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$\{[Ba_2(C_2O_4)(H_2O)_6](NCS)_2\}_n$: a layered mixed-anion barium oxalate

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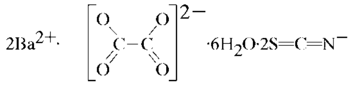
We present the first example of a compound containing Ba^{2+}, $C_2O_4{}^{2-}$, water and some additional halide or pseudo-halide anions, *viz*. hexa-μ_2-aqua-μ_6-oxalato-dibarium(II) diisothiocyanate, $\{[Ba_2(C_2O_4)(H_2O)_6](NCS)_2\}_n$. The structure consists of positively charged planar covalent layers of Ba^{2+} cations, oxalate anions and water molecules. The first coordination sphere of the Ba^{2+} cation contains six water molecules and four O atoms from two planar oxalate anions. The oxalate anion lies on an inversion centre and is coordinated to six Ba^{2+} cations, each donor O atom being bonded to two cations. Pairs of water molecules are coordinated by two Ba^{2+} cations. The layers are interspersed with non-coordinated NCS^- anions.

Comment

By varying the experimental conditions, different barium oxalate salts can be obtained. The structures of $[Ba(C_2O_4)(H_2C_2O_4)(H_2O)_2]$ (Chaix-Pluchery *et al.*, 1989), $[Ba(C_2O_4)(H_2C_2O_4)]$ (Mutin *et al.*, 1979), $[Ba_2(C_2O_4)_2(H_2O)]$ (Mutin *et al.*, 1981), $[Ba(C_2O_4)(H_2O)_2]$ (Christensen *et al.*, 1995), $[Ba(C_2O_4)(H_2O)]$ (Mutin *et al.*, 1974; Huang & Mak, 1990), $[Ba_2(C_2O_4)_2(H_2O)_7]$ (Neder *et al.*, 1997) and $[Ba_2(C_2O_4)_2(H_2C_2O_4)(H_2O)_2]$ (Mutin & Dusausoy, 1981) have been determined by single-crystal and powder diffraction. In addition, various complexes containing transition metal cations, Ba^{2+} and oxalate are known. However, there are no structurally characterized compounds containing Ba^{2+}, $C_2O_4{}^{2-}$, water and anions such as halide, pseudo-halide, chalcogenide, *etc*. In this article, we present the first example of such a compound, *viz*. $[Ba_2(C_2O_4)(H_2O)_6](NCS)_2$, (I) (Fig. 1).



$$2Ba^{2+}\cdot\left[\begin{matrix}O & & O\\ & C-C & \\ O & & O\end{matrix}\right]^{2-}\cdot 6H_2O\cdot 2S{=}C{=}N^-$$

(I)

The connectivity and dimensionality of barium oxalate structures have been analysed with the program package *TOPOS* using algorithms based on Voronoi–Dirichlet partition (Blatov *et al.*, 2000), without assumption of any atomic radii. We have found that the structure of (I) is layered, in contrast with most previously known barium oxalates, which have three-dimensional polymeric structures, the sole exception being $[Ba_2(C_2O_4)_2(H_2O)_7]$ (Neder *et al.*, 1997), which is also layered.

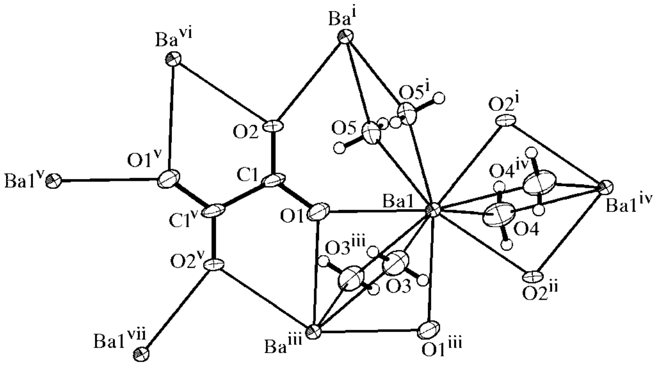


Figure 1
The coordination spheres of the Ba^{2+} and oxalate ions in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 2-y, 1-z$; (v) $1-x, -y, 1-z$; (vi) $x, y-1, z$; (vii) $1+x, y-1, z$.]

