

## METAL-ORGANIC COMPOUNDS

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## Sodium Chloranilate Trihydrate

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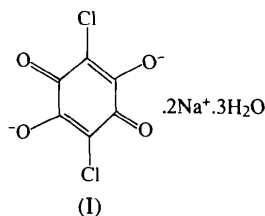
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## Abstract

In the title compound,  $2\text{Na}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}\cdot 3\text{H}_2\text{O}$ , the almost planar chloranilate ions, dianions of 3,6-dichloro-2,5-dihydroxy-*p*-benzoquinone, are parallel to the (010) plane and arranged in double chains along the [100] direction. Between the double chains, the sodium cations are situated in distorted octahedra which share edges to form chains along the [011] direction. Bond lengths within the chloranilate anion are consistent with the occurrence of two independent  $\pi$  systems.

## Comment

In the course of a study of the magnetic interactions in polyheterometallic molecular compounds (Folgado, Ibanez, Coronado, Beltran, Savariault & Galy, 1988), the sodium chloranilate salt was used as a donor of the chelating ligand. The comparison between metallic complexes thus requires a study of the structure of the sodium salt itself. Unlike the monohydrated ammonium chloranilate salt (Andersen, 1967), the sodium salt (I) crystallized with three water molecules, as was the case with the barium (Robl & Weiss, 1986) and copper salts (Cueto, Straumann, Rys, Petter, Gramlich & Rys, 1992).



The packing of the ions in the title compound, (I), is presented in the stereoview (Fig. 2). It shows that the chloranilate anions are nearly parallel to the (010) plane

(angle of  $3.98^\circ$ ) and are arranged in layers separated alternately by 3.10 and 3.44 Å. Each Na atom is situated in a distorted octahedral environment, denoted NA1 [Na(1)O<sub>5</sub>Cl] or NA2 [Na(2)O<sub>6</sub>]; these octahedra are arranged in columns in the [011] direction and share edges. In a column, the repetition order of the octahedra is –NA1–NA1–NA2–NA2–. Each pair of NA2 octahedra share an edge consisting of the O(4) and O(4<sup>x</sup>) [symmetry code: (x) 1 – x, 2 – y, 1 – z; Table 2] atoms of the chloranilate ions of adjacent layers, which accounts for the shortest distance between the layers. The other octahedral doublets, NA1–NA1 and NA1–NA2, share edges composed of water molecules and so do not directly link the chloranilate layers, giving rise to the greater interlayer distances. Fig. 1 represents the

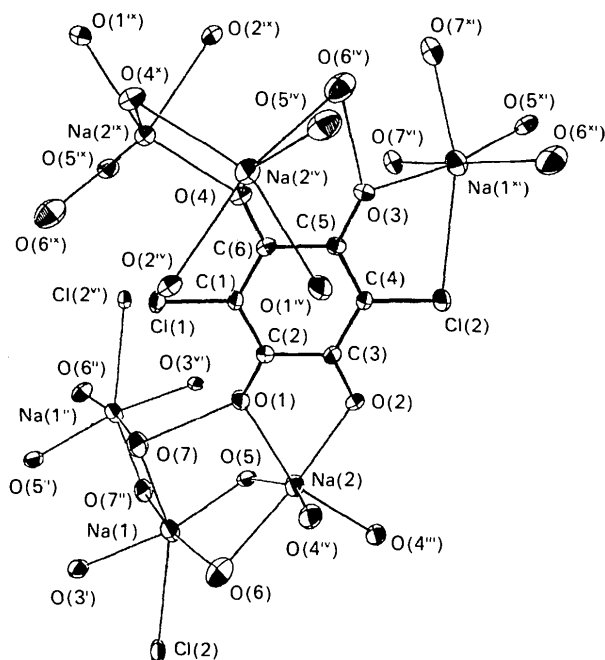


Fig. 1. Perspective view of the chloranilate anion and its environment. H atoms have been omitted. The symmetry codes are defined in Table 2.

