One-dimensional silver(I) chain of lacunary α-Keggin anions

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A novel chain-like silver polyoxotungstophosphate is formed when Ag^I metal centres, exhibiting an unusual eight-coordination fashion, bridge a monolacunary $[PW_{11}O_{39}]^{7-}$ anion to four bridging μ_2-oxygen atoms of a neighbouring lacunary α-Keggin anion.

Silver complexes of polyoxometalates have been the subject of much interest because of their potential applications as catalysts[1–3] and as structural building blocks in the preparation of new materials.[4–6] The first crystallographic description of this type of compounds was that of $[NBu_4]_4[Ag_2\{Mo_5O_{13}(OCH_3)_4(NO)\}_2]$,[7] closely followed by those of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$,[1] $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}(CH_3CN)_{17.3}(H_2O)_{1.5}$,[3] and of a family of one-dimensional chain-like materials containing the $[AgMo_8O_{26}Ag]^{2-}$ unit, such as $(^nBu_4N)_{2n}[Ag_2Mo_8O_{26}]_n$.[8] Silver salts of $[XW_{12}O_{40}]^{n-}$ (X = P or Si) have been employed in the synthesis of polyoxometalate nanowires,[4] and as templates in the isolation of silver nanoparticles.[5] $Ag_3PM_{12}O_{40}$ (M = W or Mo) was also used to prepare polyoxometalate monolayers.[6] We have been particularly interested in the synthesis of novel complexes with Keggin-type monolacunary polyoxometalates[9–11] and their use in the preparation of thin films[12] and as oxidative catalysts.[13] Here we wish to report the first member of a new family of monolacunary Keggin-type polyoxotungstates containing Ag^I metallic centres: $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]\cdot 8.25H_2O\cdot CH_3OH$.

The reaction of monolacunary $[PW_{11}O_{39}]^{7-}$ α-Keggin anions with Ag^I cations in aqueous solution led to the isolation of a new phase, isolated as very small needle-shaped single-crystals.† With the recent developments in area-detector technology of X-ray diffractometers, single-crystal diffraction data could be collected for this material and at low temperature (*ca.* 100 K), which allowed a sensible crystal solution and refinement in the acentric (and polar) $Pna2_1$ space group, leading to a formulation of the title material as $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]\cdot 8.25H_2O\cdot CH_3OH$.‡,§ A remarkable structural feature of this material is the presence of an anionic $[AgPW_{11}O_{39}]^{6-}$ unit, in which Ag^I cations physically occupy the vacant position of the lacunary α-Keggin anion (Fig. 1). This is fundamentally different from what was reported for $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$[1] and $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}(CH_3CN)_{17.3}(H_2O)_{1.5}$,[3] both containing a mixed Mo^{VI}/V^V complete Keggin anion, $[PMo_{10}V_2O_{40}]^{5-}$. The former compound, $[Ag_6(PMo_{10}V_2O_{40})]^+$ is described as a 3D macrocation, in which four crystallographically independent Ag^I moieties simply play the role of charge-balancing cations. The same occurs for the latter material, with the distinctiveness of the formation of $[Ag_6(PMo_{10}V_2O_{40})_2(CH_3CN)_{10}]^{4-}$ dimers with some Ag^I cations being coordinated to solvent molecules. Even though coordination to the lacunary position is very common among metal complexes with $[XW_{11}O_{39}]^{n-}$ anions (where X = P or Si), which may act as penta- or tetradentate ligands forming 1 : 1 or 1 : 2 complexes,[9] such feature is, to the best of our knowledge, unprecedented for Ag^I centres. We note that Ag^I metallic centres play the same role as charge-balancing cations in the title material, as a second, but only partially occupied (33.5%, see Experimental section‡), Ag(2) centre was found during the crystal refinement stages. Indeed, this Ag^I cation shares the same crystallographic region with a 66.5%-occupied K^+ [Ag(2)···K(4) of 1.42(2) Å] with the Ag···O distances to oxygen atoms belonging to neighbouring $[AgPW_{11}O_{39}]^{6-}$ units lying in the 2.37(2)–2.46(2) Å range.

