

Walid Rejik,^a Houcine Naïli,^a
Tahar Mhiri^a and
Thierry Bataille^{b*}^aLaboratoire de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, BP 802, 3018 Sfax, Tunisia, and ^bLaboratoire de Chimie du Solide et Inorganique Moléculaire (CNRS, UMR 6511), Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cedex, FranceCorrespondence e-mail:
thierry.bataille@univ-rennes1.fr**Key indicators**Single-crystal X-ray study
 $T = 292\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.044
 wR factor = 0.126
Data-to-parameter ratio = 30.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Piperazinediium hexaaquazinc(II) bis(sulfate): a structural analogue of Tutton's salts**

The crystal structure of piperazinediium hexaaquazinc(II) bis(sulfate), $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, is built from isolated $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, SO_4^{2-} and $\text{C}_4\text{H}_{12}\text{N}_2^{2+}$ ions linked together by a hydrogen-bonding network. The title compound exhibits strong analogies with some double aluminium sulfates, also known as Tutton's salts.

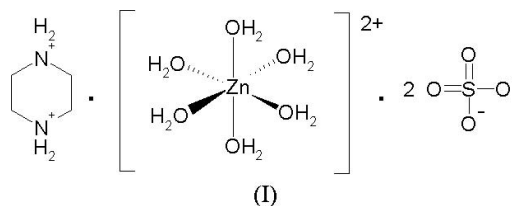
Received 14 February 2005

Accepted 24 February 2005

Online 4 March 2005

Comment

The synthesis of organically templated metal sulfates is a promising route to new microporous materials (Choudhury *et al.*, 2001; Bataille & Louër, 2002; Norquist *et al.*, 2003). In the course of our investigations on di- and trivalent metal sulfates templated by diamines (Bataille, 2003), we report here the synthesis and the structural characterization of piperazinediium hexaaquazinc(II) bis(sulfate), $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, (I).



The title compound is isostructural with the related cobalt phase (Pan *et al.*, 2003). The structure consists of Zn^{2+} cations octahedrally coordinated by six water molecules, sulfate tetrahedra and piperazinium cations lying about inversion centres, and linked together by hydrogen bonds. The chemical formula, as well as the structural model, resemble those of Tutton's salts. Indeed, the arrangement of the polyhedral units, as shown in Fig. 1, is very similar to that of, for example, $(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ (Maslen *et al.*, 1988), except that the orientation of the polyhedra differs from one phase to another. Such a relationship has also been reported in M^{II} guanidinium sulfates (Fleck *et al.*, 2004). The significant difference in unit-cell dimensions between the related phases certainly depends on the size, shape and charge of the amino group involved in the structures, *i.e.* NH_4^+ , $[\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2]^{2+}$ and $[\text{C}(\text{NH}_2)_3]^+$. Further investigations will help our understanding of the role of the amine entity in the formation of such compounds.

Experimental

Single crystals of the title compound were grown by slow evaporation at room temperature of an aqueous solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ – $\text{C}_4\text{H}_{10}\text{N}_2$ – H_2SO_4 in a 1:1:1 ratio. The product was filtered off and washed with a small amount of distilled water.

Crystal data

(C₄H₁₂N₂)[Zn(H₂O)₆](SO₄)₂
M_r = 453.74
 Monoclinic, *P*2₁/*n*
a = 12.9562 (2) Å
b = 10.6502 (2) Å
c = 13.3251 (2) Å
 β = 114.032 (1)°
V = 1679.30 (5) Å³
Z = 4

D_x = 1.795 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 15 427 reflections
 θ = 2.0–35.0°
 μ = 1.78 mm⁻¹
T = 292 (2) K
 Prism, colourless
 0.20 × 0.18 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: analytical
 (de Meulenaer & Tompa, 1965)
T_{min} = 0.708, *T_{max}* = 0.794
 27 290 measured reflections
 7387 independent reflections

5221 reflections with *I* > 2σ(*I*)
R_{int} = 0.073
 θ_{max} = 35.0°
h = -20 → 17
k = -17 → 17
l = -19 → 21

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.044
wR (*F*²) = 0.126
S = 1.04
 7387 reflections
 244 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.263P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.84 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.82 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11...O1 ⁱ	0.830 (15)	1.872 (17)	2.688 (2)	167 (3)
O11—H12...O8 ⁱⁱ	0.827 (15)	1.878 (16)	2.7038 (19)	177 (3)
O12—H21...O7 ⁱⁱⁱ	0.877 (16)	1.850 (16)	2.697 (2)	162 (2)
O12—H22...O4	0.849 (16)	1.906 (16)	2.753 (2)	176 (3)
O13—H31...O5 ⁱⁱⁱ	0.882 (15)	2.32 (2)	3.073 (3)	142.7 (19)
O13—H31...O7 ⁱⁱⁱ	0.882 (15)	2.461 (18)	3.253 (3)	150 (2)
O13—H32...O3 ^{iv}	0.872 (15)	1.954 (15)	2.821 (2)	172 (2)
O14—H41...O1	0.855 (15)	1.855 (16)	2.709 (2)	176 (2)
O14—H42...O4 ^{iv}	0.863 (16)	1.858 (16)	2.711 (2)	169 (3)
O15—H51...O6	0.849 (15)	1.888 (16)	2.736 (2)	177 (3)
O15—H52...O3 ⁱ	0.830 (16)	2.078 (17)	2.896 (2)	168 (2)
O16—H61...O5	0.868 (15)	1.855 (16)	2.718 (2)	173 (2)
O16—H62...O6 ⁱⁱ	0.876 (15)	1.886 (16)	2.7564 (19)	172 (2)
N1—H1C...O7	0.90	1.94	2.759 (2)	151
N1—H1C...O6	0.90	2.54	3.243 (2)	136
N1—H1D...O2 ^{iv}	0.90	1.89	2.766 (2)	163
N2—H2C...O2 ^{iv}	0.90	1.85	2.737 (2)	170
N2—H2D...O8 ^v	0.90	1.83	2.724 (2)	170

Symmetry codes: (i) 1 - *x*, 1 - *y*, -*z*; (ii) $\frac{1}{2}$ - *x*, *y* - $\frac{1}{2}$, 2 - *z*; (iii) 1 - *x*, 1 - *y*, 1 - *z*; (iv) $\frac{3}{2}$ - *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*; (v) $\frac{1}{2}$ - *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*.

