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Hydrogen Bonding in the Chain-like Coordination Polymer $ZnC_4O_4 \cdot 4H_2O$: A Neutron Diffraction Study

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Monoclinic crystals of $ZnC_4O_4 \cdot 4H_2O$ were grown in an aqueous silica gel: lattice constants a = 901.2(2) pm, b = 1333.6(3) pm, c = 674.6(2) pm, β = 99.33(2)°, Z = 4, space group $C2/c$. Anisotropic refinement on single-crystal neutron diffraction data led to R_w = 0.0294 including anharmonic thermal parameters for hydrogen atoms and oxygen atoms of the water molecules. The coordination polyhedron of Zn^{2-} is a slightly distorted octahedron formed by four water molecules and two $O_{squarate}$ atoms which are bound in the *trans* position to the C_4 ring of the dianion (Zn–O, 207.6(1)–212.6(1) pm). Infinite chains consisting of Zn^{2+} and $C_4O_4^{2-}$ are the main feature of the crystal structure. Adjacent chains are connected by asymmetric hydrogen bonds between H_2O and the $O_{squarate}$ atoms. The squarate dianion is ideally planar. The crystallographically independent C–O bond lengths are identical (2 × 125.0(1) pm) although the $O_{squarate}$ atoms are differently coordinated by Zn^{2+} and H. The C–C bond lengths are slightly different (146.4(1) and 146.7(1) pm).

Introduction

Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) belongs to the family of the so-called oxocarbon acids. The free acid has been used in complex chemistry. Beck *et al.* (*1*) reported various reaction pathways of squaric acid with triphenylphosphine platinum (0) compounds. The squarate dianion also provides interesting applications in structural and coordination chemistry, since due to resonance effects its four oxygen atoms are to be regarded as equivalent, potentially yielding a fourfold monodentate ligand capable of forming various coordination polymers. Squaric acid itself is a well-investigated ferroelectric (*2, 3*).

Many different types of inorganic squarates have already been studied (*4, 5*). $C_4O_4^{2-}$ is often found with less than its four oxygen atoms coordinated to metal cations (*6–10*). This, however, does not result in C–O bond lengths differing sufficiently to allow discernment between the differently coordinated $O_{squarate}$ atoms. Instead, the C–O and C–C distances are typical of completely delocalized π-electrons indicating that reso-

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nance is not disturbed by inequivalent coordination. This surprising fact can be explained by considering the water of crystallization. Close distances found between H_2O and those O_{squarate} atoms not bound to metal cations point to the existence of strong hydrogen bonds.

These assumptions were supported by the single-crystal neutron diffraction study on $BaC_4O_4 \cdot 3H_2O$ (*11*) which indicated that the bonding between the O_{squarate} atoms and noncarbon neighbors is dominated by electrostatic and ionic interactions. In connection with these results it was desirable to study squarates containing cations with higher polarizing effects than Ba^{2+}. $ZnC_4O_4 \cdot 4H_2O$ was chosen since two of the four O_{squarate} atoms are not bound to Zn^{2+} and interatomic distances indicate these oxygen atoms are involved in hydrogen bonds. $ZnC_4O_4 \cdot 4H_2O$ was first prepared and characterized by Riegler (*4*) and is a member of a family of isotypic compounds of general formula $M^{\mathrm{II}}C_4O_4 \cdot 4H_2O$ (M = Mn, Fe, Co, Ni, Zn) which can be converted during a solid-state reaction to clathrate compounds of formula $M^{\mathrm{II}}C_4O_4 \cdot 2H_2O \cdot \frac{1}{3}X$ entrapping small particles such as gases or solvent molecules (*4, 12–14*).