For Ag(1), the Ag–O and *cis* O–Ag–O bond lengths and angles are found in the 2.39(2)–2.49(2) Å and 75.1(8)–78.3(8)° ranges, respectively. As shown in Fig. 1, the Ag(1) metallic centre appears raised from the plane defined by the four terminal oxygen atoms by approximately 1.15(1) Å, with Ag(1)···P(1) being 4.344(1) Å, and

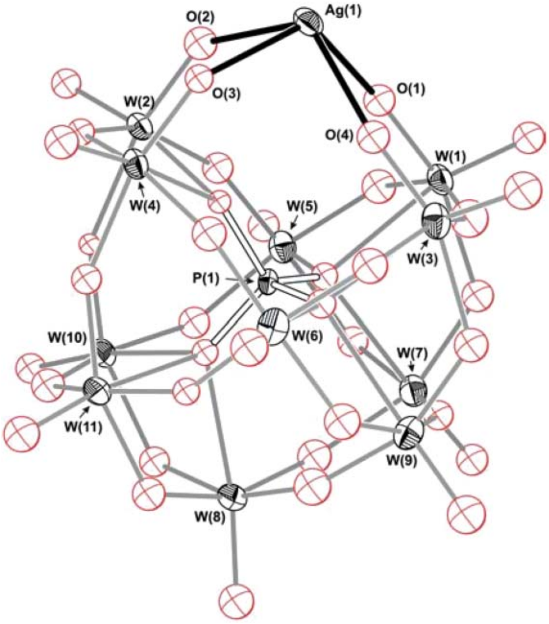

Fig. 1 Molecular structure of the anionic $[AgPW_{11}O_{39}]^{6-}$ building unit, represented with thermal ellipsoids for all W, Ag and P atoms (drawn at the 50% probability level). O atoms are represented as spheres with radius proportional to the refined U_{iso} for each atom. Selected bond lengths (Å): Ag(1)–O(1) 2.43(2), Ag(1)–O(2) 2.39(2), Ag(1)–O(3) 2.43(2), Ag(1)–O(4) 2.49(2). Selected bond angles (°): O(1)–Ag(1)–O(4) 76.7(7), O(2)–Ag(1)–O(1) 78.0(8), O(2)–Ag(1)–O(3) 78.3(8), O(2)–Ag(1)–O(4) 122.9(8), O(3)–Ag(1)–O(1) 123.9(8), O(3)–Ag(1)–O(4) 75.1(8).

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the shortest Ag(1)···W internuclear distance (within the same $[AgPW_{11}O_{39}]^{6-}$ unit) being of 3.816(1) Å [to W(2)]. The remaining geometrical aspects of the $\{WO_6\}$ distorted octahedra are typical of lacunary α-Keggin anions. The coordination sphere of Ag(1) can only be fully described once the crystal structure of the title material is taken into account. In reality, from a purely synthetic perspective, it is reasonable to assume that once the lacunary $[PW_{11}O_{39}]^{7-}$ α-Keggin anions are in the presence of Ag^I cations, $[AgPW_{11}O_{39}]^{6-}$ building units are formed and remain stable in solution (Fig. 2(a)). Crystallisation (induced by refrigeration)† leads to an ordered arrangement of these units in the solid state, in which the Ag^I lying inside the lacuna closely interact with four μ_2-oxygen atoms of a neighbouring lacunary α-Keggin anion, leading to the formation of a one-dimensional anionic $[AgPW_{11}O_{39}]_n^{6n-}$ chain running parallel to the *c*-axis of the unit cell (Fig. 2(b)). The coordination sphere of Ag(1), $\{AgO_8\}$, is thus best described as a highly distorted square antiprism (Fig. 2(c) and (d)). We note that these inter-unit Ag–O interactions are fairly long and distinct from one another, lying inside the 2.56(2)–3.00(2) Å range. This is also clearly reflected in the rather long distance of the Ag(1) centre to the average plane formed by O(14,15,20,37) atoms [*ca.* 2.03(1) Å, Fig. 2(d)].

