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Hydrogen Bonding in $Be[C_2(COO)_2] \cdot 4H_2O$—A Neutron Diffraction Study at 15 K

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Lattice constants for orthorhombic $Be[C_2(COO)_2] \cdot 4H_2O$ at 15 K are $a = 1006.4(6)$, $b = 663.0(4)$, and $c = 1263.1(7)$ pm, $Z = 4$, space group *Cmcm*. Anisotropic refinement on single crystal neutron diffraction data led to $R_w = 0.0229$. The crystal structure is made up by slightly distorted $Be(H_2O)_4^{2+}$ tetrahedra ($Be–H_2O$ 161.3 and 162.0 pm) and planar $[C_2(COO)_2]^{2-}$ anions linked together by strong ($O\cdots H_2O$ 262.0 and 263.5 pm) asymmetric hydrogen bonds. A layer-like arrangement extending parallel to (010) consisting of $[C_2(COO)_2]^{2-}$ anions and hydrogen bound water molecules of the $Be(H_2O)_4^{2+}$ tetrahedra is the primary structural feature of $Be[C_2(COO)_2] \cdot 4H_2O$. These layers are stacked in . . . *ABAB*. . . sequence and interlinked by coordinative bonds between Be^{2+} and H_2O to yield a rigid three-dimensional framework. O–H bond lengths corrected for thermal motion are 100.4 and 100.5 pm, respectively. The H–O–H angles are rather wide (111.12 and 114.36°). The anion has *mmm* symmetry. © 1992 Academic Press, Inc.

Introduction

Many inorganic derivatives of acetylene dicarboxylic acid containing polyvalent metal cations have been reported to be unstable and to tend to decompose (*1–4*). Hence structural studies are mostly available on alkaline compounds (*5–7*). Recently we prepared a stable beryllium acetylene dicarboxylate of composition $Be[C_2(COO)_2] \cdot 4H_2O$ featured by strong hydrogen bonds (*8*). In order to shed light on the particular details of these hydrogen bonds and to study influences on hydrogen bonding caused by strongly polarizing ions like Be^{2+}, we conducted a high-resolution–low-temperature neutron-diffraction study of $Be[C_2(COO)_2] \cdot 4H_2O$. Furthermore, we provide structural data of the acetylene dicarboxylate dianion of high accuracy unbiased by effects of thermal smearing and deviations from spherical of the electron density distribution around the carbon and oxygen atoms.

Experimental

A single crystal of $Be[C_2(COO)_2] \cdot 4H_2O$ grown in aqueous silica gel as described in

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TABLE I

ATOMIC PARAMETERS FOR $Be[C_2(COO)_2] \cdot 4H_2O$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Be	0.5	0.17249(11)	0.75	0.0041(2)	0.0067(2)	0.0047(2)	0	0	0
O(w1)	0.36269(7)	0.29805(11)	0.75	0.0062(2)	0.0105(2)	0.0047(2)	0.0039(2)	0	0
O(w2)	0.5	0.04365(10)	0.64102(5)	0.0042(2)	0.0098(3)	0.0069(2)	0	0	−0.0036(2)
O(1)	0.26237(4)	0.06921(7)	0.41948(3)	0.0038(1)	0.0081(2)	0.0046(1)	0.0005(1)	0.0005(1)	0.0015(1)
C(1)	0.20537(5)	0	0.5	0.0027(2)	0.0053(2)	0.0037(2)	0	0	0.0000(2)
C(2)	0.05988(5)	0	0.5	0.0026(2)	0.0088(2)	0.0067(2)	0	0	0.0009(2)
H(1)	0.31953(10)	0.35135(16)	0.68535(8)	0.0182(4)	0.00245(4)	0.0134(3)	0.0056(3)	−0.0024(3)	0.0035(3)
H(2)	0.58273(9)	−0.01127(16)	0.60977(8)	0.0134(3)	0.0236(4)	0.0186(4)	0.0032(4)	0.0025(3)	−0.0055(3)

Note. The anisotropic displacement factor takes the form $\exp(-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots))$.