In the structure of (I), positively charged planar covalent layers of Ba^{2+} cations, oxalate anions and water molecules are interspersed with NCS^- anions (Fig. 2). Ten O atoms are coordinated to each Ba^{2+} cation, four of them belonging to oxalates and six to water molecules. The oxalate anion sits on a centre of inversion and is planar, with each O atom being bonded to two Ba^{2+} cations. Each water molecule is coordi-

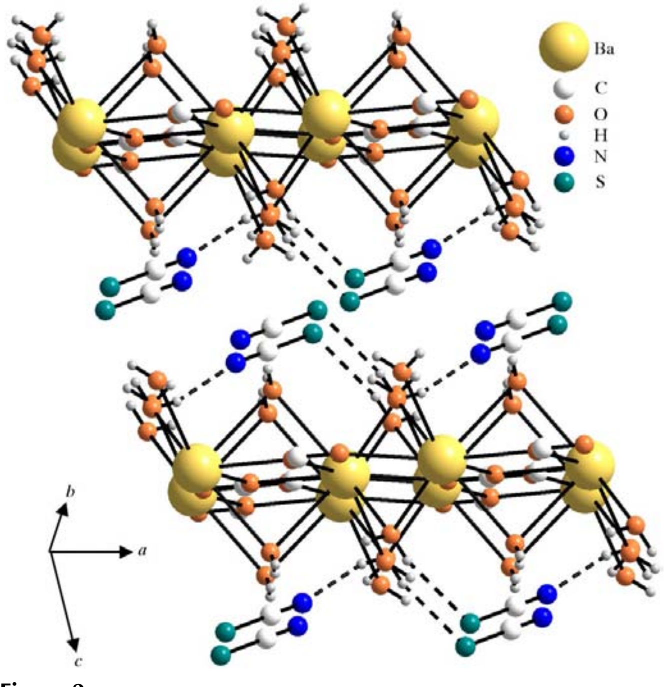


Figure 2
The crystal packing in (I). Short interlayer N···H and S···H contacts are shown with dashed lines.

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nated to two Ba^{2+} cations. Therefore, the structure of the layer can be described as $[Ba(C_2O_4)_{3/6}(H_2O)_{6/2}]^{n+}_{\infty\infty}$ or $[Ba_2(\mu_6\text{-}\eta^4\text{-}C_2O_4)(\mu_2\text{-}H_2O)_6]^{2+}$ or $A_2K^{42}M_6^2$ (A represents the central atom, K represents the coordinated ion and M represents coordinated water molecules; Porai-Koshits & Serezhkin, 1994).

Both the oxalate anion and Ba^{2+} cation centres form their own distorted triangular nets. Such motifs are typical for oxalates, according to Naumov *et al.* (1996). The topology of the layer is different from that found in $[Ba_2(C_2O_4)_2(H_2O)_7]$, where Ba^{2+} forms regular hexagonal nets and the oxalate anion centres form distorted rectangular nets.

Weak hydrogen bonds between water molecules and the N atoms of the isothiocyanate anions join the layers together in (I). The O(water)$\cdots$N distances are in the range 2.927 (12)–3.08 (2) Å. There is also a weak O(water)$\cdots$S(CN) interaction, with an S$\cdots$H distance of 2.51 (11) Å, between the isothiocyanate anion and one of the bridging water molecules.

Experimental

Compound (I) was obtained during an investigation of the $Ba(NCS)_2$–$UO_2(C_2O_4)$–H_2O system. Solid $UO_2(C_2O_4)$ was added to a hot aqueous solution of barium isothiocyanate in a 1.5:1 molar ratio, giving a clear orange solution. After slow evaporation at room temperature, orange lath-shaped crystals precipitated, which were identified as $Ba_3UO_2(C_2O_4)_2(NCS)_2\cdot 8H_2O$ (Markov & Sergeeva, 1961). These were filtered off and the remaining solution was left for some time, resulting in a light-yellow crystalline precipitate, which appeared as a mixture of a fine yellow crystalline powder and colourless opaque plate-shaped crystals of (I).