Given the aforementioned geometrical features for these linkages, interactions between neighbouring $[AgPW_{11}O_{39}]^{6-}$ units are likely to be weak. This was investigated by collecting the solid-state MAS ^{31}P NMR spectrum of the as-prepared material isolated as single-crystals, which produced a single gaussian peak centred at *ca.* −11.0 ppm. After gentle mechanical grinding in a mortar for a couple of minutes, the MAS ^{31}P NMR spectrum changed, revealing the presence of a second, highly broad (indicating site distribution), peak centred at *ca.* −10.7 ppm. Assuming *a priori* the structural robustness of the polymer building unit, it is feasible to infer that mechanical grinding partially reverts the self-assembly process, presumably leading to isolated $[AgPW_{11}O_{39}]^{6-}$ anions (Fig. 2(a) and (b)).

The anionic polymeric moieties shown in Fig. 2(b) are unusual since, on the one hand, due to the symmetry criteria imposed by the polar and acentric $Pna2_1$ space group, the $[AgPW_{11}O_{39}]^{6-}$ building units inside the unit cell are orientated so to form helical chains. The refined Flack parameter [0.00(2)][14] suggests the presence of an untwinned (by inversion) single crystal and the correct choice of the direction of the polar axis of the structure. On the other hand, even though 1D structures have been reported for lanthanide complexes with lacunary Keggin anions, namely $H_2(NH_4)_{10}[Ce_2(BW_{11}O_{39})_2(H_2O)_6]\cdot 21H_2O$,[10] and $(NH_4)_5[Ln(SiW_{11}O_{39})(H_2O)_3]\cdot nH_2O$[15] (Ln = Ce or La), in these materials the linkups between units are significantly different from what is indeed observed in the material in study: in those cases, the lanthanide centres coordinate to four terminal oxygen atoms in the lacunary position and to terminal oxygen atoms of other neighbouring lacunary Keggin anions. Individual anionic $[AgPW_{11}O_{39}]_n^{6n-}$ chains close pack in the solid state distributed in a typical herringbone fashion (Fig. 3) and interacting with the various water molecules of crystallisation *via* O–H···O hydrogen bonds (not represented).

In summary, we have isolated the first monolacunary α-Keggin-type polyoxotungstate encapsulating Ag^I cations inside the lacuna.