Experimental Details and Structure Refinement

Colorless single crystals of $ZnC_4O_4 \cdot 4H_2O$ were grown in an aqueous silica gel by the following method: A mixture of 60 ml 1 M HNO_3 and 90 ml 0.1 M $K_2C_4O_4$ was adjusted to pH 5 by slowly adding 2 M $K_2H_2SiO_4$ solution. The gelling mixture was poured into glass tubes of 1.5 cm diameter and 45 cm length and allowed to set. On top of the solidified gels 10 ml 0.25 M $Zn(NO_3)_2$ solution was placed. Within several months crystals up to approx 2 mm diameter and 1 cm length were obtained. A single crystal with well-developed faces and dimensions 1.6 × 1.6 × 3.2 mm was chosen for data collection.

Crystal Data and Data Collection

Monoclinic, a = 901.2(2) pm, b = 1333.6(3) pm, c = 674.6(2) pm, β = 99.33(2)°, $V = 800.04 \times 10^6$ pm^3 (calculated from single-crystal X-ray data, 293 K, λ = 71.07 pm (*4*)). The space group $C2/c$ (No. 15) is confirmed by structure refinement and E-statistics, Z = 4, M_r 249.47, D_x = 2.07 g·cm^{-3}. Neutron data collection carried out with the D9B four-circle diffractometer at the ILL, 296 K, λ = 84.94 pm (H3 beam tube), Cu (220) monochromator in transmission, $\lambda/2$ contamination filtered by 0.62-mm erbium foil, μ = 1.36 cm^{-1}, numerical absorption correction, anisotropic extinction correction applied according to the model of Becker and Coppens (*15*) providing allowance for secondary and primary extinction ($y_{\mathrm{min.}} = 0.12$ for $\bar{1}\bar{1}0$ and $1\bar{1}0$), $\omega - 2\theta$ scan, $\theta_{\mathrm{max.}} = 44°$, 3426 reflections recorded, 1925 unique, merging R = 0.0382, refinement on $|F|$, quantity minimized $\Sigma w(|F_o| - |F_c|)^2$, weights $\sigma_{|F|}^{-2}$ derived from counting statistics, scattering lengths from reference (*16*), reflections with $I < 3\sigma_I$ considered as unobserved (1471 reflections observed).

Starting parameters for the refinements were obtained from the X-ray structure determination (*4*). H positions were found in difference Fourier maps. For H atoms and the oxygen atoms of the water molecules anharmonic thermal parameters were refined (Gram-Charlier expansion, third-order moments, program system PROMETHEUS (*17*). C^{ijk} not differing distinctly from their e.s.d.'s in preliminary refinements were set to zero during the final cycles. Mean atomic positions of H along the covalent O–H bond were calculated from the anharmonic thermal parameters and employed for calculation of bond lengths and angles involving H. In this way, it was possible to compensate for system-

TABLE I

ATOMIC PARAMETERS FOR $ZnC_4O_4 \cdot 4H_2O$

Atom	X	Y	Z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	.75	.25	0	.0147(3)	.0111(3)	.0220(4)	.0035(2)	.0012(3)	−.0006(3)
O(*w*1)	.31922(18)	.78820(12)	.29907(18)	.0318(3)	.0309(3)	.0242(3)	.0155(3)	−.0050(3)	−.0096(3)
O(*w*2)	.62384(12)	.13026(11)	.09784(15)	.0259(3)	.0158(3)	.0342(4)	.0014(2)	.0087(3)	.0008(3)
O(1)	.55408(6)	.33302(4)	.99026(10)	.0156(2)	.0088(2)	.0343(3)	.0029(2)	.0021(2)	−.0019(2)
O(2)	.25309(6)	.45798(4)	.99523(11)	.0143(2)	.0136(2)	.0403(4)	−.0008(2)	.0061(2)	−.0006(2)
C(1)	.52663(5)	.42474(3)	.99577(7)	.0130(2)	.0083(1)	.0177(2)	.0019(1)	.0020(1)	−.0009(1)
C(2)	.38768(5)	.48143(3)	.99750(7)	.0129(2)	.0092(2)	.0197(2)	.0012(1)	.0029(1)	−.0007(1)
H(11)	.20760(30)	.34650(13)	.12977(28)	.0432(7)	.0330(6)	.0372(7)	−.0094(5)	.0049(5)	.0104(5)
H(12)	.09774(35)	.25532(23)	.12126(44)	.0368(6)	.0445(7)	.0375(7)	−.0133(5)	−.0037(5)	.0017(6)
H(21)	.15148(29)	.56439(23)	.04914(33)	.0444(6)	.0218(5)	.0521(8)	−.0015(4)	.0128(6)	−.0038(5)
H(22)	.36077(57)	.12350(32)	.26290(65)	.0942(18)	.0553(10)	.0413(11)	.0183(10)	.0256(11)	.0033(8)

