Sulfimidation of thioether groups - a versatile method for modifying and linking thia/oxa crowns

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Citation: ELSEGOOD, M.R.J., KELLY, P.F., REID, G. ... et al., 2008. Sulfimidation of thioether groups - a versatile method for modifying and linking thia/oxa crowns. Dalton Transactions, 37, pp. 5076 - 5082.

Additional Information:

- This article was published in the journal, Dalton Transactions [© Royal Society of Chemistry] and the definitive version is available at: http://dx.doi.org/10.1039/b802903b

Metadata Record: https://dspace.lboro.ac.uk/2134/15614

Version: Accepted for publication

Publisher: © The Royal Society of Chemistry

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Received (in XXX, XXX) 1st January 2007, Accepted 1st January 2007
DOI: 10.1039/b000000x

Reaction of the mixed thioether/ether crowns [9]aneO2S 1, [12]aneO3S 2 and [18]aneO2S2 3 with one mol. equiv. of the aminating agent MSH (α-mesitylsulfonylhydroxylamine) in Et2O results in the formation of the mono-sulfimidated systems [[9]aneO2(S=NH2)]+ 1a, [[12]aneO3(S=NH2)]+ 2a and [[18]aneO2S(S=NH2)]+ 3a, while using two mol. equivalents of MSH with 3 gives the disulfimidium cation [[18]aneO2(S=NH2)2]2+. All of these species have been isolated in good yields as the [mesSO3]− salts and can be readily converted readily to the [BPh4]− salts by metathesis with Na[BPh4]. Treatment of 1a or 2a with lithium diisopropylamide (LDA) and N-bromosuccinimide (NBS) at −78°C, followed by addition of a further equivalent of the parent thia/oxa crown, gives monocationic N-bridged sulfimide bicyclic compounds (4 and 5 respectively), in which the crowns are linked by the sulfimide nitrogen. Reaction of 3a with LDA and NBS leads to formation of the {([18]aneO2S2)N}+ cation 6 which exhibits an intramolecular S–N–S bridge. Crystallographic studies on representative examples of each compound type are described, together with their spectroscopic properties.

Introduction

The importance of crown ether systems systems to all areas of the chemical community continues to grow.1 Their significance stems from the range of properties they display (not the least of which is their ability to encapsulate metal cations) and has inspired the preparation of a wide range of examples of derivatised versions of archetypal crowns such as 18-crown-6.2 These are generally prepared through modification of the carbon backbones via incorporation of functionalised groups into the macrocycle. Although this can involve a range of different groups, and the resulting products can, in turn, react to derivatisate the systems still further, in all such cases the variation upon the basic crown ether unit is brought about by modification to the carbon backbone prior to cyclisation. This is because the inertness of both the backbone, and of the oxygen atoms, precludes derivatisation post ring closure.

Mixed thia/oxa crowns have been studied widely, again, mainly due to their ability to encapsulate metal cations. Thus the transition metal chemistry of [18]aneO3S and [18]aneO2S2 (3) (and, indeed, of the the Se/O and Te/O analogues of the former) has been explored extensively by one of the authors (GR).2 In contrast to the crowns containing only oxa-ether units, these mixed systems do have the potential to undergo derivatisation thanks to the presence of the more reactive thia-ether centre(s). Despite this clear possibility, post ring-closure modification of these types of macrocycles is still poorly documented. In one example, Dann et al3 reported oxidised versions of 3, formed by reacting the ‘free’ macrocycle with Chloramine-T and with hydrogen peroxide, generating [18]aneO2S(NTs)2 and [18]aneO2S(O)2 respectively. Some subsequent work on this sulfoxide was reported,4 as were studies into examples of thia-crowns bearing S=O units,5 but until a recent preliminary report on our part, no examples were known of systems wherein this methodology had been used to extend functional derivatisation of crowns.