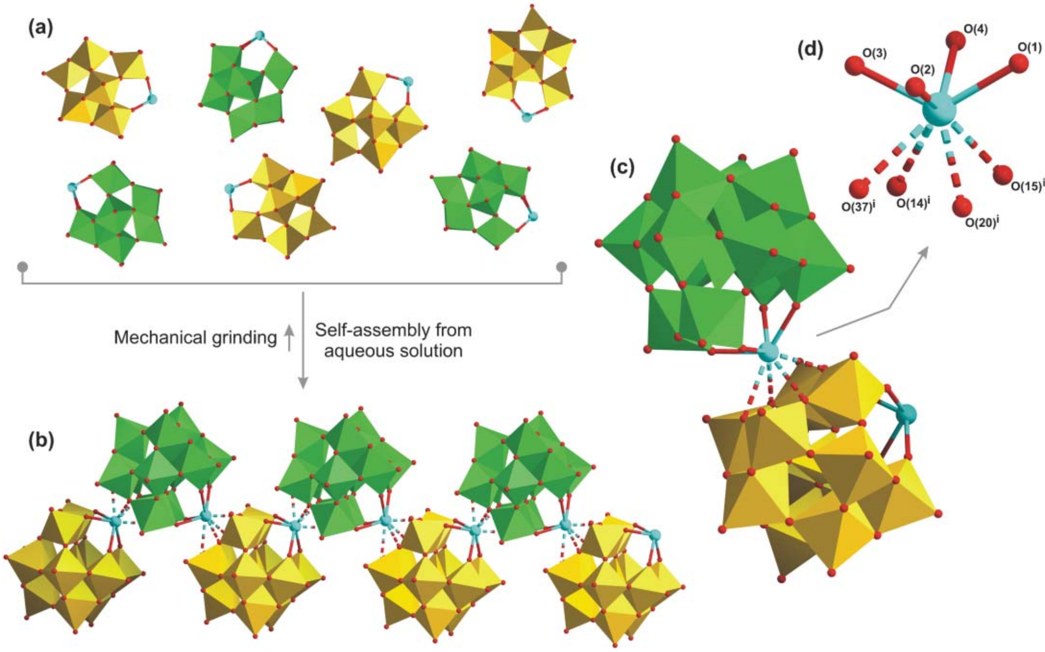

Fig. 2 (a) Schematic representation of the self-assembly process (from aqueous solution) of anionic $[AgPW_{11}O_{39}]^{6-}$ building units into a (b) one-dimensional anionic $[AgPW_{11}O_{39}]_n^{6n-}$ chain running along the [001] direction of the unit cell. (c and d) Detailed view of the highly distorted square antiprismatic coordination environment for the Ag(1) metallic centre which interconnects neighbouring $[PW_{11}O_{39}]^{7-}$ α-Keggin anions. Selected bond lengths (Å): Ag(1)–O(14)^i 2.72(2), Ag(1)–O(15)^i 2.56(2), Ag(1)–O(20)^i 2.80(2), Ag(1)–O(37)^i 3.00(2). Selected bond angles (°): O(14)^i–Ag(1)–O(15)^i 62.0(7), O(14)^i–Ag(1)–O(20)^i 72.1(6), O(14)^i–Ag(1)–O(37)^i 55.5(5), O(15)^i–Ag(1)–O(20)^i 59.9(5), O(15)^i–Ag(1)–O(37)^i 97.8(6), O(20)^i–Ag(1)–O(37)^i 54.3(5), O(1)–Ag(1)–O(14)^i 148.0(1), O(1)–Ag(1)–O(15)^i 86.3(8), O(1)–Ag(1)–O(20)^i 96.1(6), O(1)–Ag(1)–O(37)^i 139.9(7), O(2)–Ag(1)–O(14)^i 127.1(9), O(2)–Ag(1)–O(15)^i 136.5(8), O(2)–Ag(1)–O(20)^i 81.5(6), O(2)–Ag(1)–O(37)^i 71.8(6), O(3)–Ag(1)–O(14)^i 84.1(7), O(3)–Ag(1)–O(15)^i 141.3(8), O(3)–Ag(1)–O(20)^i 129.2(7), O(3)–Ag(1)–O(37)^i 75.1(6), O(4)–Ag(1)–O(14)^i 99.2(6), O(4)–Ag(1)–O(15)^i 91.5(6), O(4)–Ag(1)–O(20)^i 151.1(6), O(4)–Ag(1)–O(37)^i 142.5(6). Symmetry transformation used to generate equivalent atoms: (i) $1 - x, -y, -\frac{1}{2} + z$.

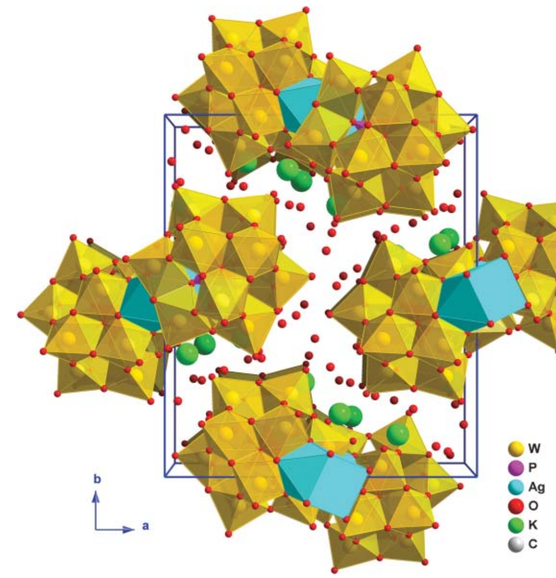

Fig. 3 Polyhedral representation of the crystal packing of $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]\cdot 8.25H_2O\cdot CH_3OH$ viewed in perspective along the [001]direction of the unit cell.

This metallic centre interacts in the solid-state with neighbouring $[AgPW_{11}O_{39}]^{6-}$ units to produce a one-dimensional, anionic $[AgPW_{11}O_{39}]_n^{6n-}$ chain. We are currently investigating the possibility of isolating other members of this new family of materials.

