

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71358 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1036]

## References

- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Jury, C. F. (1989). *Ligand Effects on the Structural, Electronic and Magnetic Properties of Copper(II) Carboxylate Complexes*. PhD thesis, Duquesne Univ., Pittsburgh, USA.
- Kawata, T., Ohba, S., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* **C48**, 1590–1594.
- Kawata, T., Uekusa, H., Ohba, S., Furukawa, T., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* **B48**, 253–261.
- MAC Science (1992). *CRYSTAN-GM. Program for X-ray Crystal Structure Analysis*. MAC Science, Tokyo, Japan.
- Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
- Steward, O. W., Kato, M., Chang, S.-C., Sax, M., Chang, C.-H., Jury, C. F., Muto, Y., Tokii, T., Taura, T., Pletcher, J. F. & Yoo, C. S. (1991). *Bull. Chem. Soc. Jpn*, **64**, 3046–3058.
- Steward, O. W., McAfee, R. C., Chang, S.-C., Piskor, S. R., Schreiber, W. J., Jury, C. F., Taylor, C. E., Pletcher, J. F. & Chen, C.-S. (1986). *Inorg. Chem.* **25**, 771–777.
- Uekusa, H., Ohba, S., Saito, Y., Kato, M., Steward, O. W., Tokii, T. & Muto, Y. (1990). *Acta Cryst.* **C46**, 1805–1812.
- Uekusa, H., Ohba, S., Tokii, T., Muto, Y., Kato, M., Husebye, S., Steward, O. W., Chang, S.-C., Rose, J. P., Pletcher, J. F. & Suzuki, I. (1992). *Acta Cryst.* **B48**, 650–667.
- Yamanaka, M., Ohba, S., Tokii, T., Jury, C. F., Steward, O. W. & Kato, M. (1993). *Acta Cryst.* **C49**, 1469–1473.

*Acta Cryst.* (1993). **C49**, 2100–2102

## Structure of Hexaaquacobalt Hydrogen Phthalate

B. M. KARIUKI AND W. JONES

*Department of Chemistry, University of Cambridge, Cambridge CB2 1EP, England*

(Received 28 September 1992; accepted 11 June 1993)

### Abstract

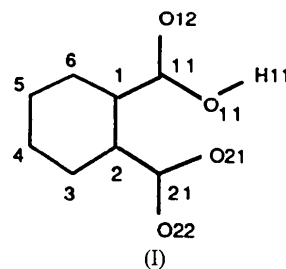
The structure of  $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_5\text{O}_4)_2$  consists of octahedrally coordinated cobalt cations with a mean Co—O distance of 2.091 (10) Å. Anion–anion and anion–water hydrogen bonding is observed.

### Comment

We have reported elsewhere on the crystal structures of various magnesium hydrogen phthalates (Kariuki

& Jones, 1989, 1990, 1992). Our principal aim has been to understand the structural influences involved in the decomposition of peracid salts, as well as the relationship between the solid intermediates observed during decomposition – some of these were amorphous. One of the phases generated during decomposition could not be obtained in a form suitable for single-crystal studies. The structure of the cobalt analogue, however, has been determined and is reported here. The powder X-ray patterns and the computer simulation of the patterns confirm that the structures are identical.

The structure consists of cobalt cations, water molecules and hydrogen phthalate anions (I).



The  $\text{Co}^{2+}$  cations occupy centres of symmetry. Each Co atom is coordinated to six molecules of water in the form of an octahedron with a mean Co—O distance of 2.091 (10) Å. There are two anions per cation. In the carboxylate group, the two C—O bond lengths are very similar [mean = 1.257 (10) Å]. The maximum deviation from the least-squares plane of the benzene ring is 0.0098 Å [C(5)]. The dihedral angle between the plane through the carboxylate group [O(21)—C(21)—O(22)] and the ring is 71.8°. The carboxylic group [O(11)—C(11)—O(12)] lies almost in the plane of the ring (dihedral angle = 7.0°), while the planes through the two carboxyl groups are at 72.2° to each other. The torsion angle H(11)—O(11)—C(11)—O(12) is  $-4.1^\circ$ .

The crystal structure is composed of layers of ions parallel to the (001) plane (Fig. 1). In the structure, double layers of anions alternate with those of the hydrated cations,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ .

