

Acta Cryst. (1998). C54, 1104–1105

Hexaaquacobalt(II) Bis(hydrogen cyclopropane-1,1-dicarboxylate)

THOMAS SCHWARZ*, ALKE PETRI, JOACHIM SCHILLING AND AXEL LENTZ

Abteilung Anorganische Chemie I, Universität Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany. E-mail: thomas.schwarz@chemie.uni-ulm.de

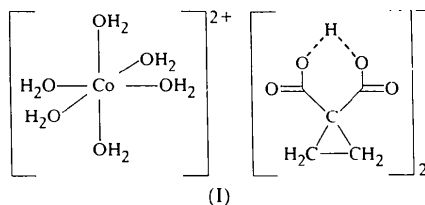
(Received 23 October 1997; accepted 17 February 1998)

Abstract

The title complex salt, [Co(H₂O)₆](C₅H₅O₄)₂, has been investigated by means of single-crystal X-ray diffraction. The structure of this compound is composed of discrete [C₃H₄(COO)(COOH)]⁻ anions and [Co(H₂O)₆]²⁺ cations. The geometrical parameters of the anion are comparable to those of the diammonium salt.

Comment

To our knowledge, there is no structural information about the salts of the first row transition metals with cyclopropane-1,1-dicarboxylic acid, but there are well known complexes with platinum (Huang *et al.*, 1990). The most important result of our investigations is the ionic character of the title compound, (I). The Co²⁺ ion is octahedrally coordinated by six water molecules. This is an interesting result because analogous transition metal complexes of cyclobutane-1,1-dicarboxylic acid show that the metal cations are coordinated by the carboxylate anions and not by the water molecules (Allan & Dalrymple, 1993).



The hydrogen cyclopropane-1,1-dicarboxylate anion possesses C_s point symmetry. The mirror plane is identical to the plane formed by the cyclopropane ring (C1—C3—C4) and also includes the acidic H atom. The exact position of the acidic H atom could not be located, but it should be bonded to those O atoms having the longer C—O distances [O4 and O4^{iv}; symmetry code: (iv) *x*, -*y*, *z*]. The values of 1.231 (4) Å for C2—O3, which is typical for a C=O double bond (Weast, 1972), and 1.290 (3) Å for C2—O4 differ significantly. As the O4...O4^{iv} distance is very short [2.490 (3) Å], the symmetrical hydrogen bond could be linear. However,

considering hybridization of the O atoms, an angular hydrogen bond is more likely. The torsion angle between the two carboxylic acid groups (O4—C2—C3—C2^{iv}) is 7.7 (9)° and the torsion angle between the carboxylic acid groups and the cyclopropane ring (O4—C2—C3—C1) is 40.1 (2)°.

The average bond length in the cyclopropane ring of the anion is 1.503 Å, in good agreement with the value found for cyclopropane-1,1-dicarboxylic acid (Meester *et al.*, 1971). The individual bond lengths within the cyclopropane ring vary from 1.460 (6) (C1—C4) to 1.525 (5) Å (C1—C3) (Table 1). The bond angles (Table 1) within this ring vary between 57.2 (3) and 61.4 (3)°. These correspond to the values found for the diammonium salt (Brehin *et al.*, 1992). The carboxylic acid groups show expected bond lengths, equal to those found from X-ray experiments of salts of various carboxylic acids (Jaulmes *et al.*, 1987). The C2—C3—C2^{iv} angle is about 120° and is consistent with *sp*² hybridization for the cyclopropyl C2 atom (McQuillin, 1972). The Co²⁺ ion is surrounded by six water molecules, forming an elongated octahedron in the O2ⁱⁱ—Co1—O2 axial direction [symmetry code: (ii) *x*, 1-*y*, *z*]. The four equatorial Co—O bond lengths are only slightly shorter than the two axial Co—O bond lengths (Table 1). The values of these bond lengths are in excellent agreement with other inorganic compounds, *e.g.* CoCl₂·6H₂O (Mizuno, 1960).

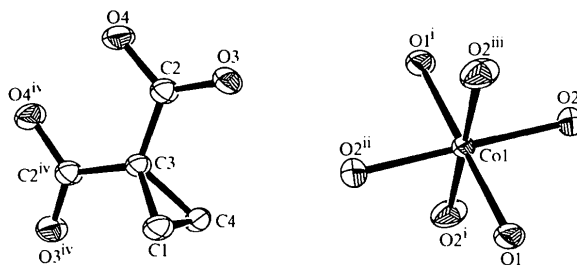


Fig. 1. ORTEP (Johnson & Burnett, 1997) drawing (30% probability ellipsoids) showing the atom-numbering scheme.

Experimental

The title compound was obtained by neutralizing cyclopropane-1,1-dicarboxylic acid (Singh & Danishefsky, 1975) with cobalt(II) carbonate in aqueous solution at 353 K. Single crystals suitable for X-ray analysis were grown by slow evaporation at room temperature.

