

# Structure of Bis(isobutylammonium) Selenite and its Sesquihydrate

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Isobutylammonium selenite and its sesquihydrate were obtained in low yields by reaction of selenium dioxide with the neat amine in the presence of small amounts of water. Both structures were determined by X-ray methods and proved to contain two independent formula units. In both cases, layer structures  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_2[\text{SeO}_3]$  are formed in which all NH hydrogen atoms act as single hydrogen bond donors, and all selenite oxygen atoms accept two hydrogen bonds. The layers contain six independent rings; the anhydrous substance has all rings of graph set  $R_4^3(10)$ , whereas the sesquihydrate has two each of  $R_4^4(12)$ ,  $R_4^2(8)$  and  $R_4^3(10)$ . The three independent water molecules of the sesquihydrate attach themselves to the layer structure by further classical hydrogen bonds to the selenite oxygen atoms.

**Key words:** Selenite, Ammonium, Hydrogen Bonds

## Introduction

There is considerable current interest in the structures of so-called “inorganic-organic hybrids”. Use of a standard search engine provides a large number of references, but these are mostly confined to compounds with organic substituents on an inorganic polymer. However, the concept has been used far more widely in some cases, *e. g.* in a recent example with cations derived from primary amines and anions based on metal complexes with carboxylate functions [1].

Our recent use of amines as reaction media for a variety of reactions such as formation of amine complexes of silver [2] led us to speculate that main group oxides might be dissolved in amines, if necessary in the presence of traces of water, to form salts of protonated amines with the corresponding oxoanions. Pilot experiments using selenium dioxide were conducted. The overall results were disappointing, in that few well-defined products could be isolated and these only in minimal yields. However, two of the products provided compensation in the form of interesting crystal structures, which are presented here: Bis(isobutylammonium) selenite **1** and its sesquihydrate. As far as we are aware, there have been few studies of selenites with protonated amines as cations; a search of the Cambridge Database [3] revealed just one such selenite, propane-1,2-diaminium selenite mono-

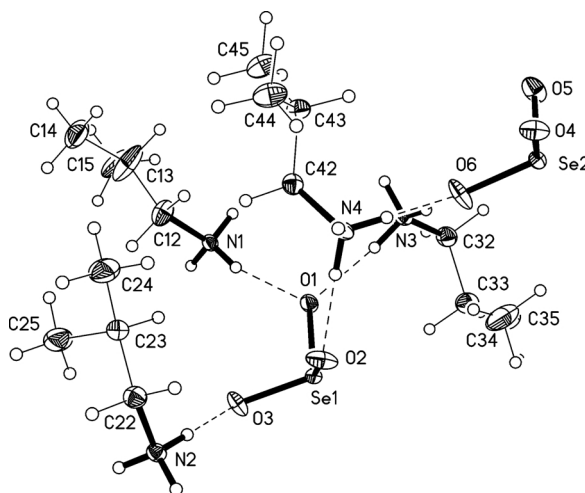


Fig. 1. The asymmetric unit (two formula units) of compound **1** in the crystal. Ellipsoids represent 30% probability levels. Dashed lines indicate hydrogen bonds.

hydrate [4], and one hydrogenselenite, 1-carbamoyl-guanidinium hydrogenselenite [5].

## Results and Discussion

The asymmetric unit of anhydrous **1** consists of two independent formula units (two selenite ions and four isobutylammonium ions); the space group is  $P2_1/c$  (Fig. 1). Bond lengths and angles may be regarded as