In that preliminary report we showed that reaction of [18]aneO2S with the aminating agent MSH resulted in the formation of the sulfimidium cation, [[18]aneO2(S=NH2)]+. (Scheme 1).6 Deprotonation and bromination, using, consecutively, lithium diisopropylamide (LDA) and N-bromosuccinimide (NBS), allowed the in situ generation of [18]aneO3(S=NBr). The known temperature-sensitive nature of dialkylsulfimides necessitated the one-pot reaction be carried out at low temperature (−78°C) and the product reacted immediately, in this case with the parent crown. This resulted in the linked crown system {[([18]aneO2S2)2N]}+, in which the two crowns are joined via a sulfimide nitrogen. Despite the additional charge on the linked crowns imparted by the S–N–S bridge, importantly we were also able to demonstrate that the molecule was still able to accommodate a sodium cation bound via the ether O atoms.

The aforementioned report thus confirmed the viability of an entirely new class of reaction within crown ether chemistry, namely significant post ring-closure derivatisation. Here we demonstrate that this technique is applicable to a range of other ring systems and, in addition, that within the dithiacrown [18]aneO2S intramolecular sulfimidation is also possible.

Experimental

Instrumentation and conditions

Infrared spectra were recorded as pressed KBr pellets over the range 4000-200 cm−1 on a Perkin-Elmer System 2000 Fourier-
transform spectrometer, $^1$H (400 MHz) and $^{13}$C($^1$H) NMR spectra (100 MHz) on a Bruker DPX-400 FT spectrometer with chemical shifts in ppm to high frequency of SiMe$_3$ and coupling constants (J) in Hz. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry; FAB mass spectra were recorded on a JEOL SX102 mass spectrometer, ES$^-$ and ES$^+$ mass spectra (MeCN solution) were recorded using a VG Biotech platform or carried out by the EPSRC Mass Spectrometry Service at the University of Wales, Swansea.

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and appropriately dried solvents. [9]aneO$_2$S and [18]aneO$_2$S$_2$ were prepared via the literature procedure, and [12]aneO$_2$S was prepared using a similar method. $^7$O-mesitylsulfonylhydroxylamine (MSH) was prepared by the literature route,\(^8\) while lithium diisopropylamidine (LDA) and N-bromosuccinimide (NBS) were used as received (Aldrich).

SAFETY NOTE!: MSH can spontaneously (and unpredictably) decompose, resulting in an explosive pressure change. Samples should be kept in small amounts in loosely sealed containers, thereby minimising the risks should decomposition occur.

Preparations

Reactions of [9]aneO$_2$S (1)

[1a][mesSO$_3$]: [9]aneO$_2$S (1.0 g, 6.75 mmol) was dissolved in Et$_2$O (15 cm$^3$), and MSH (1.82 g, 8.43 mmol) added as a solid in several portions. The mixture was stirred overnight, after which the white solid produced was filtered, washed with further Et$_2$O (2 x 25 cm$^3$) and dried in vacuo. Yield: 2.13 g (87%).

Found: C, 49.39; H, 6.95; N, 3.48. $^{13}$C$_{30}$H$_{34}$O$_2$SN requires C, 71.99; H, 6.81; N, 3.45. $^1$H NMR (d$_6$-DMSO) $\delta_H = 6.72$ (s, 2H, Ar-$H$), 6.30 (br s, 2H, S=NH$_2$), 3.30-4.11 (m, 12H, CH$_2$), 2.56 (s, 6H, 2 x CH$_3$), 2.14 (s, 3H, 1 x CH$_3$). $^{13}$C NMR (CDCl$_3$) $\delta_C = 139.0, 137.2$ (quaternary Ar-$C$), 130.8 (2 x Ar-$CH$), 71.3, 70.3 (OCH$_2$), 48.3 (CH$_2$SNH$_2$), 23.0 (2 x CH$_3$). FAB MS (3-nitrobenzyl alcohol): $m/z = 164.0$ (C$_{21}$H$_{37}$O$_7$S$_3$N requires 164.2).