Ref. (*8*) with dimensions 1.1 × 1.1 × 3.0 mm was chosen for data collection on the D9 four-circle diffractometer at the Institut Laue-Langevin, Grenoble, France, under the following experimental conditions: measuring temperature 15 K chosen to reduce the effects of thermal motion and consequently to obtain a better definition of positional parameters; orthorhombic cell with a = 1006.4(6), b = 663.0(4), c = 1263.1(7) pm (at 15 K); $V = 841.1 \times 10^6$ pm^3, M_r = 193.2, Z = 4, D_{calc} = 1.53 g cm^{-3}, space group *Cmcm* (no. 63). A marked foreshortening of the b axis is caused by cooling, whereas a and c remain nearly unaffected (295 K, X-ray data: a = 1004.7(1), b = 675.0(1), c = 1262.4(2) pm (*8*)). Data collection was carried out with thermal neutrons with mean wavelength 70.71(4) pm, Cu (220) monochromator in transmission, λ/2 contamination filtered by 0.25-mm iridium foil. A total of 1737 reflections up to θ_{max} = 42.5° were recorded within one octant of reciprocal space. A numerical absorption correction (*9*) (calculated μ = 1.06 cm^{-1}) was applied. After merging multiple measured identical reflections, a set of 1682 unique reflections was obtained (R_{merge} = 0.0203). Thereof 1347 had $I > 2\sigma_I$ and were used for structure refinement. Scattering lengths were taken from Ref. (*10*). Refinement on $|F|$ was carried out employing the program system PROMETHEUS (*11*), minimizing $\Sigma w(|F_o| - |F_c|)^2$ and assigning weights $1/\sigma^2_{|F|}$ derived from counting statistics. Starting parameters were obtained from the results of the X-ray structure analysis (*8*). No significant anharmonic motion of the hydrogen atoms could be detected. Full-matrix least-squares refinement with harmonically anisotropic displacement factors for all atoms and a six-parameter anisotropic extinction correction (*12*) converged at R = 0.0321 and R_w = 0.0229, GOF = 1.55 (60 parameters). Final atomic parameters are given in Table I. Supplementary material has been deposited.[1]

Results and Discussion

Be^{2+} is situated on Wyckoff-position 4*c* of space group *Cmcm* (point symmetry *m*2*m*). It is coordinated to four water molecules occupying a crystallographic mirror plane (2× O(w1), 2× O(w2)) in a slightly distorted tetrahedral fashion (Fig. 1). Be, O(w1), and both H(1) as well as Be, O(w2), and both H(2) lie almost perfectly within a common plane pointing to bonding forces between Be^{2+} and H_2O being mainly domi-

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[1] Further details of the structure determination have been deposited as Supplementary Publication No. CSD55664. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

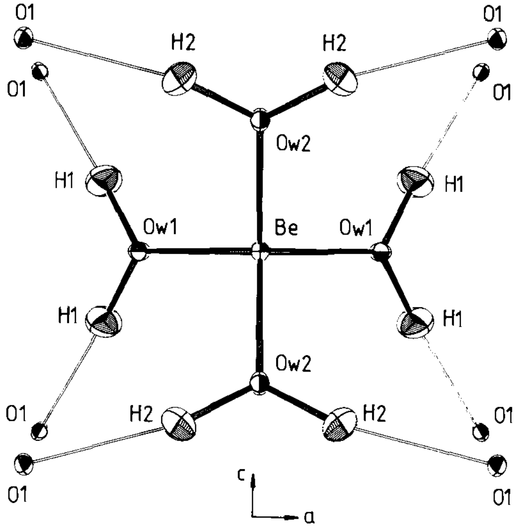

FIG. 1. The $Be(H_2O)_4^{2+}$ coordination tetrahedron with the acceptor O atoms viewed from the [010] direction (15 K, 50% probability ellipsoids). The strong attracting force of the acceptor O atoms and the desire to achieve nearly straight hydrogen bonds are obviously responsible for the wide H–O–H angles.

TABLE III

WATER AND HYDROGEN BONDS (DISTANCES IN pm, ANGLES IN (°))

	Uncorrected	With riding model correction
H(1)–O(w1)	99.0(1)	100.4
H(1)–O(1)	164.6(1)	
O(w1)–O(1)	263.5(1)	
H(2)–O(w2)	99.1(1)	100.5
H(2)–O(1)	164.8(1)	
O(w2)–O(1)	262.0(1)	
H(1)–O(w1)–H(1)′	111.12(11)	
O(w1)–H(1)–O(1)	175.70(10)	
H(2)–O(w2)–H(2)′	114.36(10)	
O(w2)–H(2)–O(1)	165.98(10)	

nated by electrostatic interactions. Be–H_2O contacts are rather short (161.3 and 162.0 pm, Table II) and cover the lower range reported for fourfold Be–O coordination (*13*). This obviously reflects water molecules with oxygen atoms being negatively polarized to a considerable extent due to strong hydrogen bonding ($H_2O \cdots O$ 262.0 and 263.5 pm, Table III) between H_2O and the oxygen atoms of the acetylene dicarboxylic acid dianion.

