Crystal structure of bis(aminoguanidinium) bis(nitrilotriacetato)zirconate, $[(\text{NH}_2)_2\text{CNHNH}_2]_2\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]_2$

E. Haussühl^{*I}, S. Haussühl^{II} and E. Tillmanns^I^I Universität Wien, Institut für Mineralogie und Kristallographie, Althanstr. 14 - Geozentrum, A-1090 Wien, Austria^{II} Universität zu Köln, Institut für Kristallographie, Zùlpicherstr. 49b, D-50674 Köln, Germany

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Abstract

$\text{C}_{14}\text{H}_{26}\text{N}_{10}\text{O}_{12}\text{Zr}$, monoclinic, $P12_11$ (No. 4), $a = 9.995(2)$ Å, $b = 10.554(2)$ Å, $c = 11.196(2)$ Å, $\beta = 92.95(3)^\circ$, $V = 1179.5$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.017$, $wR_{\text{ref}}(F^2) = 0.044$, $T = 293$ K.

Source of material

The raw material was obtained from an aqueous solution by fractional crystallization of the reaction product of aminoguanidinium-hydrogencarbonate, nitrilotriacetic acid and zirconium tetrachloride in a stoichiometric ratio at 294 K. Single crystals of optical quality were obtained by slow evaporation of an aqueous solution at about 294 K.

Discussion

The constituents of the structure are arranged in two types of layers parallel to (100). The first type consists of complex nitrilotriacetato-zirconate anions, in which the Zr cations are coordinated by six oxygen and two nitrogen atoms of the nitrilotriacetato groups. The second type is occupied by aminoguanidinium cations, which are connected by hydrogen bonds to carboxylic groups of the $\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]_2$ anions. A part of the nitrogen atoms of the aminoguanidinium cations e.g. N44, N42 exhibit large anisotropic thermal parameters. An attempt to introduce split positions did not yield smaller parameters of these distinct nitrogen atoms. The hydrogen bonds are characterized by donor acceptor distances between 2.83 Å and 3.18 Å and D–H...O angles between 120° and 172°. The static piezoelectric constant d_{222} is about 6 times larger than d_{111} of α -quartz.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.28 × 0.31 × 0.34 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	5.48 cm ⁻¹
Diffractometer, scan mode:	Nonius Kappa-CCD, ϕ/ω
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13507, 6866
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6715
$N(\text{param})_{\text{refined}}$:	439
Programs:	SHELXS-97 [1], SHELXL-97 [2], ATOMS [3]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(11A)	2a	0.787(3)	0.276(2)	0.343(2)	0.042(6)
H(11B)	2a	0.784(2)	0.424(2)	0.374(2)	0.038(5)
H(12A)	2a	0.650(2)	0.450(2)	0.515(2)	0.033(5)
H(12B)	2a	0.614(2)	0.304(2)	0.545(2)	0.041(5)
H(13A)	2a	0.589(2)	0.174(2)	0.288(2)	0.028(4)
H(13B)	2a	0.553(2)	0.162(2)	0.414(2)	0.040(5)
H(21A)	2a	0.683(2)	0.814(2)	0.155(2)	0.031(5)
H(21B)	2a	0.727(2)	0.679(2)	0.107(2)	0.040(5)
H(22A)	2a	0.585(2)	0.597(2)	-0.018(2)	0.030(4)
H(22B)	2a	0.504(2)	0.727(2)	-0.050(2)	0.027(4)
H(23A)	2a	0.414(2)	0.843(2)	0.085(2)	0.032(5)
H(23B)	2a	0.471(2)	0.841(2)	0.214(2)	0.037(5)
H(31A)	2a	-0.090(3)	0.587(3)	0.632(2)	0.061(7)
H(31B)	2a	-0.118(2)	0.631(3)	0.501(2)	0.055(7)
H(32A)	2a	0.054(2)	0.638(2)	0.384(2)	0.043(7)
H(32B)	2a	0.179(3)	0.584(3)	0.410(3)	0.082(9)