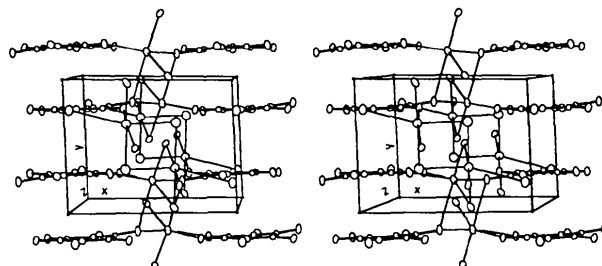


Fig. 2. Stereoview of the title structure.

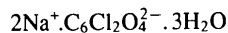
environment of a chloranilate anion. The Na(2) cations, situated at 0.21 Å from one layer in the shortest interlayer space, connect two anions of the same layer to form a chain. Moreover, each Na(2) cation establishes a bridge between two shortest-spaced layers through the atom O(4) of a chloranilate anion situated in the second layer. This constitutes a double chain of superposed parallel chloranilate anions linked by sodium cations which extends in the [100] direction. The Na(1) cations are situated between the double chains in the largest interlayer space (the distance to a layer being 0.62 Å). Each Na(1) cation is connected to a chloranilate anion through the O(3) atom and, with a very long interaction, through the Cl(2) atom [Cl(2)··Na(1) = 2.979 (1) Å]. As well as these ionic interactions, a hydrogen-bond network connects the water molecules to the O atoms of the chloranilate ions [O(5)··O(2) = 2.790 (2), O(6)··O(3) = 2.769 (2) and O(7)··O(1) = 2.758 (3) Å].

In the title structure, the interactions between the chloranilate anion and the four Na ions situated between the layers explain the deviations from planarity of the chloranilate anion. The greatest deviations are for the atoms O(1) [ $d = 0.47$  (2) Å] and O(2) [ $d = 0.37$  (1) Å] which are involved in the chelation to Na(2). The bond lengths within the chloranilate ions are characteristic of the double  $\pi$  system classically observed in such compounds (Tinti, Verdaguer, Kahn & Savariault, 1987).

## Experimental

An aqueous solution of chloranilic acid was added, while stirring, to a solution of sodium hydroxide in the molar ratio 1:2. Large crystals were obtained by slow evaporation of the solution in air. The density  $D_m$  was measured by picnometry using toluene.

### Crystal data



$$M_r = 306.995$$

Triclinic

$P\bar{1}$

$$a = 8.460$$
 (1) Å

$$b = 6.559$$
 (1) Å

$$c = 9.798$$
 (8) Å

$$\alpha = 92.05$$
 (5)°

$$\beta = 106.72$$
 (5)°

$$\gamma = 92.46$$
 (5)°

$$V = 519.6$$
 (5) Å<sup>3</sup>

$$Z = 2$$

$$D_x = 1.96$$
 Mg m<sup>-3</sup>

$$D_m = 1.95$$
 (4) Mg m<sup>-3</sup>

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction: none

Mo  $K\alpha$  radiation

$$\lambda = 0.71069$$
 Å

Cell parameters from 25 reflections

$$\theta = 15\text{--}18^\circ$$

$$\mu = 0.772$$
 mm<sup>-1</sup>

$$T = 293$$
 K

Plate

$$0.40 \times 0.35 \times 0.16$$
 mm

Violet

$$R_{\text{int}} = 0.016$$

$$\theta_{\text{max}} = 25^\circ$$

$$h = -10 \rightarrow 10$$

$$k = -7 \rightarrow 7$$

$$l = 0 \rightarrow 11$$

1931 measured reflections  
1815 independent reflections  
1736 observed reflections  
[ $I > 2\sigma(I)$ ]