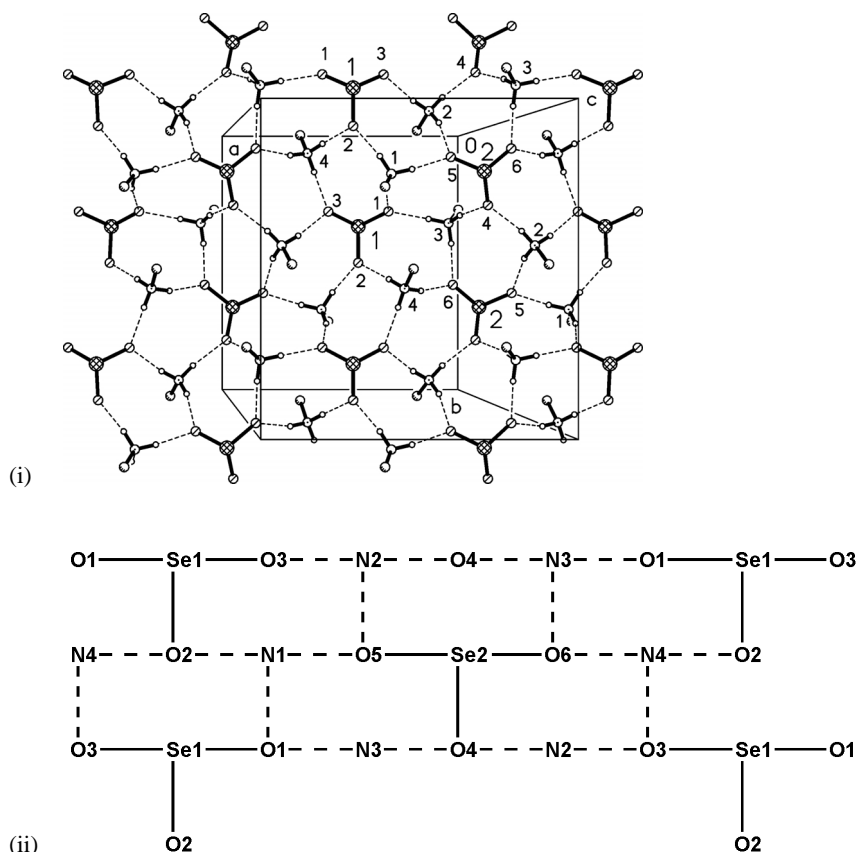


Fig. 2. Top: Packing diagram of **1** viewed perpendicular to the  $xy$  plane in the region  $z \approx 1/4$ . Classical hydrogen bonds are shown as dashed lines. Only the first carbon atoms of the isobutyl groups are shown. Numbering refers to Se atoms (large digits) or N and O atoms (small digits). Bottom: Schematic representation of the six independent rings (see text), corresponding to the top right of (i).

Table 1. Hydrogen bonds [ $\text{\AA}$  and  $^\circ$ ] for **1**.

| D-H...A                         | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------------------|--------|----------|----------|----------------------|
| N(1)-H(1B)...O(1)               | 0.91   | 1.82     | 2.695(3) | 159.2                |
| N(2)-H(2C)...O(3)               | 0.91   | 1.85     | 2.758(3) | 172.1                |
| N(3)-H(3A)...O(1)               | 0.91   | 1.85     | 2.754(3) | 174.0                |
| N(3)-H(3C)...O(6)               | 0.91   | 1.82     | 2.721(3) | 171.1                |
| N(4)-H(4A)...O(6)               | 0.91   | 1.80     | 2.686(3) | 165.0                |
| N(4)-H(4B)...O(2)               | 0.91   | 1.80     | 2.711(3) | 177.7                |
| N(1)-H(1A)...O(2) <sup>#1</sup> | 0.91   | 1.77     | 2.675(3) | 170.8                |
| N(2)-H(2A)...O(4) <sup>#1</sup> | 0.91   | 1.84     | 2.727(3) | 162.7                |
| N(1)-H(1C)...O(5) <sup>#2</sup> | 0.91   | 1.80     | 2.698(3) | 170.9                |
| N(3)-H(3B)...O(4) <sup>#2</sup> | 0.91   | 1.81     | 2.715(3) | 169.5                |
| N(2)-H(2B)...O(5) <sup>#3</sup> | 0.91   | 1.84     | 2.714(3) | 160.5                |
| N(4)-H(4C)...O(3) <sup>#4</sup> | 0.91   | 1.85     | 2.723(3) | 159.4                |

Symmetry transformations used to generate equivalent atoms:

<sup>#1</sup>  $-x+1, y-1/2, -z+1/2$ ; <sup>#2</sup>  $-x, y-1/2, -z+1/2$ ; <sup>#3</sup>  $x+1, y, z$ ;

<sup>#4</sup>  $-x+1, y+1/2, -z+1/2$ .

normal, *e. g.* Se-O 1.668–1.681(2)  $\text{\AA}$ , O-Se-O 102.2–103.8(1) $^\circ$ . The major interest attaches to the extended structure, which may be analysed in terms of classical hydrogen bonds (Table 1). All 12 hydrogen atoms of the  $\text{NH}_3$  groups act as single donors and each of the 6 selenite oxygen atoms accepts two hydrogen bonds. The overall effect is to form hydrophilic layers parallel

to the  $xy$  plane in the regions  $z \approx 1/4$  and  $3/4$  (Fig. 2); neighbouring layers are related by inversion symmetry. The hydrophobic isobutyl groups project into the space between the layers.