* Correspondence author (e-mail: eiken.haussuehl@univie.ac.at)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(33A)	2a	0.201(3)	0.479(3)	0.600(3)	0.080(9)
H(34A)	2a	0.077(3)	0.385(3)	0.724(3)	0.083(9)
H(34B)	2a	0.143(3)	0.516(4)	0.780(3)	0.080(8)
H(41A)	2a	-0.134(2)	0.491(3)	-0.040(2)	0.033(5)
H(41B)	2a	-0.208(3)	0.558(3)	-0.146(3)	0.065(8)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(42A)	2a	-0.154(3)	0.765(3)	-0.187(3)	0.085
H(42B)	2a	-0.028(3)	0.799(3)	-0.158(3)	0.08(1)
H(43A)	2a	0.076(3)	0.708(3)	0.009(3)	0.08(1)
H(44A)	2a	0.011(4)	0.568(4)	0.122(3)	0.10(1)
H(44B)	2a	0.134(4)	0.529(4)	0.065(3)	0.11(1)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	2a	0.462780(9)	0.50000(1)	0.249355(8)	0.01920(5)	0.01699(5)	0.01629(5)	0.00160(5)	0.00136(3)	0.00207(5)
N(1)	2a	0.5981(1)	0.3438(1)	0.3669(1)	0.0227(5)	0.0206(5)	0.0212(5)	0.0022(4)	0.0014(4)	0.0006(4)
N(2)	2a	0.5251(1)	0.6853(1)	0.12930(9)	0.0233(5)	0.0223(5)	0.0186(5)	-0.0018(4)	-0.0006(4)	0.0012(4)
N(31)	2a	-0.0724(2)	0.5957(2)	0.5563(2)	0.0320(8)	0.092(2)	0.0393(9)	0.0199(8)	0.0034(6)	0.0088(9)
N(32)	2a	0.0974(3)	0.5954(3)	0.4286(2)	0.059(1)	0.114(2)	0.062(1)	0.010(1)	0.028(1)	0.009(1)
N(33)	2a	0.1299(2)	0.5085(2)	0.6157(2)	0.0326(6)	0.057(1)	0.069(1)	0.014(1)	-0.0065(6)	-0.015(1)
N(34)	2a	0.0769(2)	0.4772(2)	0.7257(2)	0.068(1)	0.053(1)	0.053(1)	0.0051(9)	-0.0189(8)	0.0035(8)
N(41)	2a	-0.1595(2)	0.5588(2)	-0.0780(2)	0.0328(8)	0.048(1)	0.065(1)	-0.0137(7)	0.0072(7)	-0.0104(9)
N(42)	2a	-0.0885(2)	0.7502(3)	-0.1452(3)	0.040(1)	0.082(2)	0.138(3)	-0.029(1)	-0.026(1)	0.048(2)
N(43)	2a	0.0303(2)	0.6517(2)	0.0034(2)	0.0353(8)	0.053(1)	0.103(2)	-0.0120(8)	-0.020(1)	0.014(1)
N(44)	2a	0.0587(3)	0.5449(3)	0.0705(4)	0.034(1)	0.111(3)	0.182(4)	-0.012(1)	-0.021(2)	0.087(3)
C(3)	2a	0.0516(2)	0.5666(2)	0.5328(2)	0.0322(8)	0.047(1)	0.049(1)	0.0039(7)	0.0062(7)	-0.0066(8)
C(4)	2a	-0.0724(2)	0.6521(2)	-0.0743(2)	0.0254(7)	0.0393(9)	0.060(1)	-0.0058(6)	0.0035(7)	-0.0072(8)
C(11)	2a	0.7360(2)	0.3496(2)	0.3252(2)	0.0235(7)	0.0321(7)	0.0326(8)	0.0065(6)	0.0019(6)	0.0066(6)
C(12)	2a	0.5901(2)	0.3764(1)	0.4947(1)	0.0340(7)	0.0281(6)	0.0196(6)	0.0060(5)	-0.0023(5)	0.0019(5)
C(13)	2a	0.5413(2)	0.2158(1)	0.3441(1)	0.0375(7)	0.0175(6)	0.0308(7)	0.0024(5)	-0.0009(6)	0.0014(5)