[1a][BPh$_4$]: [1a][mesSO$_3$] (0.52 g, 1.43 mmol) was dissolved in MeOH (10 cm$^3$). Na[BPh$_4$] (0.61 g, 1.79 mmol) was dissolved separately in MeOH (5 cm$^3$) and added dropwise to the stirring crown solution. After stirring for 3 h, the resulting white precipitate was filtered, the solid recrystallised from CH$_2$Cl$_2$/Et$_2$O, refiltered and dried in vacuo. Yield: 0.59 g (85%).

Found: C, 71.34; H, 6.68; N, 2.62. $^{13}$C$_{30}$H$_{34}$O$_2$SNB.0.25CH$_2$Cl$_2$ (504.7) requires C, 71.99; H, 6.89; N, 2.78%. $^1$H NMR (d$_6$-DMSO) $\delta_H = 7.21-6.82$ (br m, 20H, BPh$_4$ Ar-$CH_2$), 3.39-4.15 (m, 12H, CH$_2$). $^{13}$C NMR (d$_6$-DMSO) $\delta_C = 163.5$ (1:1:1

Reactions of [12]aneO$_2$S$_2$ (2)

These were prepared using an anlogous method to those of 1.

[2a][mesSO$_3$]. Yield: 79%. Found: C, 49.08; H, 6.62; N, 3.30. $^{13}$C$_{14}$H$_{29}$O$_2$SN requires C, 50.10; H, 7.17; N, 3.44%. $^1$H NMR (d$_6$-DMSO) $\delta_H = 6.78$ (s, 2H, Ar-$H$), 6.04 (s, 2H, NH$_2$), 3.37-4.00 (m, 16H, $\delta_C = 142.2, 136.6, 135.9$ (quaternary Ar-$C$), 129.9 (Ar-$CH$), 70.0, 69.6, 63.8 (OCH$_2$), 49.0 (CH$_2$SNH$_2$), 22.7 (2 x CH$_3$), 20.3 (1 x CH$_3$). FAB MS (3-nitrobenzyl alcohol): $m/z = 208.0$ (C$_{21}$H$_{37}$O$_7$S$_3$N requires 208.3).

[2a][BPh$_4$] Yield: 69%. Found: C, 70.49; H, 7.01; N, 2.59. $^{13}$C$_{32}$H$_{34}$O$_2$SNB.0.25CH$_2$Cl$_2$ requires C, 70.59; H, 7.03; N, 2.55%. $^1$H NMR (d$_6$-DMSO) $\delta_H = 7.18-6.80$ (br m, 20H, BPh$_4$ Ar-$CH_2$), 3.39-4.02 (m, 16H, CH$_2$). $^{13}$C NMR (d$_6$-DMSO) requires C, 70.1, 69.7, 63.8 (OCH$_2$). FAB MS (3-nitrobenzyl alcohol): $m/z = 208.0$ (C$_{21}$H$_{37}$O$_7$S$_3$N requires 208.3).

Reactions of [18]aneO$_2$S$_2$ (3)

[3a][mesSO$_3$]: [18]aneO$_2$S$_2$ (0.750 g, 2.53 mmol) was dissolved in CH$_2$Cl$_2$/MeOH (1:1, 25 cm$^3$) separately. MSH (0.545 g, 2.53 mmol) was dissolved in CH$_2$Cl$_2$ and added dropwise to the stirring thiacrown solution. After stirring overnight, the solution was reduced to ca. 2-3 cm$^3$, after which Et$_2$O (60 cm$^3$) was added and the resulting white solid filtered and dried in vacuo. Yield: 0.799 g (62%).

