metal-organic compounds

A new polymorph of barium chloro-anilate trihydrate

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Single crystals of a new polymorph of the title compound, barium(II) 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone trihydrate, $Ba^{2+} \cdot C_6Cl_2O_4{}^{2-} \cdot 3H_2O$, have been grown in sodium metasilicate gel. Each Ba^{2+} cation is coordinated by eight O atoms. The Ba^{2+} cations are bridged by an O atom of a ligand around the centre of symmetry at Wyckoff position $4a$ and by the O atom of a water molecule around the centre of symmetry at Wyckoff position $4b$, forming a sheet parallel to the (100) plane. Loose contacts are found around one of the water molecules, as observed in the $Cmca$ form.

Comment

It has been reported that barium(II) chloranilate trihydrate [barium(II) 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone tri-hydrate] and its 3,6-dibromo analogue crystallize in the orthorhombic space group $Cmca$ (Robel & Weiss, 1986). In the crystal, there are water molecules which may be removed reversibly (Robel & Weiss, 1986). The existence of loosely bound water molecules has also been reported for the crystal of copper(II) chloranilate trihydrate (Cueto *et al.*, 1992). The presence of such water molecules is of interest from the point of view of topochemical and/or surface reactions in the crystalline state, especially because barium chloranilate particles are used in the flow-injection analysis method for the spectrophotometric determination of sulfate ion concentration in


(I)
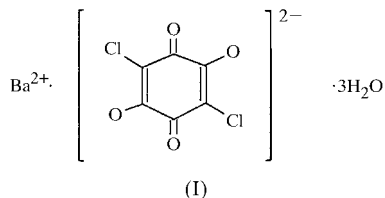
natural water (Ueno *et al.*, 1992). We report here the structure of a new polymorph of barium(II) chloranilate trihydrate, (I).

The bond lengths within the chloranilate anion are characteristic of the double π system, as exemplified by the long bond lengths for C1—C2 and C4—C5 [1.553 (10) and

1.561 (10) Å, respectively; Benchekroun & Savariault, 1995]. Each Ba^{2+} cation is coordinated by eight O atoms, with $Ba \cdots O$ distances in the range 2.719 (5)–2.934 (6) Å (Figs. 1 and 2; Table 1). The Ba^{2+} cations related by a centre of symmetry at Wyckoff position $4b$ are bridged by O4 and those related by a centre of symmetry at Wyckoff position $4a$ are bridged by O7[iii] [symmetry code: (iii) $1 - x$, $1 - y$, $-z$], forming a sheet parallel to the (100) plane. In this sheet, the anions related by a twofold screw axis along **c** overlap and are nearly parallel, with short $C \cdots C$ contacts in the range 3.266 (10)–3.368 (10) Å (Table 2). The sheets are stacked along **a**, forming rather short $Cl \cdots Cl$ contacts and a rather long contact between the O6 and O5[vi] atoms of the water molecules (Table 2). Atom O6 possibly takes part in a weak hydrogen bond, because the angle of 90.9 (2)° for $O5^{vi} \cdots O6 \cdots O7^{ii}$ [symmetry code: (ii) $1 - x$, $1 - y$, $1 - z$] satisfies a geometrical requirement for hydrogen bonding. Atom O2 does not participate in coordination with the cation, in contrast with the case of the $Cmca$ form, while it makes rather short $O \cdots O$ contacts with two water molecules (Table 2).

The space group $Pbca$ of (I) is a non-isomorphic subgroup of $Cmca$ [$Z = 8$, $a = 16.901$ (3), $b = 6.5234$ (8) and $c = 19.262$ (2) Å, and $V = 2123.7$ Å^3; Robel & Weiss, 1986]. The unit-cell volume of (I) is smaller than that of the $Cmca$ form by 0.9%. There is a similarity in the arrangements of the anions in the sheet for both forms, *i.e.* the arrangement of the anion related by a c-glide plane in (I) corresponds to that related by a b-glide plane perpendicular to the a axis in the $Cmca$ form. The arrangement of anions related by a twofold screw axis is seen in the sheets of both forms, being along the b axis for (I)
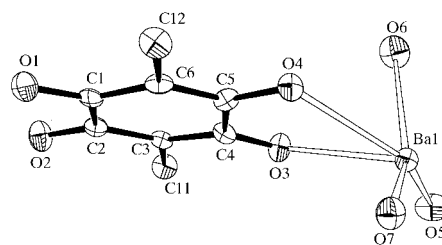
Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the asymmetric unit of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the water molecules are not shown.
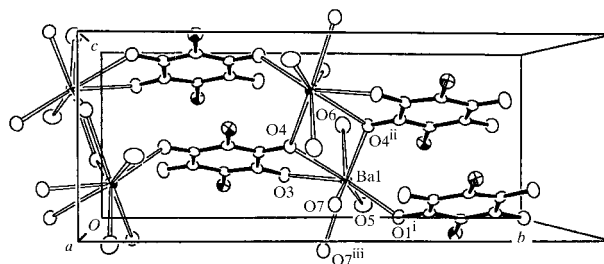
Figure 2
The arrangement of the chloroanilate anions and the coordination around the Ba^{2+} cations in (I), viewed down the a axis. The arrangement related by an a-glide plane has been omitted for clarity. Symmetry codes are as given in Table 1.

Table 1
Selected geometric parameters (Å, °).