Short Be–H_2O distances have recently been observed as well in beryllium squarate trihydrate (*14*) ($BeC_4O_4 \cdot 3H_2O$) in the range between 159.7 and 162.5 pm. These water molecules are involved in short hydrogen bonds to the squarate dianion with $H_2O \cdots O$ contacts between 260.0 and 268.5 pm. Similar results have also been obtained by a recent low temperature neutron-diffraction study (*15*) on the mineral mellite ($Al_2[C_6(COO)_6] \cdot 16H_2O$), which is a naturally occurring derivative of benzene hexacarboxylic acid (mellitic acid). The crystal structure of mellite is made up of $Al(H_2O)_6^{3+}$ octahedra linked to the heaxaanion by strong hydrogen bonds. $O \cdots O$ contacts in hydrogen bonds between water molecules bound to Al^{3+} and oxygen atoms of the $[C_6(COO)_6]^{6-}$ anion range from 257.6 to 266.4 pm.

TABLE II

THE COORDINATION OF Be (DISTANCES IN pm, ANGLES IN (°))

Be–O(w1)	161.3(1)	2×	Be–O(w2)	162.0(1)	2×
Angles *A*–Be–*B*			Distance *A*–*B*		
A/*B*					
O(w1)/O(w1)′	117.87(6)		276.4		
O(w1)/O(w2)	105.79(2)	4×	257.9		
O(w2)/O(w2)′	116.36(5)		275.3		

The H–O–H angles in $Be[C_2(COO)_2] \cdot 4H_2O$ are considerably greater than tetrahedral (111.12 and 114.36°, Table III) resembling the value found by neutron diffraction in an early study on the crystal structure of $BeSO_4 \cdot 4H_2O$ (112.7°), which contains $Be(H_2O)_4^{2+}$ tetrahedra linked to the SO_4^{2-} anions by hydrogen bonds (*16*). It has been assumed that wide H–O–H angles occur if the bisector of the lone pairs of the water molecule points toward a polyvalent metal cation (*17*). However, this obviously represents too simple a model, since it is confirmed with $Be[C_2(COO)_2] \cdot 4H_2O$ and

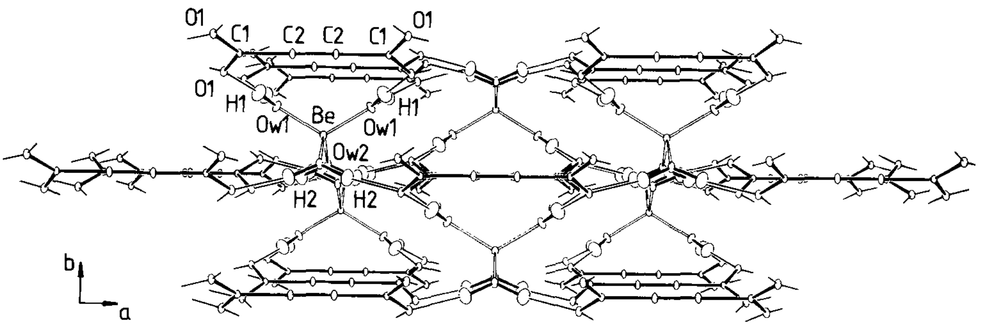

FIG. 2. Layers made up by hydrogen bonded $[C_2(COO)_2]^{2-}$ anions extending parallel to (010) are stacked in . . . *ABAB*. . . sequence and interlinked by coordinative bonds between Be^{2+} and H_2O (open bond sticks).

$BeSO_4 \cdot 4H_2O$, but not with $Al_2[C_6(COO)_6] \cdot 16H_2O$ (mellite). The crystal structure of mellite has four unique water molecules with this peculiar coordination mode. Nevertheless, three of these water molecules show H–O–H angles between 104.00 and 105.59°, resembling the value known for water molecules in the vapor phase, and only one water molecule has a considerably wider H–O–H angle (111.77°).

The $[C_2(COO)_2]^{2-}$ anions are aligned parallel to [100] with respect to the C≡C triple bond (Fig. 2). Layers of neighboring anions connected by water molecules via hydrogen bonds may be considered as the principle structural feature of $Be[C_2(COO)_2] \cdot 4H_2O$. These layers extend parallel to (010) and are stacked along [010] in . . . *ABAB*. . . sequence. Adjacent layers are linked together by coordinative bonds between H_2O and Be^{2+} yielding a rigid three-dimensional framework (Fig. 3). Despite this connection mode, a markedly anisotropic shrinkage was observed on cooling, affecting mainly the [010] direction.