Note. *w* = water oxygen atom. Anisotropic temperature factors in the form $\exp(-2\pi^2(U^{11}h^2a^{*2} + \ldots + 2U^{12}hka^*b^* + \ldots))$.

atic errors in the bond geometry as obtained in the usual harmonic treatment as a result of librations and stretch anharmonicity of the H atoms.

Final $R = 0.0290$, $R_w = 0.0294$, GOF = 1.23, 138 parameters (all reflections: $R = 0.0458$, $R_w = 0.0330$). Conventional harmonic refinement led to $R = 0.0333$, $R_w = 0.0341$, GOF = 1.41, 97 parameters (all reflections: $R = 0.0501$, $R_w = 0.0373$). Atomic parameters are listed in Tables I–III. Additional material has been deposited with the NAPS.[1]

Results and Discussion

Zn^{2+} is situated on a center of symmetry of space group *C*2/*c* (Wyckoff notation 4d). It is surrounded in a slightly distorted octahedral fashion by four water molecules (2 × O(*w*1), 2 × O(*w*2), *w* = water oxygen atom) and two O_{squarate} atoms (2 × O(1)). Interatomic distances and angles in the Zn coordination polyhedron are listed in Table IV.

The Zn–O(1) distance is the same as the Zn–O(*w*1) bond; Zn–O(*w*2) is somewhat longer. The O_{squarate} atoms are in the *trans* position with respect to the Zn octahedron. The connection of Zn^{2+} with $C_4O_4^{2-}$ which are almost ideally parallel to (001) leads to infinite chains along $[1\bar{1}0]$ and [110], respectively. Only two O_{squarate} atoms of each $C_4O_4^{2-}$ (O(1)) which are in the *trans* position with respect to the C_4 ring are bound to Zn^{2+} (Fig. 1). Thus $C_4O_4^{2-}$ acts as a twofold monodentate ligand. The chains are

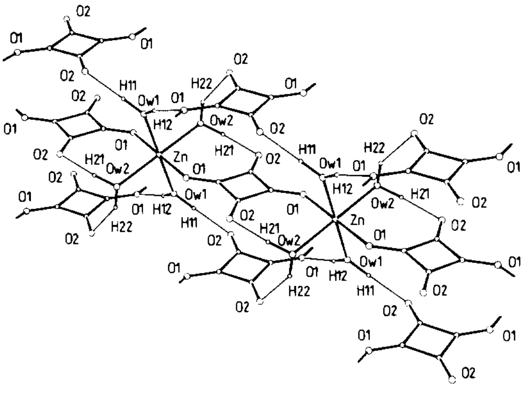

FIG. 1. Infinite chains result from the connection of Zn^{2+} with $C_4O_4^{2-}$. The chains extend along [110] and $[1\bar{1}0]$, respectively. $C_4O_4^{2-}$ is stacked along [001] in . . . *ABAB* . . . sequence. Neighboring chains are interlinked by asymmetric hydrogen bonds. (For the sake of clarity only those bonds are shown which are essential to display the connection between different chains.)