### Refinement

Refinement on  $F^2$

$$R = 0.028$$

$$wR = 0.027$$

$$S = 2.23$$

1583 reflections

175 parameters

Only H-atom  $U$ 's refined

$$w = 1.0/[\sigma^2(F) + 0.0002F^2]^{1/2}$$

3 standard reflections  
frequency: 60 min  
intensity decay: 0.04%

$$(\Delta/\sigma)_{\text{max}} = 0.03$$

$$\Delta\rho_{\text{max}} = 0.38$$
 e Å<sup>-3</sup>

$$\Delta\rho_{\text{min}} = -0.62$$
 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
Cl(1)	0.09285 (5)	0.74572 (7)	0.26928 (5)	0.0223 (2)
Cl(2)	0.01840 (8)	0.76558 (8)	0.89539 (5)	0.0276 (2)
Na(1)	-0.6345 (1)	0.6680 (1)	0.04022 (8)	0.0284 (2)
Na(2)	-0.46734 (9)	0.7951 (1)	0.40456 (8)	0.0246 (2)
O(1)	-0.2153 (2)	0.7355 (2)	0.3569 (1)	0.0248 (4)
O(2)	-0.2479 (2)	0.7580 (2)	0.6186 (1)	0.0224 (4)
O(3)	0.3298 (2)	0.7754 (2)	0.8090 (1)	0.0239 (4)
O(4)	0.3609 (2)	0.8117 (2)	0.5484 (6)	0.0261 (4)
O(5)	-0.5696 (2)	0.5010 (2)	0.2562 (2)	0.0240 (4)
O(6)	-0.6091 (2)	0.9805 (2)	0.1795 (2)	0.0318 (5)
O(7)	-0.3404 (2)	0.6816 (2)	0.0644 (2)	0.0331 (5)
C(1)	0.0746 (2)	0.7543 (3)	0.4408 (2)	0.0165 (5)
C(2)	-0.0848 (2)	0.7468 (2)	0.4570 (2)	0.0157 (5)
C(3)	-0.1039 (2)	0.7575 (3)	0.6085 (2)	0.0164 (5)
C(4)	0.0398 (2)	0.7645 (3)	0.7245 (2)	0.0177 (5)
C(5)	0.1982 (2)	0.7733 (3)	0.7076 (2)	0.0166 (5)
C(6)	0.2174 (2)	0.7815 (3)	0.5568 (2)	0.0164 (5)

Table 2. Selected interatomic distances (Å) and angles (°)

C(1)—C(2)	1.401 (3)	C(1)—C(6)	1.400 (3)
C(2)—C(3)	1.538 (3)	C(3)—C(4)	1.403 (3)
C(4)—C(5)	1.396 (3)	C(5)—C(6)	1.535 (3)
Cl(1)—C(1)	1.731 (2)	O(1)—C(2)	1.246 (2)
O(2)—C(3)	1.250 (2)	Cl(2)—C(4)	1.735 (2)
O(3)—C(5)	1.260 (3)	O(4)—C(6)	1.248 (3)
Na(1)···O(3')	2.337 (2)	Na(1)···O(5)	2.352 (2)
Na(1)···O(6)	2.388 (3)	Na(1)···O(7)	2.428 (3)
Na(1)···O(7 <sup>ii</sup> )	2.453 (3)	Na(1)···Cl(2')	2.979 (1)
Na(2)···O(1)	2.356 (2)	Na(2)···O(2)	2.396 (2)
Na(2)···O(5)	2.349 (2)	Na(2)···O(6)	2.564 (3)
Na(2)···O(4 <sup>iii</sup> )	2.300 (4)	Na(2)···O(4 <sup>iv</sup> )	2.674 (3)
O(1)···O(7)	2.758 (3)	O(2)···O(5')	2.790 (2)
O(3)···O(6 <sup>v</sup> )	2.769 (2)		
C(1)—C(2)—C(3)	118.8 (2)	C(2)—C(3)—C(4)	118.2 (2)
C(3)—C(4)—C(5)	122.6 (2)	C(4)—C(5)—C(6)	119.1 (2)
C(1)—C(6)—C(5)	118.0 (2)	C(2)—C(1)—C(6)	122.6 (2)
Cl(1)—C(1)—C(2)	118.0 (1)	Cl(1)—C(1)—C(6)	119.3 (2)
O(1)—C(2)—C(1)	124.9 (2)	O(1)—C(2)—C(3)	116.3 (2)
O(2)—C(3)—C(2)	117.0 (2)	O(2)—C(3)—C(4)	124.8 (2)
Cl(2)—C(4)—C(3)	118.3 (1)	Cl(2)—C(4)—C(5)	119.1 (2)
O(3)—C(5)—C(4)	124.4 (2)	O(3)—C(5)—C(6)	116.5 (2)
O(4)—C(6)—C(1)	125.4 (3)	O(4)—C(6)—C(5)	116.5 (3)

