Redetermination of the crystal structure of bis(guanidinium) carbonato (ethylenediaminetetraacetato) zirconate tetrahydrate, $(CN_3H_6)_2[Zr((CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)CO_3] \cdot 4H_2O$

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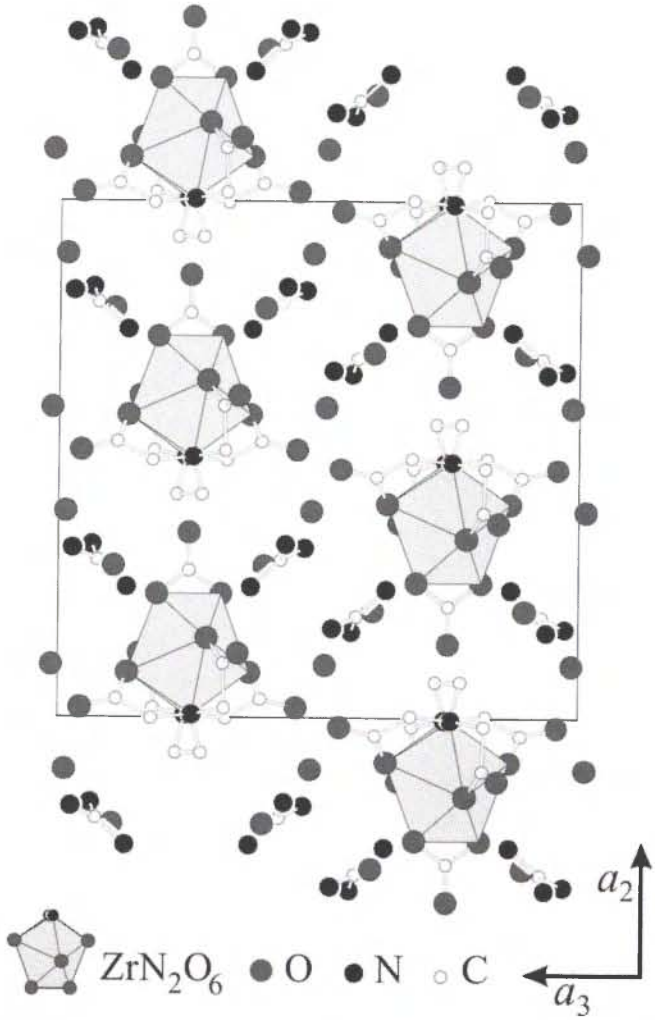

Abstract

$C_{13}H_{32}N_8O_{15}Zr$, monoclinic, $C12/c1$ (No. 15), $a = 8.894(2)$ Å, $b = 16.667(3)$ Å, $c = 16.907(3)$ Å, $\beta = 96.03(3)°$, $V = 2492.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.019$, $wR_{ref}(F^2) = 0.049$, $T = 298$ K.

Source of material

The raw material was obtained by slow evaporation of an aqueous solution of the reaction products of guanidinium carbonate and EDTA with an aqueous solution of zirconium tetrachloride in a molar ratio of about 1:1 at 295K.

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Discussion

In 1995, V. E. Mistryukov et al. reported on a crystal structure determination of bis(guanidinium) carbonato(ethylenediaminetetraacetato)zirconate trihydrate with space group *Cc* [1].

