Crystal structure of bis(dimethylammonium) zirconium bis(nitrilotriacetate) tetrahydrate, $(\text{CH}_3\text{NH}_2\text{CH}_3)_2\text{Zr}(\text{N}(\text{CH}_2\text{COO})_3)_2 \cdot 4\text{H}_2\text{O}$

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Abstract

$\text{C}_{16}\text{H}_{36}\text{N}_4\text{O}_{16}\text{Zr}$, monoclinic, $P12_11$ (No. 4), $a = 11.916(2)$ Å, $b = 9.906(2)$ Å, $c = 12.064(2)$ Å, $\beta = 111.01(3)^\circ$, $V = 1329.4$ Å³, $Z = 2$, $\rho_m = 1.584$ g cm⁻³, $R_g(F) = 0.026$, $wR_{\text{ref}}(F^2) = 0.067$, $T = 293$ K.

Source of material

The raw material was obtained by fractional crystallization of an aqueous solution of the reaction product of dimethylamine, nitrilotriacetic acid and ZrCl_4 in a stoichiometric ratio at 300 K.

Discussion

The structure is built up from layers parallel (100), which consist of dimethylammonium ions connected to interstitial water and zirconium nitrilotriacetate complexes. Hydrogen bonds are formed between the oxygen atom O14A of the first nitrilotriacetate group via the interstitial water molecules OW4, OW2, OW1, OW3 and the connecting oxygen atom O25A of the second nitrilotriacetate group. The nitrogen atom of the first amine group N30 is linked to the oxygen atoms OW1 and O16A and the second nitrogen atom N40 to OW2 and O26B, respectively. The hydrogen bonds are characterised by donor acceptor distances between 2.70 Å and 2.81 Å and D–H...A angles between 158° and 176°.

The static piezoelectric constant d_{222} is about 3 times larger than d_{111} of α -quartz. The pyroelectric effect surmounts the corresponding value of tourmaline by a factor of 3.

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.13 \times 0.14 \times 0.16$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	4.93 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, ψ
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	15847, 4609
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4368
$N(\text{param})_{\text{refined}}$:	448
Programs:	SHELXS-86 [1], SHELXL-93 [2], ATOMS [3]

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

Atom	Site	x	y	z	U_{iso}
H(31A)	2a	0.459(6)	0.409(6)	−0.065(6)	0.137
H(31B)	2a	0.387(5)	0.245(6)	−0.107(5)	0.137
H(31C)	2a	0.502(6)	0.268(6)	0.001(6)	0.137
H(32A)	2a	0.4993	0.3731	0.1974	0.105
H(32B)	2a	0.3747	0.4320	0.1901	0.105
H(32C)	2a	0.4446	0.4978	0.1159	0.105
H(41A)	2a	0.626(4)	0.619(5)	0.424(4)	0.106
H(41B)	2a	0.656(5)	0.718(6)	0.326(5)	0.106
H(41C)	2a	0.507(5)	0.714(6)	0.306(5)	0.106
H(42A)	2a	0.4644	0.8342	0.4650	0.12(1)
H(42B)	2a	0.5666	0.9160	0.5602	0.12
H(42C)	2a	0.5652	0.7580	0.5665	0.12
H(11A)	2a	−0.204(3)	0.495(3)	0.073(3)	0.037(8)
H(11B)	2a	−0.149(3)	0.639(4)	0.157(3)	0.06(1)
H(12A)	2a	0.066(3)	0.682(4)	0.146(3)	0.05(1)
H(12B)	2a	0.017(5)	0.659(7)	0.261(5)	0.11(2)
H(13A)	2a	−0.028(3)	0.553(4)	−0.020(3)	0.06(1)
H(13B)	2a	−0.099(3)	0.433(4)	−0.030(3)	0.054(9)
H(21A)	2a	0.000(4)	−0.060(5)	0.251(4)	0.07(1)
H(21B)	2a	0.032(3)	−0.078(4)	0.381(3)	0.05(1)
H(22A)	2a	−0.187(4)	−0.017(4)	0.240(3)	0.07(1)
H(22B)	2a	−0.217(3)	0.139(4)	0.273(3)	0.05(1)
H(23A)	2a	−0.105(4)	0.188(5)	0.446(4)	0.07(1)
H(23B)	2a	−0.023(3)	0.033(4)	0.500(3)	0.055(9)
H(30A)	2a	0.274(4)	0.365(5)	−0.001(4)	0.09(1)
H(30B)	2a	0.362(5)	0.239(6)	0.084(5)	0.11(2)
H(40A)	2a	0.602(4)	0.906(5)	0.391(4)	0.08(1)
H(40B)	2a	0.691(4)	0.823(5)	0.481(4)	0.08
HW(1A)	2a	0.437(4)	0.081(7)	0.224(4)	0.126
HW(1B)	2a	0.313(5)	0.009(6)	0.152(5)	0.126
HW(2A)	2a	0.626(5)	0.156(5)	0.349(5)	0.13(1)
HW(2B)	2a	0.538(5)	0.049(6)	0.370(5)	0.13
HW(3A)	2a	−0.288(5)	0.266(7)	−0.066(6)	0.12(2)
HW(3B)	2a	−0.283(4)	0.280(6)	−0.176(4)	0.10(2)
HW(4A)	2a	−0.284(4)	0.335(5)	0.470(4)	0.09(1)
HW(4B)	2a	−0.278(4)	0.356(5)	0.374(4)	0.09