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[1] See NAPS Document No. 04572 for 12 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

TABLE II

ANHARMONIC THERMAL PARAMETERS

Atom	C^{111}	C^{222}	C^{333}	C^{112}	C^{122}	C^{113}	C^{133}	C^{223}	C^{233}	C^{123}
O(*w*1)	0.051(35)	0.021(10)	0	0.038(13)	0.051(9)	−0.044(26)	0	−0.042(12)	0	−0.047(12)
O(*w*2)	0	0.019(8)	0	0.013(9)	−0.014(6)	0	−0.051(35)	0	0	0
H(11)	−0.118(64)	0	0	−0.057(24)	0.038(16)	0.097(50)	0	0	0	−0.063(23)
H(12)	0.253(64)	0.115(23)	0.250(186)	0	−0.085(18)	0	−0.171(69)	0.075(24)	0.073(51)	−0.085(27)
H(21)	−0.242(64)	−0.047(15)	0	0.039(22)	0	0	−0.096(73)	−0.042(22)	0.071(48)	0.101(23)
H(22)	2.427(236)	0.114(34)	0.791(289)	0.622(73)	0.170(37)	1.274(145)	0.659(167)	0.088(35)	0.145(74)	0.317(52)

Note. Gram-Charlier expansion; coefficients multiplied by 10^5.

stacked along [001] in . . . *ABAB* . . . sequence. Neighboring $C_4O_4^{2-}$ are in close contact with each other. The distance between two adjacent $C_4O_4^{2-}$ is $c/2 \cdot \sin \beta$ = 333 pm and similar to the distance between layers of graphite (335 pm).

The chains are interlinked by hydrogen bonds. There are four unique asymmetric hydrogen bonds, all involving O_{squarate} atoms as the proton acceptor. Three hydrogen bonds occur between different chains. One is an intrachain hydrogen bond (O(*w*2)–H(21)–O(2)) (see Fig. 1). O(2) which is not bound to Zn^{2+} acts as proton acceptor three times. One acceptor distance, however, is rather long (H(22)–O(2)′, 214.8 pm; see Table V). The two others (H(21)–O(2), 174.9 pm; H(11)–O(2), 180.9 pm) are shorter than the acceptor distance with O(1) (H(12)–O(1), 184.9 pm).

The environment of O(2) by H (Fig. 2) is similar to that found in $BaC_4O_4 \cdot 3H_2O$ (*11*) for the O_{squarate} atom not bound to Ba^{2+}. Chains within one layer parallel to (001) are connected via the hydrogen bonds O(2)–H(11)–O(*w*1)–H(12)–O(1) as shown in Fig. 1. $C_4O_4^{2-}$ belonging to neighboring layers are interlinked by the hydrogen bonds O(2)–H(21)–O(*w*2)–H(22)–O(2)′. At the same time O(*w*2)–H(21)–O(2) is the intrachain bond. Three H_2O–O_{squarate} distances are rather similar (271.6–280.6 pm). The fourth, however, belonging to the hydrogen bond involving H(22), is considerably longer (298.6 pm).

The OHO angles, except for O(*w*1)–H(11)–O(2), are markedly bent, in particular the angle at H(22) (146.16°). Likewise the HOH angles vary: The angle with O(*w*1) is close to tetrahedral, whereas the angle

TABLE III

MEAN POSITIONS OF H ALONG THE COVALENT O–H BOND

Atom	*X*	*Y*	*Z*
H(11)	.20800	.34736	.12872
H(12)	.09598	.25462	.11957
H(21)	.15177	.56369	.04863
H(22)	.36043	.12335	.25986

TABLE IV

THE COORDINATION OF Zn^{2+}

Zn–O(1)	207.6(1)	2×	
Zn–O(*w*1)	207.6(1)	2×	
Zn–O(*w*2)	212.6(1)	2×	
	Angles *A*–Zn–*B*		
A/*B*			Distance *A*–*B*
O(1)/O(1)′	180		415.2
O(1)/O(*w*1)	91.14(4)	2×	296.5
O(1)/O(*w*1)′	88.86(4)	2×	290.7
O(1)/O(*w*2)	94.85(3)	2×	309.5
O(1)/O(*w*2)′	85.15(3)	2×	284.4
O(*w*1)/O(*w*1)′	180		415.3
O(*w*1)/O(*w*2)	91.48(5)	2×	301.0
O(*w*1)/O(*w*2)′	88.52(5)	2×	293.3
O(*w*2)/O(*w*2)′	180		425.3

Note. Distances in pm; angles in degrees; *w* = water oxygen atom.

