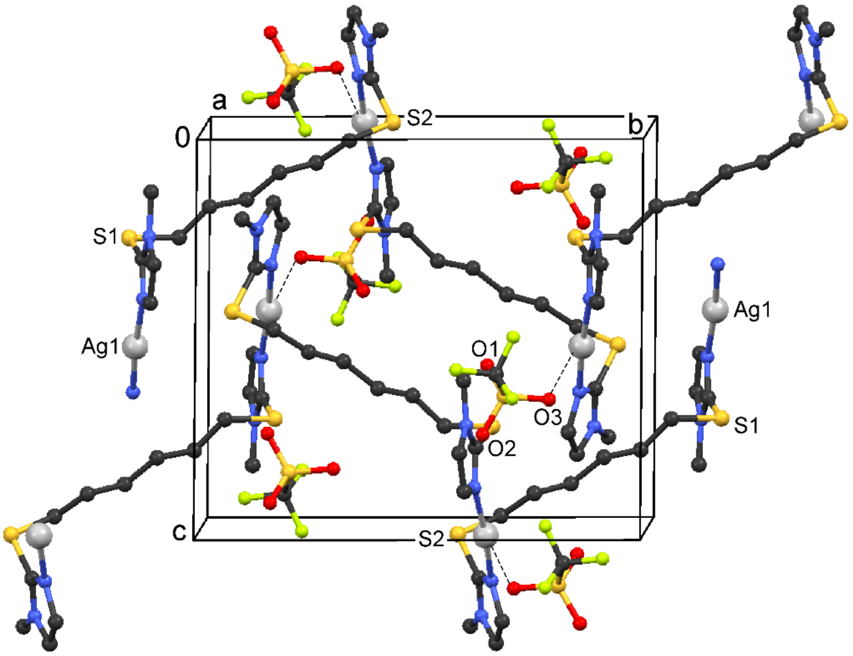


Figure 2. Packing and short contacts in the crystal structure of poly[silver(I)-μ-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] triflate] (**3b**)

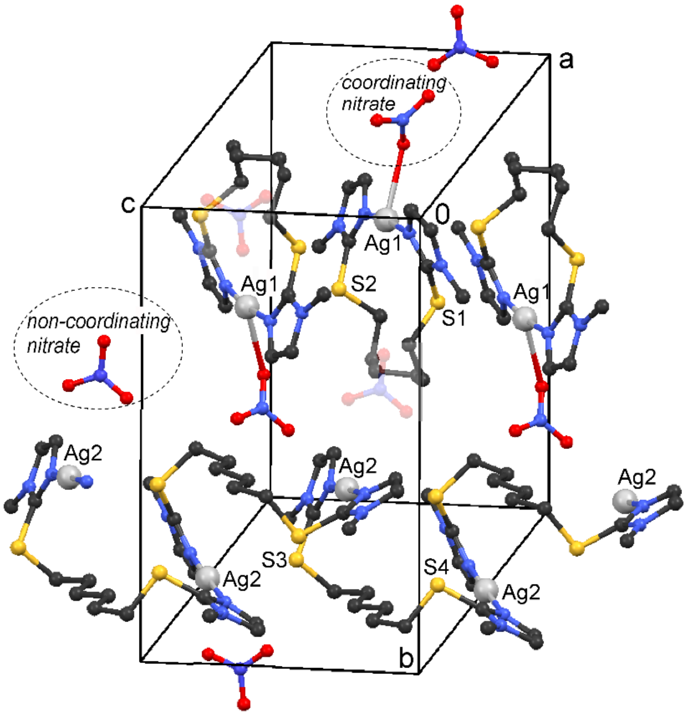


Figure 3. Linear and cyclic motifs in the crystal structure of poly[silver(I)-μ-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] nitrate] / *cyclo*-[1,6-bis(1-methylimidazol-2-ylthio)-κ^2*N*-hexane]nitratosilver(I) (**3c**)

	3a	**3b**	**3c**
Chemical formula	$C_{14}H_{22}AgN_4S_2\cdot F_6P$	$C_{14}H_{22}AgN_4S_2\cdot F_3CSO_3$	$C_{28}H_{44}Ag_2N_8S_4\cdot N_2O_6$
M_r	563.31	567.41	960.71
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
T (K)	176	173	193
a (Å)	11.4105 (3)	11.9969 (4)	24.495 (2)
b (Å)	14.6410 (4)	14.4345 (5)	15.9416 (14)
c (Å)	13.3257 (4)	13.4063 (4)	9.6366 (8)
β (°)	109.101 (1)	108.488 (1)	90.421 (3)
V (Å^3)	2103.6 (1)	2201.7 (2)	3762.9 (6)
Z	4	4	4
μ (mm^{-1})	1.29	1.25	1.32
Crystal size (mm)	0.17×0.11×0.09	0.17×0.12×0.10	0.16×0.09×0.06
Measured	36300	58340	26704
Independent	4124	4207	6271
Observed reflections	3700	3920	3783
R_{int}	0.033	0.030	0.091
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.611	0.589
$R_1(I > 2\sigma I)$	0.029	0.022	0.059
wR_2(all data)	0.070	0.055	0.140