Found: C, 48.29; H, 6.81; N, 3.45. $^{13}$C$_{12}$H$_{26}$S$_2$O$_4$N$_2$ requires C, 47.89; H, 7.09; N, 2.63%. $^1$H NMR (d$_6$-DMSO) $\delta_H = 6.78$ (s, 2H, Ar-$CH_2$), 6.04 (s, 2H, NH$_2$), 3.37-5.00 (m, 16H, CH$_2$), 2.52 (s, 6H, 2 x Ar-$CH_3$), 2.18 (s, 3H, Ar-$CH_3$). ES$^-$ MS (MeCN): $m/z = 312.5$ (C$_{10}$H$_{14}$NO$_2$S$_2$ requires 312.5).

[3a][BPh$_4$]: [[18]aneO$_2$S$_2$(NH$_2$)$_2$][MSH]$_2$ (0.529 g, 0.73 mmol), was dissolved in MeOH (10 cm$^3$). Separately, Na[BPh$_4$] (0.250 g, 0.75 mmol) was dissolved in MeOH (5 cm$^3$) and added dropwise to the stirring sulfimide solution. A bright white solid appeared almost immediately, the mixture was allowed to stir for ca. 1 h, after which the solid was filtered and dried in vacuo. Yield: 0.395 g (86%).

Found: C, 67.64; H, 5.24; N, 1.82; $^{13}$C$_{10}$H$_{16}$BO$_2$N$_2$ requires C, 68.45; H, 7.34; N, 2.22%. $^1$H NMR (d$_6$-DMSO) $\delta_H = 7.40-6.82$ (br m, 20H, BPh$_4$ Ar-$CH_2$), 3.43-4.05 (m, 24H, CH$_2$). ES$^-$ MS (MeCN): $m/z = 312.5$ (C$_{10}$H$_{14}$NO$_2$S$_2$ requires 312.5).
[3b][mesSO3]4 was prepared using the same method as used for [4b][mesSO4]4 except that 2.25 equivalents of MSH were employed. Yield: 0.834 g (71%). Found: C, 48.36; H, 6.84; N, 3.78. C30H38O10S2N2⋅0.25CH2Cl2 requires C, 48.56; H, 6.80; N, 3.74%. IR υmax/cm−1: 3498, 3205, 2935, 1455, 1208, 1179, 1089, 1016, 858, 682, 549. 1H NMR (d6-DMSO): δH = 6.77 (s, 4H, Ar–C–H), 3.36–4.08 (m, 24H, CH2), 2.51 (s, 12H, CH3), 2.18 (s, 6H, CH3). 13C{1H} NMR (d6-DMSO): δC = 142.4, 136.5, 135.9 (quaternary Ar), 129.9 (Ar–C–H), 69.1, 69.0, 62.1 (OCH2), 47.5 (SCH2), 22.7 (2 CH3), 20.3 (1 CH3). FAB MS: m/z = 328.5 (C12H26S2O4N2 requires 328.5).

[3b][BPh4]2 was prepared by metathesis of [3a][mesSO4]4 with Na[BPh4] in analogous manner to salts of [3a][BPh4]. Yield: 0.415 g (90%). Found: C, 73.11; H, 6.99; N, 3.01. C69H67B2N2O4S2 requires C, 73.34; H, 7.26; N, 3.74%. IR υmax/cm−1: 3340, 2926, 2871, 1578, 1478, 1426, 1391, 1203, 1153, 1087, 940, 927, 858, 736, 707. 1H NMR (d6-DMSO): δH = 7.40–6.72 (br m, 40H, Ar–H), 3.20–3.98 (m, 24H, CH2). 13C{1H} NMR (d6-DMSO): δC = 164.1–162.6 (1:1:1:1 q, BPh4, ipso–C), 135.5, 125.3, 121.5 (Ar–C), 69.1, 62.1 (OCH2), 47.6 (H,N;SCH2). ES+ MS (MeCN): m/z = 328.5 (C12H26S2O4N2 requires 328.5).

X-Ray Crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 1. Data for [2a][BPh4] and [6][BPh4] were collected using a Bruker AXS SMART 1000 CCD area-detector diffractometer using sealed-tube graphite-monochromated Mo–Kα radiation and narrow frame exposures (0.3°). Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. All structures were solved by direct methods and refined on F2 values for all unique data by full-matrix least-squares.