TABLE V

WATER AND HYDROGEN BONDS

	With mean positions along O–H	With refined coordinates	
		Anharmonically	Harmonically
O(*w*1)–H(11)	97.9(2)	96.5	96.4
O(*w*1)–H(12)	97.5(3)	95.4	96.3
O(*w*2)–H(21)	99.4(3)	98.4	97.6
O(*w*2)–H(22)	95.2(4)	93.1	95.9
O(2)–H(11)	180.9(2)		
O(1)–H(12)	184.9(3)		
O(2)–H(21)	174.9(3)		
O(2)′–H(22)	214.8(4)		
H(11)–O(*w*1)–H(12)	109.08(25)	H(21)–O(*w*2)–H(22)	104.23(32)
H(11)–O(*w*1)–Zn	128.40(16)	H(21)–O(*w*2)–Zn	112.94(16)
Zn–O(*w*1)–H(12)	121.27(21)	Zn–O(*w*2)–H(22)	112.71(28)
O(*w*1)–H(11)–O(2)	178.42(23)	O(*w*2)–H(21)–O(2)	163.23(21)
O(*w*1)–H(12)–O(1)	166.39(28)	O(*w*2)–H(22)–O(2)′	146.16(37)
O(*w*1)–O(1)	280.6(2)	O(*w*2)–O(2)	271.6(1)
O(*w*1)–O(2)	278.7(2)	O(*w*2)–O(2)′	298.6(1)

Note. Distances in pm; angles in degrees.

with O(*w*2) resembles the value known from free water molecules. The bond lengths of the covalent O–H bonds increase in the sequence H(22), H(12), H(11), H(21). This increase reflects the different strengths of the hydrogen bonds expressed in terms of H_2O–$O_{squarate}$ distances as well as the H–$O_{squarate}$ acceptor distances.

$C_4O_4^{2-}$ is situated on a center of symmetry. An unweighted least-squares plane fitted to $C_4O_4^{2-}$ shows that it is ideally planar (max. deviation from plane, 0.2 pm). The two unique C–C distances barely deviate outside the limits of experimental error (146.4 and 146.7 pm, see Table VI). The two unique C–O bond lengths are even identical (2 × 125.0 pm) although the coordination of the $O_{squarate}$ atoms is completely different. The CCC angles deviate slightly from 90°. Somewhat greater deviations from the ideal value of 135° are observed for the OCC angles. Thus the bonding geometry of $C_4O_4^{2-}$ corresponds very well to a system of completely delocalized π-electrons. Zn^{2+} is in plane with the squarate dianion. If H(12) is considered a least-squares plane can be fitted to Zn^{2+}, H(12), O(1), and C(1) (max. deviation from plane, 10.93 pm for O(1)) which is inclined by 17.69° to the plane of the squarate dianion. This is comparable to the situation observed with $BaC_4O_4 \cdot 3H_2O$ (*11*) which provides two unique $O_{squarate}$ atoms coordinated to one Ba^{2+} and one H each.

Although Ba^{2+} and Zn^{2+} show rather different behavior in coordination chemistry, the environments of the $O_{squarate}$ atoms with regard to metal cations and protons stemming from hydrogen bonds are surprisingly similar. This supports the idea that the squarate dianion tries to form structures where it is surrounded by positively charged particles accepting metal cations as well as the protons of hydrogen bonds (*10, 11, 18*). The results obtained from this work