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

The structure was solved by the Patterson method using *SHELXS86* (Sheldrick, 1985). All H atoms, located by difference Fourier synthesis, were left riding with the distances to their parent atoms constrained; a global isotropic displacement parameter was refined. The full-matrix least-squares refinements were carried out using *SHELX76* (Sheldrick, 1976). Molecular graphics were produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: PA1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Cs[CB<sub>10</sub>H<sub>13</sub>] at 293 K

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## Abstract

The unit cell of the room-temperature phase of Cs[CB<sub>10</sub>H<sub>13</sub>], caesium 8,9:10,11-di- $\mu$ -hydro-undeca-hydro-7-carba-*nido*-undecaborate(1<sup>-</sup>), is found to be very similar to that of  $\gamma$ -Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] at 299 K reported previously [Rius, Romerosa, Teixidor, Casabó & Miravittles (1991). *Inorg. Chem.* **30**, 1376–1379], but the packing of the carborane anion cages around the Cs<sup>+</sup> ions is distorted further from ideal octahedral geometry and the uncapped pentagonal faces of the cages lie

parallel to the *a* axis. No evidence of increased conductivity in two higher-temperature phases has been found for this compound.

## Comment

A study of three polymorphs of Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] in the temperature range 293–323 K has been reported previously (Rius, Romerosa, Teixidor, Casabó & Miravittles, 1991). The structure at 299 K has been described as a distorted hexagonal close-packed arrangement of anions with Cs<sup>+</sup> cations at the octahedrally coordinated sites. With increasing temperature, a transition to a conducting phase occurred between 471.8 and 495 K, associated with a change in the anion packing arrangement about Cs<sup>+</sup> from distorted octahedral ( $\gamma$ ,  $\beta$  phases) to tetrahedral ( $\alpha$  phase, conducting) and disorder of the Cs<sup>+</sup> ions along the *c* axis of the tetragonal cell. The structure of Cs[CB<sub>10</sub>H<sub>13</sub>], (I), at 293 K was determined in order to investigate the effects of slight changes in the electronic configuration, symmetry and H-atom geometry of the carborane anion on the structure and conductivity of the carborano caesium salts, while keeping the overall charge and carborane cage geometry constant.

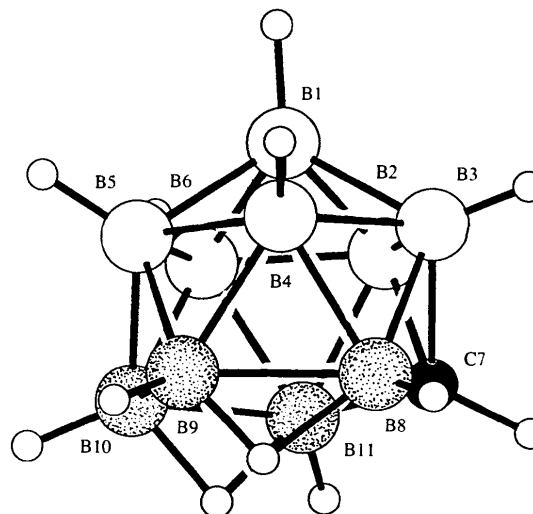
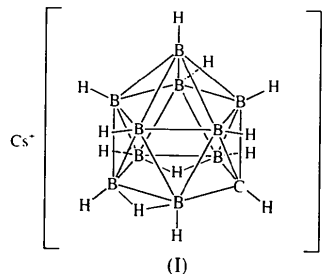


Fig. 1. A *PLUTO* (Motherwell & Clegg, 1978) plot of the [CB<sub>10</sub>H<sub>13</sub>]<sup>-</sup> anion with the atomic numbering scheme. This anion displays internal mirror symmetry, in contrast to [C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>, which has only one bridging H atom on the pentagonal ring.