Bonds of the types (a) anion–anion and (b) anion–water are found in the crystal. Bonds of the latter type result in the formation of [anion—Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>—anion] ‘sandwiches’. The anion–anion hydrogen bonding occurs between carboxylic and carboxylate groups of neighbouring ions, forming chains parallel to the *a* axis.

Similar hydrogen-bonding contacts and crystal-packing features are observed in another polymorph of hexaaquacobalt hydrogen phthalate (Adiwidjaja, Rossmannith & Küppers, 1978). These two crystal forms fall in the class of hydrogen phthalates displaying ‘sandwich’ packing (Kariuki & Jones, 1992).

A third modification (Küppers, 1990) is characterized by intramolecular hydrogen bonding and packs in 'sheets'.

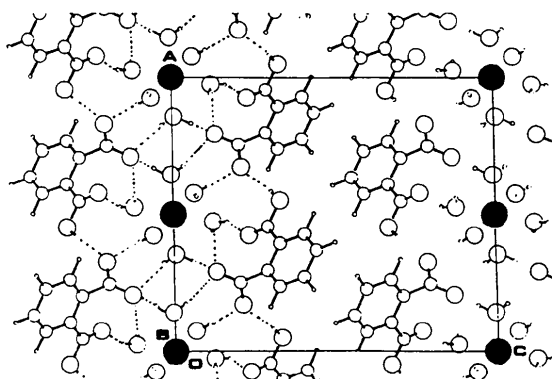
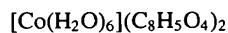


Fig. 1. Structure viewed along the *b* axis (*PLUTO*; Motherwell & Clegg, 1978). The filled circles represent cobalt cations and the broken lines show hydrogen-bonding contacts.

## Experimental

### Crystal data



$M_r = 497.28$

Monoclinic

$P2_1/a$

$a = 12.760(6) \text{ \AA}$

$b = 5.319(4) \text{ \AA}$

$c = 14.933(8) \text{ \AA}$

$\beta = 91.05(4)^\circ$

$V = 1013.3 \text{ \AA}^3$

$Z = 2$

$D_x = 1.61 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9 - 14^\circ$

$\mu = 0.913 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Plates

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

Pink

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction: none

2072 measured reflections

1779 independent reflections

1173 observed reflections

$[F > 3\sigma(F)]$

$R_{\text{int}} = 0.07$

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

$h = -15 \rightarrow 15$

$k = 0 \rightarrow 6$

$l = 0 \rightarrow 17$

2 standard reflections

frequency: 180 min

intensity variation: none

### Refinement

Refinement on  $F$

$R = 0.056$

1173 reflections

171 parameters

No weights applied

$(\Delta/\sigma)_{\text{max}} = 0.285$

$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.19 \text{ e \AA}^{-3}$

Atomic scattering factors from *SHELX76* (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and temperature factors ( $\text{\AA}^2$ )