The packing within a layer may be analysed in terms of two topologically equivalent chains of residues parallel to the  $x$  axis (horizontal in Fig. 2i) connected by hydrogen bonds. The first chain has the repeat unit (excluding hydrogen atoms) O1-Se1-O3...N2...O4...N3 and the second O5-Se2-O6...N4...O2...N1. Further chains, antiparallel to the first two, are generated by the  $2_1$  screw axis. The chains are linked by the remaining selenite oxygen atoms and by further hydrogen bonds to form rings of graph set  $R_4^3(10)$  and connectivity O-Se-O...HNH...O...HNH. There are six independent rings of this type (*e. g.* the horizontal group of three rings at the top right-hand edge of Fig. 2 and those immediately below them; *cf.* the schematic view of Fig. 2ii).

It is noteworthy that the two independent formula units are topologically equivalent. Often, independent formula units can be distinguished in

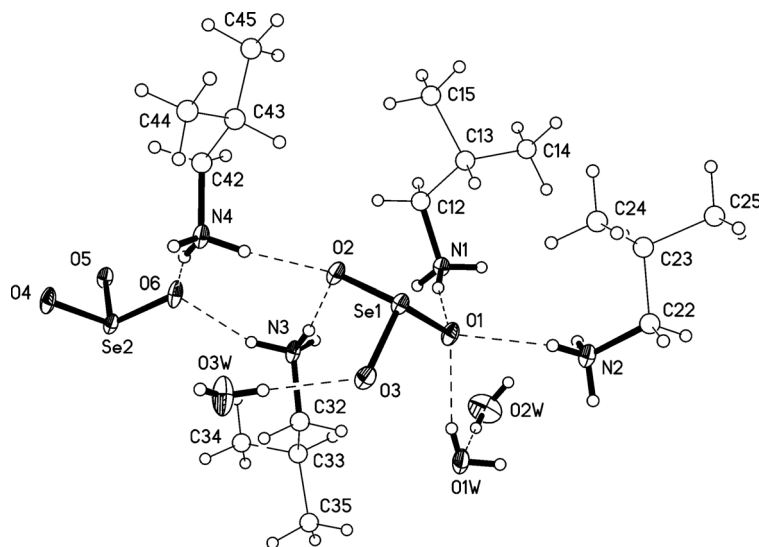


Fig. 3. The asymmetric unit (two formula units) of compound  $1 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  in the crystal. Ellipsoids represent 30% probability levels. Dashed lines indicate hydrogen bonds.

Table 2. Hydrogen bonds [ $\text{\AA}$  and  $^\circ$ ] for  $1 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ .

| D-H...A                          | d(D-H)    | d(H...A) | d(D...A) | <(DHA) |
|----------------------------------|-----------|----------|----------|--------|
| N(1)-H(1C)...O(1)                | 0.91      | 1.90     | 2.794(4) | 168.1  |
| N(2)-H(2A)...O(1)                | 0.91      | 2.08     | 2.802(4) | 135.9  |
| N(3)-H(3B)...O(2)                | 0.91      | 1.83     | 2.731(5) | 170.9  |
| N(3)-H(3C)...O(6)                | 0.91      | 1.90     | 2.779(4) | 160.8  |
| N(4)-H(4A)...O(2)                | 0.91      | 1.89     | 2.776(4) | 163.6  |
| N(4)-H(4B)...O(6)                | 0.91      | 1.90     | 2.787(5) | 164.2  |
| O(1W)-H(O2)...O(1)               | 0.793(19) | 2.04(2)  | 2.816(5) | 165(5) |
| O(2W)-H(O3)...O(1W)              | 0.795(19) | 2.21(3)  | 2.984(5) | 164(6) |
| O(3W)-H(O6)...O(3)               | 0.792(19) | 2.03(2)  | 2.820(5) | 175(6) |
| N(1)-H(1A)...O(4) <sup>#1</sup>  | 0.91      | 2.00     | 2.812(4) | 147.3  |
| N(2)-H(2C)...O(4) <sup>#1</sup>  | 0.91      | 1.87     | 2.777(4) | 178.2  |
| O(2W)-H(O4)...O(4) <sup>#1</sup> | 0.802(19) | 2.02(2)  | 2.815(5) | 172(7) |
| N(1)-H(1B)...O(3) <sup>#2</sup>  | 0.91      | 1.86     | 2.723(4) | 157.3  |
| N(3)-H(3A)...O(3) <sup>#2</sup>  | 0.91      | 1.87     | 2.772(4) | 169.2  |
| N(2)-H(2B)...O(5) <sup>#3</sup>  | 0.91      | 1.86     | 2.761(5) | 170.8  |
| O(1W)-H(O1)...O(5) <sup>#3</sup> | 0.812(19) | 2.07(2)  | 2.851(4) | 161(5) |
| N(4)-H(4C)...O(5) <sup>#4</sup>  | 0.91      | 1.91     | 2.803(4) | 167.5  |
| O(3W)-H(O5)...O(6) <sup>#4</sup> | 0.797(19) | 2.08(2)  | 2.857(5) | 166(5) |