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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	0.05404(2)	0.30111(3)	0.26766(2)	0.0264(1)	0.0260(1)	0.0284(1)	0.0005(1)	0.00934(9)	0.0034(1)
N(1)	2a	-0.0223(2)	0.5045(2)	0.1453(2)	0.033(1)	0.033(1)	0.031(1)	0.004(1)	0.012(1)	0.0029(9)
N(2)	2a	-0.0345(2)	0.1054(2)	0.3337(2)	0.034(1)	0.031(1)	0.034(1)	-0.004(1)	0.012(1)	0.001(1)
N(30)	2a	0.3650(3)	0.3231(4)	0.0469(3)	0.043(2)	0.074(3)	0.067(2)	0.008(2)	0.020(1)	0.012(2)
N(40)	2a	0.6212(2)	0.8273(4)	0.4391(3)	0.032(1)	0.071(3)	0.057(2)	0.004(1)	0.009(1)	-0.000(2)
C(11)	2a	-0.1462(3)	0.5331(4)	0.1405(3)	0.031(2)	0.048(2)	0.038(2)	0.011(1)	0.010(1)	0.004(1)
C(12)	2a	0.0606(3)	0.6165(3)	0.2043(3)	0.048(2)	0.028(2)	0.053(2)	-0.003(1)	0.015(2)	0.003(1)
C(13)	2a	-0.0199(3)	0.4782(3)	0.0245(3)	0.045(2)	0.038(2)	0.030(2)	0.007(1)	0.016(1)	0.006(1)
C(14)	2a	-0.1724(3)	0.4645(3)	0.2398(3)	0.034(2)	0.034(2)	0.043(2)	-0.002(1)	0.014(1)	-0.003(1)
C(15)	2a	0.1840(3)	0.5678(3)	0.2815(3)	0.042(2)	0.033(2)	0.038(2)	-0.003(1)	0.012(1)	-0.000(1)
C(16)	2a	0.0840(3)	0.3870(3)	0.0312(2)	0.036(2)	0.031(2)	0.033(2)	-0.005(1)	0.014(1)	-0.002(1)
C(21)	2a	0.0404(3)	-0.0134(3)	0.3327(3)	0.053(2)	0.028(2)	0.060(2)	0.001(1)	0.026(2)	0.003(2)
C(22)	2a	-0.1601(3)	0.0873(4)	0.2497(3)	0.033(2)	0.051(2)	0.039(2)	-0.010(1)	0.012(1)	0.001(1)
C(23)	2a	-0.0312(3)	0.1331(3)	0.4562(2)	0.044(2)	0.046(2)	0.031(2)	-0.006(1)	0.015(1)	0.002(1)
C(24)	2a	0.1648(3)	0.0218(3)	0.3374(3)	0.052(2)	0.035(2)	0.044(2)	0.010(2)	0.025(2)	0.008(1)
C(25)	2a	-0.1795(3)	0.1501(3)	0.1311(3)	0.034(2)	0.039(2)	0.039(2)	-0.005(1)	0.011(1)	-0.004(1)
C(26)	2a	0.0773(3)	0.2171(3)	0.5242(2)	0.040(2)	0.033(2)	0.031(2)	0.006(1)	0.014(1)	0.004(1)