Crystal data

$[Ba_2(C_2O_4)(H_2O)_6](NCS)_2$
$M_r = 586.96$
Triclinic, $P\bar{1}$
$a = 6.8990$ (9) Å
$b = 6.9441$ (6) Å
$c = 9.6383$ (10) Å
$\alpha = 85.517$ (8)°
$\beta = 71.498$ (9)°
$\gamma = 67.037$ (8)°
$V = 402.63$ (8) Å^3

$Z = 1$
$D_x = 2.421$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 9$–15°
$\mu = 5.16$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.11 × 0.11 × 0.06 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.428$, $T_{\max} = 0.819$
1539 measured reflections
1411 independent reflections
1291 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 25.0°$
$h = -7 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.157$
$S = 1.19$
1411 reflections
109 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 5.3664P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.70$ e Å^{-3}
$\Delta\rho_{\min} = -1.81$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ba1—O1	2.723 (8)	Ba1—O5	2.856 (8)
Ba1—O1$^{\rm i}$	2.771 (8)	Ba1—O5$^{\rm ii}$	2.864 (9)
Ba1—O2$^{\rm ii}$	2.730 (8)	C1—C1$^{\rm v}$	1.55 (2)
Ba1—O2$^{\rm iii}$	2.762 (8)	C1—O1	1.266 (14)
Ba1—O3	2.916 (10)	C1—O2	1.246 (13)
Ba1—O3$^{\rm i}$	2.972 (10)	N1—C2	1.122 (17)
Ba1—O4	2.899 (10)	C2—S1	1.637 (12)
Ba1—O4$^{\rm iv}$	3.074 (11)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $-x, 2-y, 1-z$; (v) $1-x, -y, 1-z$.

After being located from a difference electron-density map, the positions of the water H atoms were refined with the O—H and H$\cdots$H distances restrained to 0.82 (2) and 1.36 (2) Å, respectively, to give reasonable H—O—H angles, and with a $U_{\rm iso}$ value of 0.05 Å^2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TOPOS*4.0 (Blatov *et al.*, 2000); software used to prepare material for publication: local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1090). Services for accessing these data are described at the back of the journal.

References

Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (2000). *J. Appl. Cryst.* **33**, 1193.

Chaix-Pluchery, O., Mutin, J. C., Bouillot, J. & Niepce, J. C. (1989). *Acta Cryst.* C**45**, 1699–1705.

Christensen, A. N., Hazell, R. G., Bell, A. M. T. & Altomare, A. (1995). *J. Phys. Chem. Solids*, **56**, 1359–1362.

Enraf–Nonius (1988). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.

Huang, S.-H. & Mak, T. C. W. (1990). *Z. Kristallogr.* **190**, 305–308.

Markov, V. P. & Sergeeva, T. V. (1961). *Zh. Neorg. Khim.* **6**, 368–375. (In Russian.)

Mutin, J. C., Aubry, A., Bertrand, G., Joly, E. & Protas, J. (1974). *C. R. Acad. Sci. Ser. C*, **278**, 1001–1004.

Mutin, J. C. & Dusausoy, Y. (1981). *J. Solid State Chem.* **38**, 394–405.

Mutin, J. C., Dusausoy, Y. & Protas, J. (1981). *J. Solid State Chem.* **36**, 356–364.

Mutin, J. C., Watelle, G. & Dusausoy, Y. (1979). *J. Solid State Chem.* **27**, 407–421.

Naumov, D. Yu., Podberezskaya, N. V., Boldyreva, E. V. & Virovets, A. V. (1996). *Zh. Strukt. Khim.* **37**, 550–578. (In Russian.)

Neder, R., Burghammer, M., Schulz, H., Christensen, A. N., Krane, H. G., Bell, A. M. T., Hewat, A. W. & Altomare, A. (1997). *Z. Kristallogr.* **212**, 305–326.

Porai-Koshits, M. A. & Serezhkin, V. N. (1994). *Zh. Neorg. Khim.* **39**, 1109–1132. (In Russian.)

Sheldrick, G. M. (1976). *SHELX*76. University of Cambridge, England.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

m356 Eugenia V. Peresypkina *et al.* • $[Ba_2(C_2O_4)(H_2O)_6](NCS)_2$ *Acta Cryst.* (2004). C**60**, m355–m356