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup>  $x-1, -y+1/2, z-1/2$ ; <sup>#2</sup>  $x, -y+1/2, z-1/2$ ; <sup>#3</sup>  $x-1, y, z$ ; <sup>#4</sup>  $x, -y+1/2, z+1/2$ .

terms of topologically differing structural roles in the packing [6].

The asymmetric unit of the sesquihydrate of **1** also consists two independent formula units (two selenite ions, four isobutylammonium ions and three water molecules); the space group is again  $P2_1/c$  (Fig. 3). Bond lengths and angles may again be regarded as normal, *e. g.* Se-O 1.682–1.699(3)  $\text{\AA}$ , O-Se-O 101.7–103.2(1) $^\circ$ .

The extended structure of  $1 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  is again a layer structure (Fig. 4i), but the layers are now par-

allel to the  $xz$  plane at  $y \approx 1/4$  and  $3/4$ . Hydrogen bond data are presented in Table 2. It is convenient to begin by analysing the packing without the water molecules. Again, all 12 hydrogen atoms of the  $\text{NH}_3$  groups act as single donors and each of the 6 selenite oxygen atoms accepts two hydrogen bonds. However, there the similarity to structure **1** ends. At the top of Fig. 4i, in the region  $x \approx 1$ , two horizontal chains of residues (parallel to the  $z$  axis) can be recognised. Within each chain, translation and *c*-glide operators are involved. The upper chain contains only selenite 1 and cation 1 (referred to the numbering of the Se and N atoms) and the repeat unit (excluding hydrogen atoms) O1-Se1-O3...N1; the lower only selenite 2 and cation 2, with repeat unit O5-Se2-O4...N2. The chains are crosslinked by hydrogen bonds to form rings of graph set  $R_4^4(12)$ , atom sequence (O-Se-O...HNH...)<sub>2</sub> and  $R_4^2(8)$ , atom sequence (O...HNH)<sub>2</sub>, numbered 1 and 3 in the schematic summary (Fig. 4ii). This first pattern repeats by translation at the bottom of the Figure ( $x \approx 0$ ). In the region  $x \approx 1/2$ , cations 3 and 4 link with selenite oxygen atoms to form further  $R_4^4(12)$  rings (no. 4), which alternate with further  $R_4^2(8)$  rings (no. 2) parallel to the  $z$  axis to form the second pattern. Between these two patterns, two independent  $R_4^3(10)$  rings, analogous to those in the anhydrous material, are formed (nos. 5 and 6).

The water molecules 1 and 2 are attached to the same side of ring no. 3 (Fig. 4iii), whereby O1, O4 and O5 act as acceptors. Water molecule 3 bridges one corner of the large ring no. 2, whereby O3 and O6 are