Data for [3b][BPh4], [4b][BPh4] and [5][BPh4] were collected at 93 K by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optics) and Mercury CCD system. At least a full hemisphere of data was collected using ω or ω/φ scans. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were performed with full-matrix least-squares based on F2 by using the program SHELXTL.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC XXX XXXX. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).
Results and discussion

Reaction of crowns 1 and 2 with MSH in Et₂O results in rapid formation of the [mesSO₃]- salts of the aminated cations ([9]aneO₂S(NH₂)₂)⁺ 1a and ([12]aneO₂S(NH₂)₂)⁺ 2a, both of which precipitate from the ether as waxy, colourless solids (Scheme 2). In both cases, treatment of a methanolic solution of the material with a slight excess of Na[BPh₄] readily precipitates the corresponding [BPh₄]⁻ salts; these are more crystalline in nature and more readily handled. The sulfimidation and metathesis reactions proceed very cleanly, giving yields often in excess of 80%. Such results echo those we reported previously for the analogous reaction of the larger crown [18]aneO₅S,¹¹ thereby confirming that the reaction amplitudes are equally viable for all ring sizes.

Slow diffusion of Et₂O into a CDCl₃/dmso solution of [2a][BPh₄] generated crystals suitable for X-ray crystallography, and the latter technique confirms the expected structure (Fig.2). The S–N bond length in this case (1.635(14) Å) is in the range expected for sulfimidium units. The sulfimidium NH₂ unit is oriented exo to the ring, with no intra- or intermolecular H-bonding interactions to the ether O atoms evident.

Four resonances are seen in the solution ¹³C{¹H} NMR spectrum as expected (indicating the time-averaged symmetry in solution). Also as expected, within the spectrum of [2a][BPh₄] resonances associated with the SCH₂ carbon atom are most affected by the sulfimidation reaction, shifting substantially (by ca. 15 ppm) to high frequency – undoubtedly a consequence of the presence of formally S(IV) in the product (cf. S(II) in the parent crown).

The ease with which colourless, powdered [BPh₄]⁻ salts of 2a can be obtained by metathesis is a key to further reactivity. Not only are such compounds easier to handle than the corresponding [mesSO₃]⁻ salts, they also possess inert counterions; in our experience the [mesSO₃]⁻ is often less than reactivity. Not only are such compounds easier to handle than the corresponding [mesSO₃]⁻ salts, they also possess inert counterions; in our experience the [mesSO₃]⁻ is often less than reactivity.

In the case of 1a the corresponding [BPh₄]⁻ salts of 1a and 2a can be obtained by metathesis, is a key to further reactivity. Not only are such compounds easier to handle than the corresponding [mesSO₃]⁻ salts, they also possess inert counterions; in our experience the [mesSO₃]⁻ is often less than reactivity.

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The reaction of MSH with 3 also generates small amounts of the dication which results from oxidation of both ring sulfurs by MSH (as shown by mass spectrometry). This product may be prepared directly by reaction of [18]aneO₂S₂ with two equivalents of MSH, thereby generating {([18]aneO₂S₂(NH₂))⁺ (3a) in good yield (Scheme 2). As with the previous examples, addition of a slight excess of Na[BPh₄] to solutions of the [mesSO₃]⁻ salt results in the formation of [3a][BPh₄].

The latter was characterised by ¹H NMR and IR spectroscopy, ES+ MS and by microanalysis.