C(14)	2a	0.7319(1)	0.3791(1)	0.1922(1)	0.0247(6)	0.0233(6)	0.0330(7)	0.0022(5)	0.0067(5)	0.0021(5)
C(15)	2a	0.4500(2)	0.4243(1)	0.5172(1)	0.0341(7)	0.0181(5)	0.0209(5)	0.0011(5)	0.0025(5)	0.0009(4)
C(16)	2a	0.3968(2)	0.2185(1)	0.2959(1)	0.0347(7)	0.0257(6)	0.0253(6)	-0.0047(5)	0.0045(5)	0.0013(5)
C(21)	2a	0.6658(1)	0.7205(1)	0.1631(1)	0.0265(6)	0.0306(7)	0.0279(7)	-0.0072(5)	-0.0030(5)	0.0047(5)
C(22)	2a	0.5081(2)	0.6488(1)	0.0014(1)	0.0323(7)	0.0294(6)	0.0169(5)	-0.0029(5)	0.0020(5)	0.0024(5)
C(23)	2a	0.4320(2)	0.7906(1)	0.1552(1)	0.0354(7)	0.0203(6)	0.0255(6)	0.0018(5)	-0.0010(5)	0.0018(5)
C(24)	2a	0.7047(2)	0.6759(1)	0.2886(1)	0.0313(7)	0.0217(6)	0.0289(7)	-0.0009(5)	-0.0049(6)	0.0009(5)
C(25)	2a	0.3874(1)	0.5628(1)	-0.0171(1)	0.0293(6)	0.0270(6)	0.0195(6)	0.0017(5)	-0.0015(5)	-0.0011(5)
C(26)	2a	0.3027(2)	0.7442(1)	0.2040(1)	0.0319(7)	0.0242(6)	0.0271(6)	0.0084(5)	0.0006(5)	0.0034(5)
O(14A)	2a	0.8293(1)	0.3598(1)	0.1331(1)	0.0320(6)	0.0600(8)	0.0489(7)	0.0139(6)	0.0166(5)	0.0114(6)
O(14B)	2a	0.6218(1)	0.4281(1)	0.14845(9)	0.0266(5)	0.0290(5)	0.0233(4)	0.0049(4)	0.0047(4)	0.0014(4)
O(15A)	2a	0.4008(1)	0.4113(1)	0.61420(9)	0.0454(6)	0.0362(5)	0.0230(5)	0.0059(5)	0.0089(4)	0.0080(4)
O(15B)	2a	0.3919(1)	0.4853(1)	0.42872(8)	0.0338(4)	0.0325(6)	0.0217(4)	0.0110(5)	0.0067(3)	0.0071(4)
O(16A)	2a	0.3265(1)	0.1245(1)	0.3033(1)	0.0489(7)	0.0352(6)	0.0595(8)	-0.0181(6)	-0.0030(6)	0.0137(6)
O(16B)	2a	0.3597(1)	0.3210(1)	0.2408(1)	0.0308(5)	0.0254(5)	0.0338(6)	-0.0051(4)	-0.0035(4)	0.0059(4)
O(24A)	2a	0.8162(1)	0.7017(1)	0.3334(1)	0.0342(6)	0.0465(7)	0.0453(7)	-0.0087(5)	-0.0154(5)	0.0083(5)
O(24B)	2a	0.6174(1)	0.6083(1)	0.34058(9)	0.0367(5)	0.0244(5)	0.0226(5)	-0.0038(4)	-0.0046(4)	0.0027(4)
O(25A)	2a	0.3244(1)	0.5598(1)	-0.1139(1)	0.0491(7)	0.0500(7)	0.0241(5)	-0.0100(6)	-0.0131(5)	0.0041(5)
O(25B)	2a	0.36132(9)	0.4928(1)	0.07308(8)	0.0316(4)	0.0328(5)	0.0246(4)	-0.0075(6)	-0.0054(3)	0.0054(5)
O(26A)	2a	0.1987(1)	0.8028(1)	0.1887(2)	0.0393(7)	0.0439(7)	0.075(1)	0.0181(6)	0.0073(7)	0.0219(7)
O(26B)	2a	0.3138(1)	0.6409(1)	0.2669(1)	0.0313(5)	0.0305(5)	0.0337(5)	0.0119(4)	0.0099(4)	0.0118(4)

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