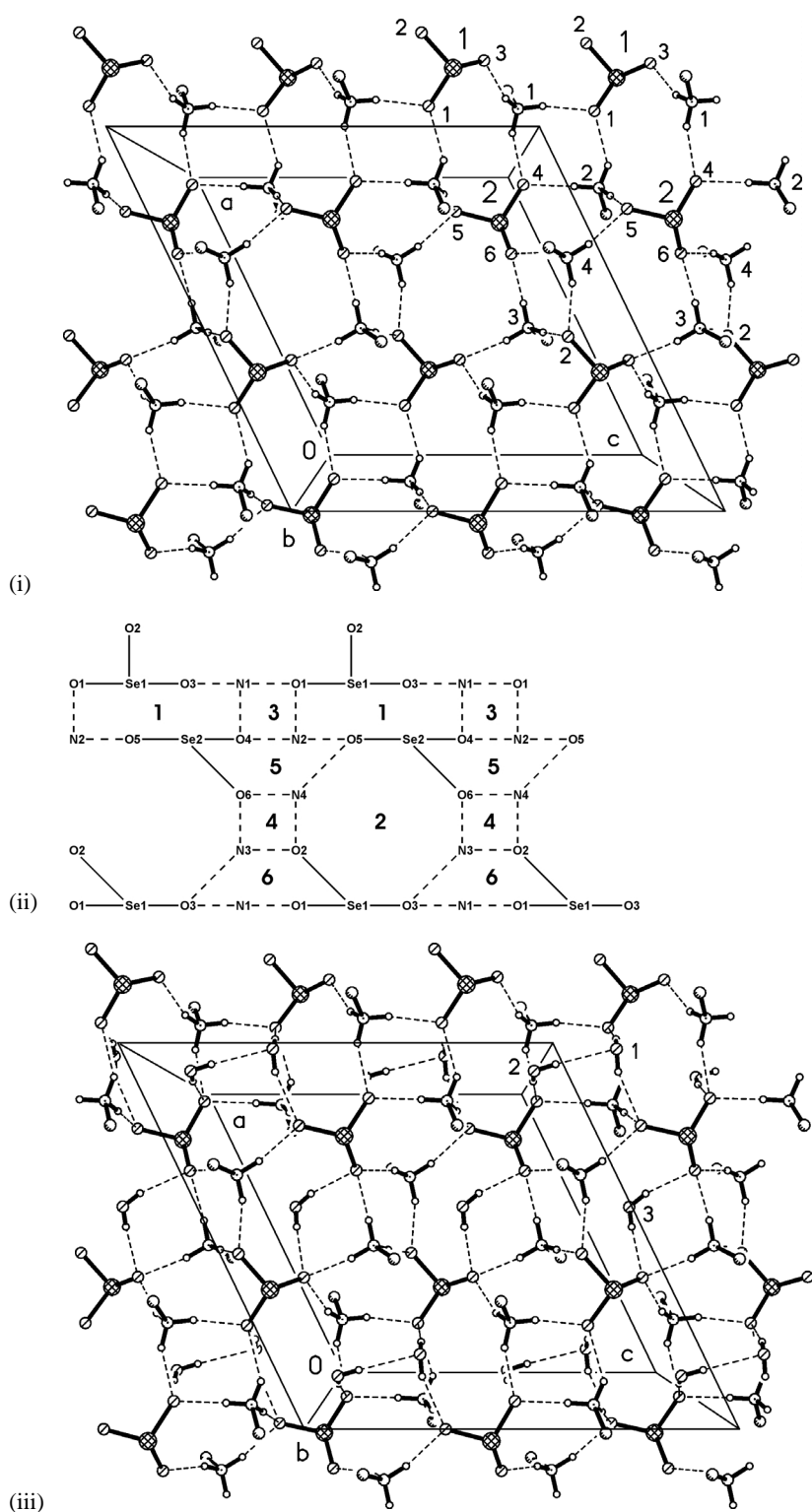


Fig. 4. Top: Packing diagram of  $1 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  viewed parallel to the  $y$  axis in the region  $y \approx 1/4$ . Water molecules are omitted. Hydrogen bonds are shown as dashed lines. Only the first carbon atoms of the isobutyl groups are shown. Numbering refers to Se atoms (large digits) or N and O atoms (small digits). Centre: Schematic representation of the upper part of the diagram (see text). Bottom: Complete packing including waters. Only the water oxygen atoms are numbered.

Table 3. Crystallographic data.