Ba1—O1^i	2.750 (5)	Ba1—O7^{iii}	2.829 (6)
Ba1—O3	2.719 (5)	Cl1—C3	1.729 (7)
Ba1—O4	2.760 (5)	Cl2—C6	1.738 (7)
Ba1—O4^{ii}	2.755 (5)	O1—C1	1.244 (8)
Ba1—O5	2.794 (6)	O2—C2	1.242 (8)
Ba1—O6	2.898 (7)	O3—C4	1.239 (8)
Ba1—O7	2.934 (6)	O4—C5	1.263 (8)
Ba1—O4—Ba1^{ii}	111.70 (16)	Ba1—O7—Ba1^{iii}	106.95 (18)

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

Table 2
Contact distances (Å).

O2$\cdots$O5^{iv}	2.750 (8)	C5$\cdots$O2^{viii}	3.349 (9)
O2$\cdots$O7^v	2.795 (7)	C6$\cdots$Cl1^{viii}	3.266 (10)
O1$\cdots$O7^v	2.865 (7)	C6$\cdots$C2^{viii}	3.368 (10)
O6$\cdots$O5^{vi}	2.931 (9)	C2$\cdots$C3^{viii}	3.280 (10)
O6$\cdots$O7^{vii}	2.943 (9)	Cl2$\cdots$Cl1^{ix}	3.228 (3)
O1$\cdots$C5^{viii}	3.322 (9)	Cl2$\cdots$Cl1^x	3.398 (3)

Symmetry codes: (iv) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (v) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ix) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (x) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

and along the *a* axis for the *Cmca* form. In both forms, the sheets related by a glide plane are stacked, along an *a*-glide plane in (I) and a *c*-glide plane in the *Cmca* form. Thus, the *a*, *b* and *c* axes of (I) correspond to the *c*, *a* and *b* axes, respectively, of the *Cmca* form.

Differential scanning calorimetry measurements for (I) in the temperature range 273–443 K showed broad endothermic anomalies at around 363 and 403 K on heating. Since these thermal anomalies are irreversible, they are attributable to dehydration. This dehydration phenomenon corresponds to that observed at temperatures of 313–363 and 368–383 K for the bromo analogue from thermogravimetry measurements (Robel & Weiss, 1986). This shows that the water molecules in (I) are more tightly bound than in the bromo analogue. The lower and higher temperature regions have been assigned to the hydration of one and two water molecules per formula unit, respectively (Robel & Weiss, 1986).

Experimental

The formation of crystals of (I) was accomplished by the reaction of BaCl$_2$ and C$_6$H$_2$Cl$_2$O$_4$ in sodium metasilicate gel. Chloranilic acid was dissolved in NaOH aqueous solution in equal concentrations of 0.1 *M*. The solution (20 ml) was mixed with 0.5 *M* Na$_2$SiO$_3$·9H$_2$O solution (20 ml). The mixed solution was placed in a test tube of length 200 mm and inner diameter 30 mm. For gelation, 2 *M* acetic acid (about 10 ml) was then added to the solution. The gelation period was 24 h. After the gel had set, 0.1 *M* BaCl$_2$·2H$_2$O solution (30 ml) was carefully layered on top of the set gel. The test tube was kept at 313 K for 30 d. Dark-red prismatic crystals of (I) formed in the gel.

Crystal data

Ba^{2+}·C$_6$Cl$_2$O$_4$$^{2-}$·3H$_2$O	Mo $K\alpha$ radiation
$M_r = 398.35$	Cell parameters from 25
Orthorhombic, *Pbca*	reflections
$a = 17.258$ (4) Å	$\theta = 10.2$–11.0°
$b = 17.614$ (4) Å	$\mu = 4.29$ mm^{-1}
$c = 6.925$ (2) Å	$T = 298$ K
$V = 2105.1$ (8) Å^3	Prismatic, dark red
$Z = 8$	$0.46 \times 0.21 \times 0.09$ mm
$D_x = 2.514$ Mg m^{-3}	

Data collection

Rigaku AFC-5*R* diffractometer	$R_{int} = 0.023$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -2 \rightarrow 22$
(North *et al.*, 1968)	$k = -2 \rightarrow 22$
$T_{min} = 0.351$, $T_{max} = 0.680$	$l = -1 \rightarrow 8$
3563 measured reflections	3 standard reflections
2415 independent reflections	every 97 reflections
2110 reflections with $I > 0.5\sigma(I)$	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.060$	$\Delta\rho_{max} = 2.60$ e Å^{-3}
$wR = 0.065$	$\Delta\rho_{min} = -1.78$ e Å^{-3}
$S = 1.670$	Extinction correction:
2110 reflections	Zachariasen (1967)
146 parameters	Extinction coefficient:
H-atom parameters not defined	2.14 (7) $\times 10^{-6}$
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$	

The H atoms of the water molecules were not found in a difference Fourier map and were not included in the refinement. The maximum $\Delta\rho$ was 0.74 Å from Ba1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure corporation, 1997–1999); program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*-3 (Farrugia, 1997).

References

Benchekroun, R. & Savariault, J.-M. (1995). *Acta Cryst.* C**51**, 186–188.
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Cueto, S., Straumann H.-P., Rys, P., Petter, W., Gramlich, V. & Rys, F. S. (1992). *Acta Cryst.* C**48**, 458–460.
Farrugia. L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Molecular Structure Corporation (1990). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive. The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1997–1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Robel, C. & Weiss, A. (1986). *Z. Naturforsch. Teil B*, **41**, 1495–1501.
Ueno, K., Sagara, F., Higashi, K., Yataka, K., Yoshida, I. & Ishii, D. (1992). *Anal. Chim. Acta*, **261**, 241–245.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.