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Notes and references

† *Synthesis*: Chemicals were readily available from commercial sources and were used as received without further purification. $K_7[PW_{11}O_{39}]\cdot nH_2O$ was prepared by adaptation of the method of Haraguchi *et al.*[16] An aqueous solution of $K_7[PW_{11}O_{39}]\cdot nH_2O$ (0.1 mmol in *ca.* 5 cm^3 of water) was added to silver nitrate (0.17 g, 0.1 mmol) dissolved in *ca.* 5 cm^3 of distilled water, leading to the formation of a yellow precipitate which was filtered off. To the filtered mother-liquor 2 cm^3 of methanol were added and after refrigeration over a period of several days golden-brown crystals of the title compound were grown and manually harvested. Selected FT-IR data (from KBr disk; Aldrich 99%+): ν(W=O) at 952, ν(W–O–W) at 904, 858, 809 and 734 cm^{-1}, and ν(P–O) at 1085 and 1043 cm^{-1}.

‡ A suitable single-crystal of $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]\cdot 8.25H_2O\cdot CH_3OH$ (**I**), was mounted on a glass fibre.[17] Data were collected at 100(2) K (at the Unidade de Raios-X, RIAIDT, University of Santiago de Compostela, Spain) on a Bruker SMART 1000 CCD diffractometer (Mo-Kα graphite-monochromated radiation, λ = 0.7107 Å), controlled by the SMART software package.[18] Images were processed using the SAINTPlus software package,[19] and data were corrected for absorption with SADABS.[20] The structure was solved by the direct methods of SHELXS-97,[21] and refined by full-matrix least squares on F^2 using SHELXL-97.[22] Non-hydrogen atoms have been directly located from difference Fourier maps but only the heaviest elements (P, Ag, W and some K) could be refined with sensible anisotropic displacement parameters. When refined anisotropically, the majority of the oxygen atoms belonging to the $[AgPW_{11}O_{39}]^{6-}$ units gave large tensors in more than one direction, indicating thermal disorder. Instead, these atoms have been refined using independent isotropic displacement parameters. One crystallographic region was found to be partially occupied by K$^+$ and Ag$^+$ cations (which do not share the same crystal coordinates). These cations have been refined with a linked free variable for the site occupancies which ultimately refined to *ca.* 66.5% and 33.5 for K$^+$ and Ag$^+$, respectively. Only the former cation could be reasonably refined using anisotropic displacement parameters. The structure contains a total of 12 crystallographic independent water molecules of crystallisation, all directly located from difference Fourier maps whose site occupancy add up to 8.25 molecules per formula unit (individual site occupancies were found from unrestrained refinement). These molecules were refined using a common isotropic displacement parameter.

Hydrogen atoms associated with the charge-balancing H$^+$, the water molecules of crystallisation and the methanol molecule could not be located from difference Fourier maps and no attempt was made to place these in calculated positions. However, these hydrogen atoms have been added to the empirical formula of the compound. The last difference Fourier map synthesis showed the highest peak (3.646 e Å^{-3}) and the deepest hole (−3.451 e Å^{-3}) located at 0.20 Å from O(6W) and 0.89 Å from W(4), respectively.

§ *Crystal data*: $CH_{22.50}Ag_{1.34}K_{3.67}O_{48.25}PW_{11}$ (including 22.5 H-atoms from the charge balancing H$^+$, water molecules of crystallisation and methanol molecules), M = 3147.32, orthorhombic, space group $Pna2_1$, Z = 4, a = 17.746(3), b = 20.587(4), c = 13.232(3) Å, V = 4834.1(16) Å^3, μ(Mo-Kα) = 27.042 mm^{-1}, D_c = 4.324 g cm^{-3}, brown prisms with crystal size of 0.17 × 0.05 × 0.04 mm. Of a total of 44989 reflections collected, 11 355 were independent (R_{int} = 0.1000). Final $R1$ = 0.0604 [$I > 2\sigma(I)$] and $wR2$ = 0.1538 (all data). Data completeness to theta = 28.25°, 98.0%. A total number of 5236 Friedel pairs have been used in the refinement as independent data. CCDC 605319. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605973b