Crystal data

[Co(H₂O)₆](C₅H₅O₄)₂
M_r = 425.20

Mo Kα radiation
λ = 0.71073 Å

Monoclinic

A2/m $a = 6.4014 (11) \text{ \AA}$ $b = 9.2804 (12) \text{ \AA}$ $c = 13.606 (2) \text{ \AA}$ $\beta = 93.126 (18)^\circ$ $V = 807.1 (2) \text{ \AA}^3$ $Z = 2$ $D_x = 1.750 \text{ Mg m}^{-3}$ $D_m = 1.72 \text{ Mg m}^{-3}$ D_m measured by pycnometry

Data collection

Stoe IPDS diffractometer

Rotation scans

Absorption correction: none

2853 measured reflections

680 independent reflections

657 reflections with

 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.107$ $S = 1.210$

680 reflections

65 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 1.4573P]$ where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 490 reflections

 $\theta = 1.45\text{--}24.2^\circ$ $\mu = 1.138 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Prism

 $0.3 \times 0.2 \times 0.1 \text{ mm}$

Light red

 $R_{\text{int}} = 0.034$ $\theta_{\text{max}} = 24.06^\circ$ $h = -7 \rightarrow 7$ $k = -10 \rightarrow 10$ $l = -15 \rightarrow 15$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.612 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.250 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

additional mirror plane which led to space group *A2/m*. An adequate absorption correction would have been desirable in this case, but because of lack of suitable software at the time of data collection it was not applied and it was decided not to apply refined absorption methods retrospectively. The H atoms were geometrically set as idealized CH₂ groups using a riding model.

Data collection: *IPDS* (Stoe & Cie, 1995). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON92* (Spek, 1992). Software used to prepare material for publication: *PLATON92* and *PLUTON* (Spek, 1990).

One of us (AP) would like to thank the Fonds der Chemischen Industrie (FCI) for financially supporting the work described in this manuscript.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1008). Services for accessing these data are described at the back of the journal.

References

- Allan, J. R. & Dalrymple, J. (1993). *Thermochim. Acta*, **221**, 205–210.
- Brehin, P., Kozelka, J. & Bois, C. (1992). *Acta Cryst.* **C48**, 2094–2096.
- Huang, Z., Li, C., Feng, J., Tang, W. & Zhou, Z. (1990). *Wuji Huaxue Xuebao*, **6**, 287–294.
- Jaulmes, P. S., Laruelle, P. & Fabregue, E. (1987). *Acta Cryst.* **C43**, 238–241.
- Johnson, C. K. & Burnett, M. N. (1997). *ORTEP*III. Version 1.0.2. University of Glasgow, Scotland.
- Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
- Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.
- McQuillin, F. J. (1972). *Alicyclic Chemistry*, p. 13. Cambridge University Press.
- Meester, M. A. M., Schenk, H. & MacGillavry, C. H. (1971). *Acta Cryst.* **B27**, 630–634.
- Mizuno, J. (1960). *J. Phys. Soc. Jpn.* **15**, 1412–1420.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Singh, R. K. & Danishefsky, S. (1975). *J. Org. Chem.* **40**, 2969–2970.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Spek, A. L. (1992). *PLUTON92. Molecular Graphics Program*. University of Utrecht, The Netherlands.
- Stoe & Cie (1995). *IPDS Software*. Version 2.86. Stoe & Cie, Darmstadt, Germany.
- Weast, R. C. (1972). In *Handbook of Chemistry and Physics*, 53rd ed. Cleveland, USA: CRC Press.

Table 1. Selected geometric parameters (\AA , $^\circ$)

Col—O1	2.056 (3)	C1—C3	1.525 (5)
Col—O2	2.081 (2)	C2—C3	1.500 (3)
O3—C2	1.231 (4)	C3—C4	1.524 (5)
O4—C2	1.290 (3)		
O1 ⁱ —Col—O1	180.0	O3—C2—C3	121.3 (2)
O1—Col—O2 ⁱⁱ	90.29 (9)	O4—C2—C3	116.2 (3)
O1—Col—O2 ⁱⁱⁱ	89.71 (9)	C2 ^{iv} —C3—C2	119.8 (3)
O2 ⁱⁱ —Col—O2	90.39 (14)	C2 ^{iv} —C3—C1	116.09 (18)
O2 ⁱⁱⁱ —Col—O2	89.61 (14)	C2—C3—C1	116.09 (18)
C4—C1—C3	61.4 (3)	C4—C3—C1	57.2 (3)
O3—C2—O4	122.5 (3)		

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

Different space groups were tried and it turned out that, although space group *A2* had twice as many parameters as *A2/m*, the *R* values were nearly identical. In addition, the Le Page symmetry test (Le Page, 1987, 1988) pointed towards an