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Co(1)	0.5000	0.0	0.0	0.025 (1)
O(1)	0.5258 (4)	0.1789 (11)	-0.1215 (4)	0.032 (3)
O(2)	0.6446 (4)	-0.1938 (14)	-0.0050 (4)	0.048 (4)
O(3)	0.5764 (4)	0.2952 (11)	0.0647 (4)	0.036 (3)
O(12)	0.9241 (4)	0.2967 (11)	0.2328 (4)	0.042 (3)
O(11)	1.0492 (4)	0.1893 (13)	0.3323 (4)	0.042 (3)
O(21)	0.7923 (3)	-0.0569 (10)	0.1313 (3)	0.035 (3)
O(22)	0.6725 (4)	0.1359 (12)	0.2117 (3)	0.043 (3)
C(2)	0.7968 (5)	-0.1117 (14)	0.2899 (4)	0.027 (4)
C(6)	0.9278 (5)	-0.1751 (16)	0.4063 (5)	0.035 (4)
C(21)	0.7529 (4)	0.0007 (18)	0.2049 (4)	0.029 (3)
C(11)	0.9550 (5)	0.1634 (15)	0.2924 (5)	0.030 (4)
C(1)	0.8937 (5)	-0.0475 (13)	0.3303 (4)	0.025 (4)
C(3)	0.7381 (5)	-0.2981 (17)	0.3279 (5)	0.039 (4)
C(5)	0.8689 (6)	-0.3652 (17)	0.4432 (5)	0.042 (4)
C(4)	0.7728 (6)	-0.4230 (17)	0.4038 (5)	0.046 (5)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O(1)—Co(1)	2.080 (10)	O(2)—Co(1)	2.116 (10)
O(3)—Co(1)	2.077 (10)	C(4)—C(5)	1.385 (13)
C(11)—O(12)	1.199 (10)	C(11)—O(11)	1.340 (10)
C(21)—O(21)	1.254 (9)	C(21)—O(22)	1.259 (10)
C(21)—C(2)	1.503 (11)	C(1)—C(2)	1.408 (11)
C(3)—C(2)	1.371 (12)	C(1)—C(6)	1.386 (11)
C(5)—C(6)	1.380 (13)	C(1)—C(11)	1.485 (12)
C(4)—C(3)	1.381 (13)		
O(2)—Co(1)—O(1)	92.2 (6)	O(3)—Co(1)—O(1)	88.9 (6)
O(3)—Co(1)—O(2)	89.1 (6)	C(5)—C(4)—C(3)	120.7 (9)
C(3)—C(2)—C(21)	116.1 (7)	C(3)—C(2)—C(1)	118.7 (7)
C(5)—C(6)—C(1)	121.4 (8)	O(22)—C(21)—O(21)	123.4 (7)
C(2)—C(21)—O(21)	119.6 (7)	C(2)—C(21)—O(22)	116.8 (6)
O(11)—C(11)—O(12)	123.4 (8)	C(1)—C(11)—O(12)	124.1 (7)
C(1)—C(11)—O(11)	112.5 (7)	C(6)—C(1)—C(2)	119.5 (7)
C(11)—C(1)—C(2)	119.0 (7)	C(11)—C(1)—C(6)	121.5 (7)
C(4)—C(3)—C(2)	121.2 (8)	C(4)—C(5)—C(6)	118.5 (8)
C(1)—C(2)—C(21)	125.2 (7)		

The material was obtained by reacting a mixture of basic cobalt(II) carbonate  $[\text{2CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}]$ , phthalic acid (mol ratio 1:6) and water. This was heated until foaming stopped (after about 30 min). The filtrate was then kept at 328 K to evaporate off the solvent.

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). All non-H atoms were assigned anisotropic thermal parameters. The positions of the ring H atoms were fixed geometrically and the difference Fourier synthesis map revealed the locations of the carboxylic and water protons.

Support of the Cambridge Commonwealth Trust (studentship for BMK) and Interlox Ltd is appreciated.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71391 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1032]

## References

- Adiwidjaja, G., Rossmanith, E. & Küppers, H. (1978). *Acta Cryst.* **B34**, 3079–3083.  
 Kariuki, B. M. & Jones, W. (1989). *Acta Cryst.* **C45**, 1297–1299.

- Kariuki, B. M. & Jones, W. (1990). *Mol. Cryst. Liq. Cryst.* **186**, 45–52.
- Kariuki, B. M. & Jones, W. (1992). *Mol. Cryst. Liq. Cryst.* **211**, 233–255.
- Küppers, H. (1990). *Z. Kristallogr.* **192**, 97.
- Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

*Acta Cryst.* (1993). **C49**, 2102–2107

## Structures of 2,6-Bis(aminomethyl)pyridine (bamp) Complexes of Fe<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Mn<sup>II</sup>, Co<sup>III</sup> and Cu<sup>II</sup>

PIERRE BONHÔTE, MICHEL FERIGO,  
HELEN STOECKLI-EVANS\* AND WERNER MARTY †

*Institut de Chimie, Université de Neuchâtel,  
Avenue de Bellevaux 51, CH-2000 Neuchâtel,  
Switzerland*

(Received 18 September 1992; accepted 27 April 1993)

### Abstract

The structures of bis[2,6-bis(aminomethyl)pyridine]iron dichloride hydrate [(I), Febamp], bis[2,6-bis(aminomethyl)pyridine]nickel dichloride hydrate [(II), Nibamp], bis[2,6-bis(aminomethyl)pyridine]zinc dichloride hydrate [(III), Znbamp], bis[2,6-bis(aminomethyl)pyridine]manganese dichloride hydrate [(IV), Mnbamp], bis[2,6-bis(aminomethyl)pyridine]cobalt trichloride hemihydrate [(V), Cobamp] and chloro[2,6-bis(aminomethyl)pyridine]copper perchlorate [(VI), Cubamp] are reported. The bamp ligand complexes in a tridentate manner and except in the case of Cu<sup>II</sup>, which is mono-tridentate coordinated, the complexes are all bis-tridentate. The Fe<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> complexes are isomorphous. In general, the *M*—N(pyridine) distances are shorter than normal, while the *M*—N(amino) distances are slightly longer than normal.