1 F. X. Liu, C. Marchal-Roch, P. Bouchard, J. Marrot, J. P. Simonato, G. Herve and F. Secheresse, *Inorg. Chem.*, 2004, **43**, 2240–2242.
2 J. S. Yadav, B. V. S. Reddy, P. Sridhar, J. S. S. Reddy, K. Nagaiah, N. Lingaiah and P. S. Saiprasad, *Eur. J. Org. Chem.*, 2004, 552–557.
3 J. T. Rhule, W. A. Neiwert, K. I. Hardcastle, B. T. Do and C. L. Hill, *J. Am. Chem. Soc.*, 2001, **123**, 12101–12102.
4 Z. H. Kang, E. Wang, M. Jiang and S. Y. Lian, *Nanotechnology*, 2004, **15**, 55–58.
5 S. Mandal, D. Rautaray and M. Sastry, *J. Mater. Chem.*, 2003, **13**, 3002–3005; A. Troupis, A. Hiskia and E. Papaconstantinou, *Angew. Chem., Int. Ed.*, 2002, **41**, 1911–1914.
6 M. Kinne and M. A. Barteau, *Surf. Sci.*, 2000, **447**, 105–111.
7 R. Villanneau, A. Proust, F. Robert and P. Gouzerh, *Chem. Commun.*, 1998, 1491–1492.
8 H. Abbas, A. L. Pickering, D. L. Long, P. Kogerler and L. Cronin, *Chem.–Eur. J.*, 2005, **11**, 1071–1078.
9 A. M. V. Cavaleiro, J. Jesus and H. I. S. Nogueira, in *Metal Clusters in Chemistry*, ed. P. Braunstein, P. Raithby and L. Oro, 1999, vol. 1, p. 442.
10 F. L. Sousa, F. A. A. Paz, C. Granadeiro, A. M. V. Cavaleiro, J. Rocha, J. Klinowski and H. I. S. Nogueira, *Inorg. Chem. Commun.*, 2005, **8**, 924–927.
11 F. L. Sousa, F. A. A. Paz, A. M. V. Cavaleiro, J. Klinowski and H. I. S. Nogueira, *Chem. Commun.*, 2004, 2656–2657.
12 F. L. Sousa, A. S. Ferreira, R. A. S. Ferreira, A. M. V. Cavaleiro, L. D. Carlos, H. I. S. Nogueira and T. Trindade, *J. Alloys Compd.*, 2004, **374**, 371–376; F. L. Sousa, A. Ferreira, R. A. S. Ferreira, A. M. V. Cavaleiro, L. D. Carlos, H. I. S. Nogueira, J. Rocha and T. Trindade, *J. Nanosci. Nanotechnol.*, 2004, **4**, 214–220.
13 W. P. Griffith, N. Morley-Smith, H. I. S. Nogueira, A. G. F. Shoair, M. Suriaatmaja, A. J. P. White and D. J. Williams, *J. Organomet. Chem.*, 2000, **607**, 146–155; N. M. Gresley, W. P. Griffith, A. C. Laemmel, H. I. S. Nogueira and B. C. Parkin, *J. Mol. Catal. A: Chem.*, 1997, **117**, 185–198; W. P. Griffith, R. G. H. Moreea and H. I. S. Nogueira, *Polyhedron*, 1996, **15**, 3493–3500.
14 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876–881.
15 M. Sadakane, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed.*, 2000, **39**, 2914–2916.
16 N. Haraguchi, Y. Okaue, T. Isobe and Y. Matsuda, *Inorg. Chem.*, 1994, **33**, 1015–1020.
17 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615–619.
18 SMART, *Bruker Molecular Analysis Research Tool v 5.054©*, Bruker AXS, Madison, WI, USA, 1997–98.
19 SAINTPlus, *Data Reduction and Correction Program v. 6.01©*, Bruker AXS, Madison, WI, USA, 1997–98.
20 G. M. Sheldrick, *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, USA, 1998.
21 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, 1997.
22 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.