S	1.07	1.06	1.02
Parameters	255	264	455
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.11, −0.66	0.64, −0.52	0.88, −0.51
CCDC no.	1577446	1577445	1577447

EXPERIMENTAL

Reagents and solvents were purchased from Sigma-Aldrich. NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Bruker Alpha FT instrument. Single crystal diffraction data were recorded with a Bruker D8 Quest Photon 100 diffractometer using MoKα radiation. Absorption corrections were applied (multi-scan). Structure solution and refinement was performed by direct methods with the program SHELXL-2014.[6] Visualization of the structures and measurements of distances and angles was performed with the program Mercury.[7] CCDC 1577445–1577447 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

1,6-Bis(1-methylimidazol-2-ylthio)hexane bis(hydrobromide) (1a). A solution of 1,6-dibromohexane (10.0 g, 41 mmol) in CH_2Cl_2 (15 mL) was added dropwise to methimazole (9.8 g, 86 mmol) in CH_2Cl_2 (100 mL). The mixture was stirred for 72 h, and the resulting colorless precipitate was collected. The product was washed with CH_2Cl_2 and vacuum-dried (yield: 14.6 g, 76%). Mp 185 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 1.31–1.36 (m, 4H), 1.45–1.55 (m, 4H), 3.15 (t, *J*=7.2 Hz, 4H), 3.80 (s, 6H), 7.77 (d, *J*=1.8 Hz, 2H), 7.83 (d, *J*=1.8 Hz, 2H); ^{13}C NMR (DMSO-*d*$_6$): δ 27.0, 29.0, 34.5, 35.0, 121.0, 125.3, 140.0; IR (neat): ν 3145, 3108, 2933, 2862, 2770, 2703, 1622, 1697, 1626, 1567, 1489, 1472, 1452, 1420, 1355, 1294, 1274, 1205, 1159, 1088, 1026, 914, 880, 774, 744, 667, 511, 459, 413 cm^{-1}.

1,6-Bis(1-methylimidazol-2-ylthio)hexane bis(hydrohexafluoridophosphate) (1b). The bromide **1a** (1.0 g, 2.1 mmol) was dissolved in H_2O (30 mL), NH_4PF_6 (0.69 g, 4.3 mmol) was added, and the resulting precipitate was stirred, filtered and washed with cold H_2O. Vacuum-drying gave a white solid (0.64 g, 58%). Mp 117 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 1.31–1.36 (m, 4H), 1.49–1.54 (m, 4H), 3.12 (t, *J*=7.2 Hz, 4H), 3.79 (s, 6H), 7.75 (d, *J*=2.0 Hz, 2H), 7.80 (d, *J*=2.0 Hz, 2H); ^{13}C NMR (DMSO-*d*$_6$): δ 27.0, 29.0, 34.4, 35.0, 121.2, 125.3, 140.0; IR (neat): ν 3323, 3185, 3160, 1626, 1580, 1496, 1473, 1436, 1424, 1357, 1298, 1276, m1207, 1159, 1098, 870, 823, 761, 736, 695, 662, 606, 554, 510, 471, 458 cm^{-1}.

1,6-Bis(1-methylimidazol-2-ylthio)hexane (2). The bromide **1a** (5.0 g, 11 mmol) was dissolved in H_2O (50 mL), $NaHCO_3$ (1.87 g, 22 mmol) was added, and the mixture was stirred until the evolution of gas ceased and a second liquid phase was formed. The mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic phases were dried over Na_2SO_4 and taken to dryness under reduced pressure. The liquid residue crystallized on vacuum-drying (1.24 g, 94%). Mp 56 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 1.30–1.35 (m, 4H), 1.48–1.55 (m, 4H), 2.94 (t, *J*=7.2 Hz, 4H), 3.56 (s, 6H), 6.91 (d, *J*=1.3 Hz, 2H), 7.21 (d, *J*=1.3 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 27.3, 29.1, 32.8, 33.3, 123.0, 128.4, 140.1; IR (neat): ν 3119, 3096, 3007, 2966, 2926, 2858, 1678, 1591, 1517, 1460, 1437, 1416, 1390, 1376, 1358, 1332, 1282, 1191, 1148, 1122, 1087, 1034, 958, 915, 785, 752, 738, 694, 679, 509, 460, 412 cm^{-1}.