A TLS analysis (*18*) applied to Be and the four water oxygen atoms of its coordination tetrahedron showed significant rigid body movement even at 15 K (R_g = 0.0358). The *L* tensor elements indicate a small librational movement with an amplitude of approx 2.5° with respect to an axis running through Be and parallel to [101]. Translational motion is most pronounced in the [010] direction for both the Be coordination tetrahedron and the $[C_2(COO)_2]^{2-}$ anion. The latter librates along an axis defined by the C≡C triple bond (R_g = 0.1184) with an amplitude of approx 4°. The corresponding terms for bond length correction are negligible (0.1–0.2 pm). Similar rigid body motions were found at room temperature from X-ray data, however with higher amplitudes (*8*). The inclination of the anions to the (010) plane is virtually unaffected on cooling (24.3° at 15 K, 23.7° at 295 K (X-ray)). Hence the marked foreshortening of the crystallographic *b* axis is caused by diminution of the considerably anisotropic thermal motion.

The acetylene dicarboxylic acid dianion is planar with *mmm* symmetry. The C≡C triple bond length (120.5 pm, Table IV) corresponds well with the value claimed by spectroscopic results (121 pm) (*19*). However, it is in evident contrast to the X-ray refinement that gave 118.8 pm (*8*). This artificial foreshortening is obviously caused by significant deviations from spherical of the electron density distribution of the *sp* hybridized carbon atoms. This bias consequently affects the C–C single bond length outside the corresponding limits of experi-

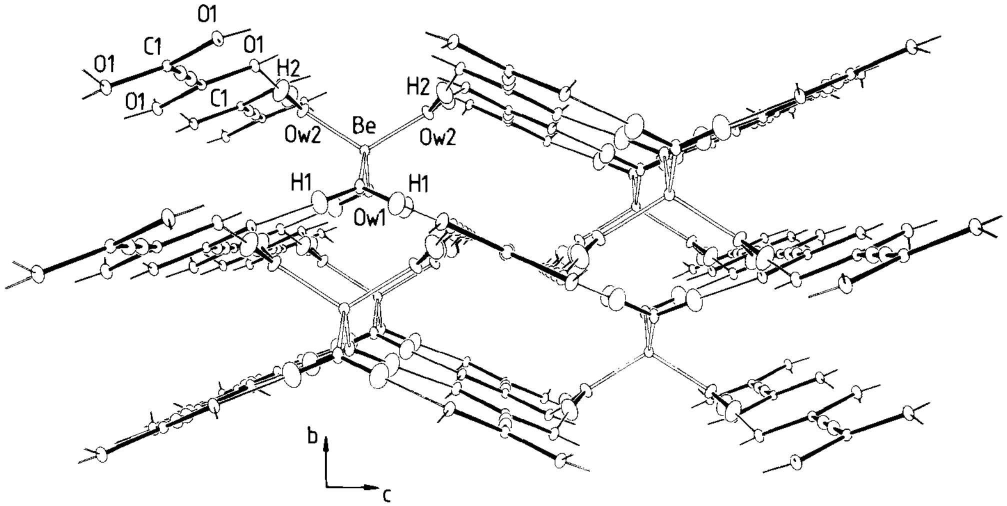

FIG. 3. A view parallel to the C≡C triple bond ([100] direction) shows the corrugation of the hydrogen bonded layers.The $[C_2(COO)_2]^{2-}$ anions are inclined to the (010) plane by 24°.

TABLE IV

THE ACETYLENEDICARBOXYLIC ACID DIANION (DISTANCES IN pm, ANGLES IN (°))

	Neutron 15 K	X-ray 295 K (*8*)
C(1)-O(1)′	125.5(1)	125.0(2)
C(1)-C(2)	146.4(1)	147.5(2)
C(2)-C(2)′	120.5(1)	118.8(3)
O(1)-C(1)-O(1)′	125.58(5)	126.08(18)
O(1)-C(1)-C(2)	117.21(3)	116.96(10)
C(1)-C(2)-C(2)′	180.0	180.0

mental error as well (neutron, 146.4 pm; X-ray, 147.5 pm). The distance between the two carbon atoms of the carboxylate groups, however, remains nearly the same (neutron, 413.3 pm; X-ray, 413.8 pm). The differences of the C–O bond lengths found by the complementary neutron and X-ray diffraction are less pronounced (125.5 and 125.0 pm, respectively).

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