| Compound                                       | <b>1</b>  | <b>1</b> · 1½H <sub>2</sub> O                                     |
|--|---|---|
| Formula  | C <sub>8</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> Se | C <sub>8</sub> H <sub>27</sub> N <sub>2</sub> O <sub>4.5</sub> Se |
| <i>M<sub>r</sub></i>                           | 275.25  | 302.28  |
| Habit  | colourless tablet   | colourless tablet   |
| Crystal size [mm]                              | 0.3 × 0.2 × 0.1   | 0.25 × 0.17 × 0.07  |
| Crystal system                                 | monoclinic  | monoclinic  |
| Space group                                    | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                |
| Cell constants:                                |   |   |
| <i>a</i> [Å]                                   | 10.9618(8)  | 11.8833(16)   |
| <i>b</i> [Å]                                   | 11.7892(8)  | 24.196(3)   |
| <i>c</i> [Å]                                   | 21.8125(16)   | 12.0447(16)   |
| β [°]  | 97.744(4)   | 115.748(4)  |
| <i>V</i> [Å <sup>3</sup> ]                     | 2793.1  | 3119.3  |
| <i>Z</i>                                       | 8   | 8   |
| <i>D<sub>x</sub></i> [g cm <sup>−3</sup> ]     | 1.309   | 1.287   |
| μ [mm <sup>−1</sup> ]                          | 2.7   | 2.4   |
| <i>F</i> (000)                                 | 1152  | 1272  |
| <i>T</i> [°C]                                  | −140  | −140  |
| 2θ <sub>max</sub>                              | 60  | 56.6  |
| Transmissions                                  | 0.59–0.78   | 0.64–0.85   |
| No. of refl.:                                  |   |   |
| measured                                       | 50532   | 54634   |
| indep.   | 8176  | 7720  |
| <i>R</i> <sub>int</sub>                        | 0.060   | 0.090   |
| Parameters                                     | 257   | 328   |
| Restraints                                     | 0   | 271   |
| <i>wR</i> ( <i>F</i> <sup>2</sup> , all refl.) | 0.102   | 0.109   |
| <i>R</i> ( <i>F</i> , ≥ 4σ( <i>F</i> ))        | 0.039   | 0.050   |
| <i>S</i>                                       | 1.03  | 1.05  |
| Max. Δρ (eÅ <sup>−3</sup> )                    | 1.5   | 0.64  |

acceptors. The interactions with the water molecules break the exact topological equivalence between the two independent formula units. It is noteworthy that water 1 accepts only one classical hydrogen bond (from water 2) and waters 2 and 3 none at all; because of problems with disorder of isobutyl groups (see below), C–H···O interactions are not analysed in detail, but some H···O contacts of *ca.* 2.5 Å are observed.

Neither structure is closely related to that of propane-1,2-diaminium selenite monohydrate [4], in which selenites and water molecules are linked into a polymeric chain, extended to a double layer structure by N–H···O hydrogen bonds.

## Experimental Section

Isobutylamine was obtained commercially and used without further purification. Compound **1**: 0.2 g selenium dioxide in 20 mL amine containing 1 drop of water was stirred for 3 h, the suspension filtered and layered with diethyl ether. Sesquihydrate of **1**: 0.05 g selenium dioxide was refluxed in 10 mL amine containing 2 drops of water. The resulting clear solution was layered with diethyl ether. In both cases a few small colourless crystals formed after several months.

## X-ray structure determinations

Crystals were mounted in inert oil on glass fibres. Data were measured using MoK<sub>α</sub> radiation on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were performed with the program SADABS. The structures were refined anisotropically on *F*<sup>2</sup> using all reflections (program SHELXL-97 [7]). Water H atoms were located and refined freely but with O–H distances restrained equal; NH<sub>3</sub> and ordered CH<sub>3</sub> groups were refined as idealised rigid groups allowed to rotate but not tip; other H atoms were included using a riding model. Two isobutyl groups of the sesquihydrate are disordered over two positions and were refined with appropriate restraints. Crystal data and numerical details of refinement are given in Table 3.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-609324 (**1**), 609325 (**1** · 1½H<sub>2</sub>O). Copies may be requested free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

- [1] A. M. Beatty, B. A. Helfrich, G. A. Hogan, B. A. Reed, *Crystal Growth and Design* **6**, 122 (2006).
- [2] P. G. Jones, C. Wölper, *Dalton Trans.* 1762 (2005).
- [3] F. H. Allen, *Acta Crystallogr.* **B58**, 380 (2002).
- [4] M. J. Todd, W. T. A. Harrison, *Acta Crystallogr.* **E61**, o1538 (2005).

- [5] L. K. Ritchie, W. T. A. Harrison, *Acta Crystallogr.* **E59**, o1296 (2003).
- [6] For a recent example, see S. V. Narayanan, H. Hopf, P. G. Jones, *Acta Crystallogr.* **E62**, o2125 (2006).
- [7] G. M. Sheldrick, SHELXL-97, a program for refining crystal structures, University of Göttingen, Germany (1997).