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bromination, the presence of the second thioether S atom enables the pendant S=NBr group to bridge across the molecule to form the \{\textit{[18]aneO_2S_2(NH_2)}\}_2^+ cation (6) via an intramolecular process. The spectroscopic features of this product parallel those for the other species in this work, with the ES' MS clearly showing the cation peak two mass units below that for the sulfidium cation \{\textit{[18]aneO_2S_2(NH_2)}\}_2^+ as expected. Crystals of [6][BPh_4] suitable for X-ray crystallography were grown by vapour diffusion of Et_2O into a CDCl_3/dmso solution. As Fig. 6 shows, the molecule forms a ‘basket’ shape, with the S=NS linkage bridged over the molecule. The nitrogen atom lies, on average 2.96 Å above the plane of the four oxygen atoms. The S=N bond lengths are very similar to each other [1.6465(17) and 1.6469(17) Å], and to those of other compounds containing ‘bridged’ sulfimide groups (vide supra). As Fig.6 highlights, the structure of the cation effectively consists of two, fused, 11-membered macrocycles, and it is worth noting that the individual macrocycles are themselves unique. The formation of this cation thus mirrors the formation of \{\textit{[9]aneS(NH_2)S_2(μ-N)}\}_2^+ in the reaction of \textit{[9]aneS} with excess MSH. In the latter case the formation of the transannular bridge was unexpected; it most likely occurs \textit{via} loss of [NH_4] from the initial product, \{\textit{[9]ane(SNH_2)_3}\}_2^+. In contrast, the formation of (6) is a rational synthesis that can be expected to be applicable to all crown systems bearing two sulfur atoms.

Conclusions

The formation of the simple sulfimidium derivatives of crowns 1-3 confirms the general viability of MSH as aminating agent for mixed thia/oxa crown systems. In conjunction with the preliminary work on reactions of \textit{[18]aneO_2S} it confirms that this constitutes a very effective new route for derivatisation of such crowns. The amenable bridging reactions have great potential for further utilisation, both from the point of view of the linked crown systems such as 4 and the intramolecularly bridged species such as 6. In terms of the former class of compound, it is clear that a wide variety of arrangements is possible, depending upon the crowns chosen as starting materials. The demonstrated ability of the larger ring systems to coordinate to a Na+ guest ion indicates that a significant new area of macrocyclic coordination chemistry should result from this approach. In terms of the intramolecular bridge motif it is clear that many variations on 6 should be possible. The presence of unique macrocycles within this structure also suggests that linking of the ends of chain thia/oxa ethers should be possible, with sulfimide nitrogen atoms forming bridges that generate new cyclic structures. Work on all these fascinating possibilities is underway.