The aqua H atoms were located in a difference map and refined with O—H distance restraints of 0.85 (1) Å and H...H distance restraints of 1.39 (1) Å, and with *U_{iso}* = 1.2*U_{eq}*(O). H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.97 Å, N—H = 0.90 Å and *U_{iso}* = 1.2*U_{eq}*(C,N).

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Berndt, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999).

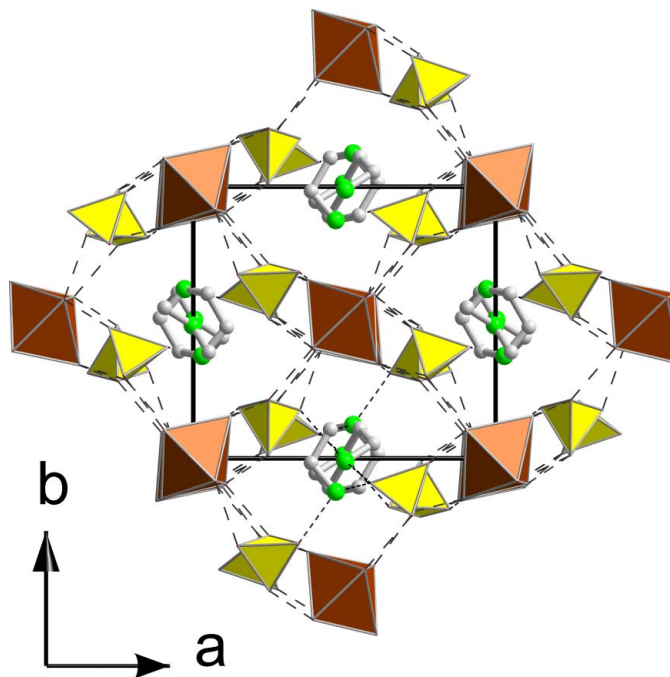


Figure 1

Projection of the structure of (I) along the *c* axis, showing the hydrogen-bonding network between [Zn(H₂O)₆]²⁺ (brown octahedra), SO₄²⁻ (yellow tetrahedra) and C₄H₁₂N₂²⁺ ions. The hydrogen bonds formed from water molecules are represented by thick dashed lines, while those involving N atoms are shown by thin ones. H atoms have been omitted for clarity.

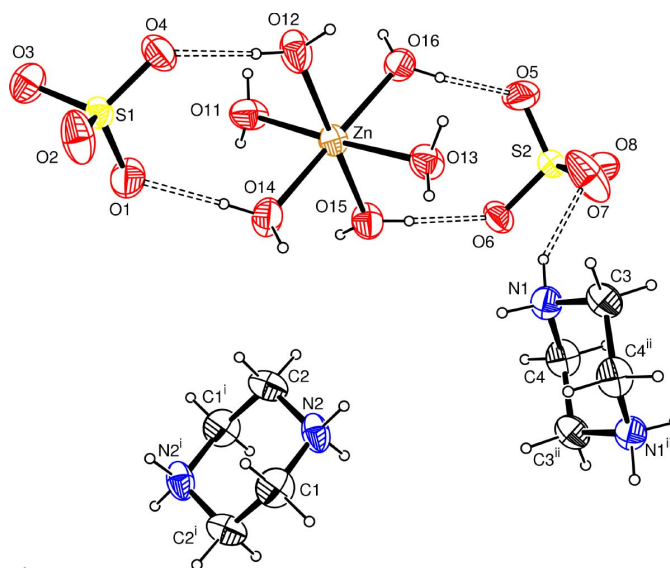


Figure 2

A part of the crystal structure of (I), showing the asymmetric unit (expanded by symmetry to give complete organic cations) and atom numbering. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) 1 - *x*, 2 - *y*, -*z*; (ii) 1 - *x*, 2 - *y*, 1 - *z*.]

The authors thank Dr T. Roisnel (Centre de Diffraction X, Université de Rennes I) for collecting the diffraction data.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bataille, T. (2003). *Acta Cryst.* **C59**, m459–m461.
- Bataille, T. & Louër, D. (2002). *J. Mater. Chem.* **12**, 3487–3493.
- Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
- Choudhury, A., Krishnamoorthy, J. & Rao, C. N. R. (2001). *Chem. Commun.* pp. 2610–2611.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fleck, M., Bohaty, L. & Tillmans, E. (2004). *Solid State Sci.* **6**, 469–477.
- Maslen, E. N., Ridout, S. C., Watson, K. J. & Moore, F. H. (1988). *Acta Cryst.* **C44**, 409–412.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Norquist, A. J., Doran, M. B., Thomas, P. M. & O'Hare, D. (2003). *Dalton Trans.* pp. 1168–1175.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pan, J.-X., Yang, G.-Y. & Sun, Y.-Q. (2003). *Acta Cryst.* **E59**, m286–m288.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.