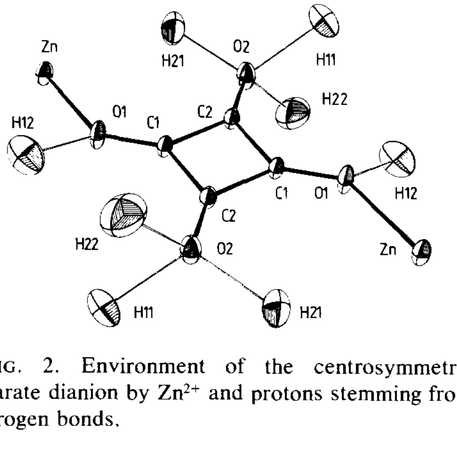

FIG. 2. Environment of the centrosymmetric squarate dianion by Zn^{2+} and protons stemming from hydrogen bonds.

TABLE VI

THE SQUARATE DIANION

C(1)–O(1)	125.0(1)	C(1)–C(2)	146.4(1)
C(2)–O(2)	125.0(1)	C(1)–C(2)′	146.7(1)
O(1)–C(1)–C(2)	132.78(4)	O(2)–C(2)–C(1)	134.42(4)
O(1)–C(1)–C(2)′	136.88(4)	O(2)–C(2)–C(1)′	135.92(4)
C(2)–C(1)–C(2)′	90.34(3)	C(1)–C(2)–C(1)′	89.66(3)
C(1)–O(1)–H(12)	119.68(10)	C(2)–O(2)–H(21)	109.50(9)
C(1)–O(1)–Zn	133.83(4)	C(2)–O(2)–H(11)	119.59(9)
Zn–O(1)–H(12)	103.80(9)	C(2)–O(2)–H(22)	118.11(13)
		H(21)–O(2)–H(11)	112.83(11)
		H(21)–O(2)–H(22)	112.05(14)
		H(11)–O(2)–H(22)	82.57(13)

Note. Distances in pm; angles in degrees.

are in agreement with the assumption that the bonding between the squarate dianion and its noncarbon neighbors is mainly determined by ionic and electrostatic interactions. A thorough discussion of these effects should be made possible by a precise electron density determination or X–X synthesis.

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References

1. W. Beck, F. Goetzfried, and M. W. Chen, *Chem. Ber.* **111,** 3719 (1978).
2. E. J. Samuelsen, U. Buchenau, M. Dieter, K. Ehrhardt, E. Fjahr, and H. Grimm, *Phys. Scr.* **25,** 685 (1982).
3. U. Deininghaus, H. Fisher, P. K. Kahol, and M. Mehring, *Phys. Rev. B* **31,** 305 (1985).
4. E. Riegler, Dissertation, Universität München, Munich (1979).
5. C. Robl, Dissertation, Universität München, Munich (1984).
6. C. Robl and A. Weiss, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **41,** 1341 (1986).
7. J. A. C. van Ooijen, R. Reedijk, and A. L. Spek, *Inorg. Chem.* **18,** 1184 (1979).
8. C. Robl and A. Weiss, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **41,** 1490 (1986).
9. C. Robl and A. Weiss, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **41,** 1485 (1986).
10. C. Robl, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **43,** 99 (1988).
11. C. Robl and W. F. Kuhs, *J. Solid State Chem.* **73,** 172 (1988).
12. I. Alt, Dissertation, Universität München, Munich (1984).
13. A. Weiss, E. Riegler, and C. Robl, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **41,** 1329 (1986).
14. A. Weiss, E. Riegler, and C. Robl, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **41,** 1333 (1986).
15. P. J. Becker and P. Coppens, *Acta Crystallogr. Sect. A* **30,** 129 (1974).
16. L. Koester and H. Rauch, Summary of Neutron Scattering Lengths, IAEA Contract 2517/RB (1981).
17. U. H. Zucker, E. Perenthaler, W. F. Kuhs, R. Bachmann, and H. Schulz, *J. Appl. Crystallogr.* **16,** 358 (1983).
18. C. Robl, V. Gnutzmann, and A. Weiss, *Z. Anorg. Allg. Chem.* **549,** 187 (1987).