Poly[silver(I)-*μ*-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] hexafluoridophosphate] (3a). Ag_2O (50 mg, 0.24 mmol) was added to a solution of hexafluoridophosphate **1b** (0.30 g, 0.50 mmol) in MeOH (10 mL). The suspension was stirred at room temperature protected from light for 18 h. The resulting precipitate was filtered, washed with MeOH (5 mL) and Et_2O (3×2 mL) and vacuum-dried. Yield: 115 mg (86%). Single crystals were obtained from acetone/H_2O. Mp 198 °C. ^{1}H NMR (DMSO-d_6): δ 1.43–1.54 (m, 8H), 2.97 (t, *J*=5.6 Hz, 4H), 3.83 (s, 6H), 7.26 (d, *J*=1.5 Hz, 2H), 7.63 (d, *J*=1.5 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 25.5, 27.3, 34.6, 34.8, 125.7, 129.7, 140.8; IR (neat): ν 3158, 3136, 2936, 2864, 1528, 1464, 1414, 1341, 1286, 1158, 1088, 875, 832, 765, 740, 728, 688, 556, 507, 468, 433 cm^{-1}.

Poly[silver(I)-*μ*-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] triflate] (3b). AgOTf (0.41 g, 1.6 mmol) was added to a solution of base **2** (0.5 g, 1.6 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at room temperature protected from light for 24 h. The solvent was removed under reduced pressure, and the liquid residue crystallized on vacuum-drying. Yield: 0.73 g (81%). Single crystals were obtained by diffusion of Et_2O into CH_2Cl_2. Mp 167 °C. ^{1}H NMR (DMSO-d_6): δ 1.46 (m, 8H), 2.97 (t, *J*=5.6 Hz, 4H), 3.83 (s, 6H), 7.26 (d, *J*=1.5 Hz, 2H), 7.62 (d, *J*=1.5 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 25.9, 27.8, 34.8, 120.7 (q, *J*=322 Hz), 125.6, 129.6, 140.8; IR (neat): ν 3151, 3122, 2943, 2927, 2885, 2847, 1532, 1465, 1437, 1416, 1361, 1342, 1254, 1221, 1185, 1155, 1027, 954, 902, 883, 840, 797, 770, 755, 735, 689, 635, 627, 571, 531, 516, 488, 433 cm^{-1}.

Poly[silver(I)-*μ*-[1,6-bis(1-methylimidazol-2-ylthio)-κ*N*-hexane] nitrate] / *cyclo*-[1,6-bis(1-methylimidazol-2-ylthio)-κ^2*N*-hexane]nitratosilver(I) (3c). A solution of $AgNO_3$ (0.55 g, 3.2 mmol) in H_2O (10 mL) was added to base **2** (1.0 g, 3.2 mmol) in EtOH (10 mL). The mixture was stirred for 1 h, and the solvent was removed under reduced pressure to give a colorless liquid which crystallized on vacuum-drying. Yield: 1.08 g (70%). Mp 54 °C. ^{1}H NMR (DMSO-d_6): δ 1.05–1.52 (m, 8H), 2.97 (t, *J*=5.6 Hz, 4H), 3.83 (s, 6H), 7.26 (d, *J*=1.5 Hz, 2H), 7.63 (d, *J*=1.5 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 25.8, 27.6, 34.7, 34.8, 125.7, 129.7, 140.7; IR (neat): ν 3513, 3102, 2929, 2916, 2853, 2408, 2361, 1746, 1662, 1525, 1461, 1409, 1322, 1276, 1195, 1148, 1097, 1084, 1042, 947, 922, 874, 827, 802, 776, 752, 740, 724, 687, 639, 627, 561, 522, 506, 455, 429 cm^{-1}.

REFERENCES

1. A. I. Siriwardana, I. R. Crossley, A. A. J. Torriero, I. M. Burgar, N. F. Dunlop, A. M. Bond, G. B.

Deacon, and D. R. MacFarlane, *J. Org. Chem.*, 2008, **73**, 4676.

2. F. Freeman, M. C. Keindl, H. N. Po, E. Brinkman, and J. A. Masse, *Synthesis*, 1989, 714.
3. C.-L. Chen, B.-S. Kang, and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3.
4. A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, and M. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155.
5. A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.
6. G. M. Sheldrick, *Acta Crystallogr.*, 2015, C**71**, 3.
7. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.