### Comment

In our search for ligands that will coordinate in a bis-tridentate fashion to 3*d* metals and Zn, we investigated the structural features of the title compounds. The 2,6-bis(aminomethyl)pyridine (bamp) ligand was originally

synthesized by Lions & Martin (1957) starting from 2,6-dimethylpyridine. They also synthesized the Fe<sup>II</sup> and Ni<sup>II</sup> bis-complexes  $[M(\text{bamp})_2]^{2+}$ . Schwarzenbach, Boesch & Egli (1971) synthesized the same ligand starting from 2,6-pyridinedicarbonitrile and prepared compounds of the form  $[\text{Co}(\text{bamp})X_3]^{3+}$ , where *X* = H<sub>2</sub>O, Cl, NO<sub>2</sub>. Tinner & Marty (1977) used bamp to selectively produce meridional coordination in Co<sup>III</sup> complexes when other ligands were present, however,  $[\text{Co}(\text{bamp})_2]^{3+}$  was a major reaction product. Here, we describe the systematic investigation of the crystal structures of complexes of bamp with Fe<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Mn<sup>II</sup>, Co<sup>III</sup> and Cu<sup>II</sup> [(I)–(VI), respectively]. With the exception of the bis-complexes of Mn<sup>II</sup> (IV) and Zn<sup>II</sup> (III), the syntheses of these complexes have been described previously (Lions & Martin, 1957; Schwarzenbach *et al.*, 1971; Tinner & Marty, 1977; Couturier & Petitfaux, 1975), but their crystal structures have not been reported. bamp behaves as a tridentate ligand in all six complexes and except in the case of Cu<sup>II</sup> (VI), which is mono-tridentate coordinated, the complexes are all bis-tridentate. The Fe<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> complexes [(I), (II) and (III)] are isomorphous, with two molecules per asymmetric unit. The unit cell contains eight molecules with approximate C<sub>2</sub> symmetry and four with crystallographic C<sub>2</sub> symmetry (Fig. 1). The geometry of the metal centres is distorted octahedral in all three complexes. The Mn<sup>II</sup> complex (IV) crystallizes in the same space group, is also a bis-tridentate complex, but is not isomorphous with the previous three complexes. The cation has crystallographic C<sub>2</sub> symmetry (Fig. 2) and the geometry of the metal centre is distorted octahedral. In the case of the Co<sup>III</sup> complex (V), the geometry of the metal centre is also distorted octahedral and the complex has only approximate C<sub>2</sub> symmetry (Fig. 3). In the Cu<sup>II</sup> complex (VI), the coordination is best described as square pyramidal (Fig. 4). The Cu atom is displaced by 0.118 (2) Å from the best plane through atoms N1, N2, N3 and C11 [planar to within 0.014 (2) Å]. The apical position is occupied by atom C11<sup>i</sup> of a molecule related by the twofold screw axis in the *c* direction. The Cu···C11<sup>i</sup> distance is 2.936 (1) Å, while Cu···C11<sup>ii</sup> (atom C11<sup>ii</sup> is displaced by one unit cell in the *c* direction) is 3.695 (1) Å. The Cu···Cu<sup>i</sup> distance is 4.079 (1) Å. This situation is illustrated in Fig. 5.

A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed a number of structures with the ligand 2-aminomethylpyridine. In Table 4 we compare the geometry of the various metal centres in the two series of compounds. While the N—*M*—N bond angles are similar, it can be seen that in general the *M*—N(py) distances in the title compounds are shorter than those in the 2-aminomethylpyridine complexes. Likewise, the *M*—N(amino) distances are generally longer. This could be an indication of a higher degree of delocalization in the *M*—N(py) bond for the bamp complexes. The conformations of the chelate rings in the bamp complexes

† Deceased.