Acknowledgements

This work was supported by the EPSRC (EP/C510100); we acknowledge the use of the EPSRC Mass Spectrometry Service at the University of Wales, Swansea.
Fig. 1 The structure of crowns 1-3.
Scheme 1 Linkage reactions of [18]aneO,S performed in our initial study.\textsuperscript{11}
Scheme 2  Sulfimidation reactions of 1-3 using MSH.
Scheme 3 Bridging reactions of crown sulfimidium salts. \(i\) LDA, NBS (-78°C) followed by addition of parent crown; \(ii\) LDA, NBS (-78°C).
Fig. 2 View of the structure of the cation within [2a][BPh₄] (in all figures crossed lined atoms are oxygen; most H atoms and any disorder are omitted for clarity).
Fig. 3 View of the structure of the cation in [4][BPh₄].
Fig. 4 X-ray crystal structure of the cation within [5][BPh₄]·CHCl₃ with atom numbering scheme.
Fig. 5 X-ray crystal structure of the dication within [3b][BPh$_4$]$_2$. 
Fig. 6 The X-ray crystal structure of one of the independent cations in [6][BPh₄].
Table 1. Crystallographic parameters$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>[2a][BPh₄]</th>
<th>[4][BPh₄]</th>
<th>[5][BPh₄]</th>
<th>[3b][BPh₄]₂</th>
<th>[6][BPh₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₃₂H₃₈BNO₃S</td>
<td>C₃₆H₄₄BNO₄S₂</td>
<td>C₄₁H₅₃BCl₃NO₆S₂</td>
<td>C₆₅H₇₅B₂N₂O₄S₂</td>
<td>C₅₈H₄₄BNO₄S₂</td>
</tr>
<tr>
<td>M</td>
<td>527.50</td>
<td>629.65</td>
<td>837.12</td>
<td>966.90</td>
<td>629.65</td>
</tr>
<tr>
<td>Crystal dimensions</td>
<td>0.23 × 0.21 × 0.13</td>
<td>0.15 × 0.15 × 0.15</td>
<td>0.13 × 0.03 × 0.03</td>
<td>0.10 × 0.10 × 0.08</td>
<td>0.65 × 0.32 × 0.12</td>
</tr>
<tr>
<td>Crystal morphology and colour</td>
<td>Block, colourless</td>
<td>Prism, colourless</td>
<td>Needle, colourless</td>
<td>Prism, colourless</td>
<td>Block, colourless</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic,</td>
</tr>
<tr>
<td>Space Group</td>
<td>P₂₁/n</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>P</td>
</tr>
<tr>
<td>a/Å</td>
<td>12.9446(3)</td>
<td>10.7110(11)</td>
<td>14.046(3)</td>
<td>12.854(3)</td>
<td>10.6347(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.0724(3)</td>
<td>27.872(2)</td>
<td>11.934(2)</td>
<td>12.341(3)</td>
<td>14.3378(7)</td>
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<tr>
<td>c/Å</td>
<td>18.1166(5)</td>
<td>11.0118(12)</td>
<td>25.163(6)</td>
<td>16.969(4)</td>
<td>22.9147(11)</td>
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<tr>
<td>α°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>78.764(2)</td>
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<tr>
<td>β°</td>
<td>98.060(4)</td>
<td>101.127(3)</td>
<td>98.981(6)</td>
<td>108.861(10)</td>
<td>81.805(2)</td>
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<tr>
<td>γ°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>V/Å³</td>
<td>2803.16(18)</td>
<td>3225.6(6)</td>
<td>4166.5(16)</td>
<td>2547.2(11)</td>
<td>3229.5(3)</td>
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<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
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<tr>
<td>µ/mm⁻¹</td>
<td>0.149</td>
<td>0.206</td>
<td>0.367</td>
<td>0.155</td>
<td>0.206</td>
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<tr>
<td>θ Range/°</td>
<td>1.82 to 30.56</td>
<td>2.02 to 25.35</td>
<td>1.89 to 25.38</td>
<td>2.54 to 25.35</td>
<td>0.91 to 28.90</td>
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<tr>
<td>Measured reflections</td>
<td>32677</td>
<td>20502</td>
<td>22437</td>
<td>14321</td>
<td>28453</td>
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<tr>
<td>Independent reflections</td>
<td>8548</td>
<td>5821</td>
<td>6919</td>
<td>4600</td>
<td>14816</td>
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<tr>
<td>Rₘᵢₜ</td>
<td>0.0260</td>
<td>0.0278</td>
<td>0.0567</td>
<td>0.1030</td>
<td>0.0238</td>
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<tr>
<td>R [Fᵡ² &gt; 2σ(Fᵡ²)]$^a$</td>
<td>0.0438</td>
<td>0.0375</td>
<td>0.1066</td>
<td>0.0849</td>
<td>0.0464</td>
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<tr>
<td>wR² [all data]$^b$</td>
<td>0.1206</td>
<td>0.0927</td>
<td>0.2964</td>
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<td>0.1268</td>
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<tr>
<td>Largest difference map features/eÅ³</td>
<td>0.524, −0.303</td>
<td>0.294, −0.315</td>
<td>0.889, −0.846</td>
<td>1.132, −0.361</td>
<td>0.570, −0.349</td>
</tr>
</tbody>
</table>

$^a$ R = Σ |Fₒ| - |F_c| / Σ |Fₒ|. $^b$ wR² = {Σ [w(Fₒ² − F_c²)]²} / {Σ [w(Fₒ²)]²}⁰.⁵