Our attempts to solve the structure of that species yielded the centrosymmetric space group *C2/c*. This was confirmed by the absence of a measurable piezoelectric effect. From the difference Fourier-map and in addition from thermogravimetric runs we found that four water molecules are present per formula unit. The constituents of the structure are arranged in two types of layers parallel to (001). The first type is alternately occupied by guanidinium cations and interstitial water. The second type consists of complex carbonato(ethylenediaminetetraacetato)zirconate anions, in which the Zr-cations are coordinated by six oxygen and two nitrogen atoms of the carbonato(ethylenediaminetetraacetato) groups. The ionic interactions between these layers are reinforced by a 3-dimensional network of hydrogen bonds which are characterized by D···A distances between 2.82 Å and 3.11 Å and D–H···A angles of about 160°.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.27 × 0.29 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.27 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, ω/2θ
$2\theta_{max}$:	53.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7602, 2711
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2564
$N(param)_{refined}$:	233
Programs:	SHELXS-97 [2], SHELXL-97 [3], ATOMS [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	8*f*	0.297(2)	0.507(1)	0.870(1)	0.038(4)
H(11B)	8*f*	0.152(2)	0.481(1)	0.812(1)	0.039(4)
H(12A)	8*f*	0.224(2)	0.443(1)	0.667(1)	0.046(5)
H(12B)	8*f*	0.157(2)	0.529(1)	0.679(1)	0.046(5)
H(13A)	8*f*	0.372(2)	0.384(1)	0.763(1)	0.032(4)
H(13B)	8*f*	0.470(2)	0.4305(9)	0.830(1)	0.031(4)
H(21A)	8*f*	–0.279(2)	0.872(1)	0.968(1)	0.043(5)
H(21B)	8*f*	–0.352(2)	0.819(1)	0.904(1)	0.058(6)
H(22A)	8*f*	–0.025(3)	0.858(1)	1.008(1)	0.059(7)
H(22B)	8*f*	0.065(3)	0.812(1)	0.963(1)	0.056(6)
H(23A)	8*f*	–0.206(2)	0.740(1)	0.840(1)	0.048(5)
H(23B)	8*f*	–0.052(3)	0.730(1)	0.864(1)	0.060(7)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
HW(1A)	8*f*	0.112(3)	0.438(2)	0.519(2)	0.080(8)
HW(1B)	8*f*	0.051(3)	0.390(2)	0.469(2)	0.09(1)
HW(2A)	8*f*	0.264(4)	0.751(2)	0.913(2)	0.103(8)
HW(2B)	8*f*	0.332(3)	0.825(2)	0.919(2)	0.103(8)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	4*e*	1/2	0.626106(9)	3/4	0.0236(1)	0.0178(1)	0.0238(1)	0	0.00176(6)	0
N(1)	8*f*	0.3419(1)	0.50499(7)	0.75657(7)	0.0294(5)	0.0230(5)	0.0294(5)	–0.0010(4)	0.0045(4)	0.0019(4)
N(21)	8*f*	–0.2740(2)	0.83464(9)	0.9365(1)	0.0392(7)	0.0424(8)	0.0500(8)	0.0051(6)	0.0052(6)	–0.0093(7)
N(22)	8*f*	–0.0188(2)	0.8277(1)	0.9734(1)	0.0386(8)	0.067(1)	0.0463(8)	–0.0012(7)	0.0018(6)	–0.0181(8)
N(23)	8*f*	–0.1274(2)	0.75237(9)	0.86962(9)	0.0400(8)	0.0386(7)	0.0470(8)	0.0059(6)	0.0012(6)	–0.0100(6)
C(1)	4*e*	1/2	0.7845(1)	3/4	0.033(1)	0.0232(9)	0.043(1)	0	0.0056(8)	0
C(2)	8*f*	–0.1399(2)	0.80473(8)	0.92713(8)	0.0365(7)	0.0305(7)	0.0334(7)	0.0002(6)	0.0060(6)	0.0025(5)
C(11)	8*f*	0.2389(2)	0.51760(9)	0.81878(9)	0.0340(7)	0.0300(7)	0.0376(8)	–0.0016(6)	0.0117(6)	0.0037(6)
C(12)	8*f*	0.2499(2)	0.49805(9)	0.67816(9)	0.0329(7)	0.0321(7)	0.0362(7)	–0.0078(6)	–0.0011(6)	–0.0003(6)
C(13)	8*f*	0.4336(2)	0.43116(8)	0.77406(9)	0.0388(7)	0.0188(6)	0.0383(8)	–0.0013(5)	0.0057(6)	0.0029(5)
C(14)	8*f*	0.1883(2)	0.60411(9)	0.81617(8)	0.0297(7)	0.0324(7)	0.0337(7)	0.0007(5)	0.0048(5)	0.0004(6)
C(15)	8*f*	0.3265(2)	0.53502(8)	0.61120(8)	0.0363(7)	0.0270(6)	0.0315(7)	–0.0021(5)	–0.0036(5)	0.0017(5)
O(11)	4*e*	1/2	0.85746(9)	3/4	0.082(1)	0.0216(7)	0.067(1)	0	0.003(1)	0
O(12)	8*f*	0.4537(1)	0.73902(5)	0.68798(6)	0.0369(5)	0.0246(5)	0.0338(5)	–0.0002(4)	–0.0005(4)	0.0040(4)
O(14A)	8*f*	0.0732(1)	0.62378(7)	0.84525(8)	0.0373(6)	0.0426(6)	0.0566(7)	0.0053(5)	0.0193(5)	0.0018(5)
O(14B)	8*f*	0.2765(1)	0.65340(6)	0.78424(6)	0.0297(5)	0.0260(5)	0.0473(6)	0.0016(4)	0.0099(4)	0.0022(4)
O(15A)	8*f*	0.2844(2)	0.51894(8)	0.54207(6)	0.0705(8)	0.0524(7)	0.0315(6)	–0.0232(6)	–0.0108(5)	0.0026(5)
O(15B)	8*f*	0.4319(1)	0.58665(6)	0.63209(6)	0.0389(5)	0.0302(5)	0.0278(5)	–0.0085(4)	0.0016(4)	0.0010(4)
O(1W)	8*f*	0.0583(2)	0.3989(1)	0.5133(1)	0.068(1)	0.069(1)	0.0566(9)	–0.0280(8)	0.0099(7)	–0.0053(7)
O(2W)	8*f*	0.2459(2)	0.7934(1)	0.8951(2)	0.072(1)	0.077(1)	0.130(2)	–0.010(1)	0.047(1)	–0.037(1)

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