C(31)	2a	0.4261(6)	0.304(1)	-0.0385(6)	0.097(3)	0.142(5)	0.134(4)	0.002(6)	0.079(3)	-0.018(6)
C(32)	2a	0.4262(4)	0.4144(5)	0.1462(4)	0.075(3)	0.076(3)	0.084(3)	-0.007(2)	-0.004(2)	0.009(3)
C(41)	2a	0.5983(5)	0.7057(7)	0.3644(5)	0.063(3)	0.095(4)	0.097(4)	0.007(2)	0.016(2)	-0.024(3)
C(42)	2a	0.5480(4)	0.8345(7)	0.5142(4)	0.058(2)	0.171(6)	0.076(3)	0.001(3)	0.033(2)	-0.009(3)
O(14A)	2a	-0.2715(2)	0.4761(3)	0.2472(2)	0.035(1)	0.060(2)	0.070(2)	0.005(1)	0.026(1)	0.004(1)
O(14B)	2a	-0.0856(2)	0.3924(2)	0.3123(2)	0.039(1)	0.034(1)	0.036(1)	0.0035(9)	0.0164(9)	0.0032(8)
O(15A)	2a	0.2749(2)	0.6343(3)	0.2960(2)	0.052(1)	0.053(2)	0.066(2)	-0.020(1)	0.011(1)	0.012(1)
O(15B)	2a	0.1843(2)	0.4549(2)	0.3351(2)	0.041(1)	0.037(1)	0.040(1)	-0.008(1)	0.0040(9)	0.0084(9)
O(16A)	2a	0.1187(2)	0.3812(2)	-0.0537(2)	0.050(1)	0.051(1)	0.038(1)	0.006(1)	0.023(1)	0.004(1)
O(16B)	2a	0.1287(2)	0.3159(2)	0.1253(2)	0.0392(9)	0.042(1)	0.042(1)	0.009(1)	0.0205(8)	0.011(1)
O(24A)	2a	0.2496(2)	-0.0545(3)	0.3804(3)	0.072(2)	0.058(2)	0.094(2)	0.035(1)	0.047(2)	0.039(2)
O(24B)	2a	0.1726(2)	0.1347(2)	0.2858(2)	0.043(1)	0.039(1)	0.055(1)	0.011(1)	0.027(1)	0.017(1)
O(25A)	2a	-0.2770(2)	0.1368(3)	0.0496(2)	0.039(1)	0.071(2)	0.049(1)	-0.010(1)	0.002(1)	0.004(1)
O(25B)	2a	-0.0916(2)	0.2208(2)	0.1221(2)	0.038(1)	0.036(1)	0.033(1)	-0.0045(9)	0.0107(9)	0.0005(8)
O(26A)	2a	0.1101(2)	0.2277(2)	0.6321(2)	0.057(1)	0.050(1)	0.033(1)	-0.000(1)	0.016(1)	0.000(1)
O(26B)	2a	0.1275(2)	0.2802(2)	0.4595(2)	0.039(1)	0.046(1)	0.0318(9)	-0.008(1)	0.0075(8)	0.0055(9)
OW(1)	2a	0.3367(2)	0.0903(3)	0.1670(2)	0.044(1)	0.054(2)	0.060(2)	-0.003(1)	0.020(1)	-0.002(1)
OW(2)	2a	0.5777(3)	0.0639(3)	0.3119(3)	0.059(2)	0.061(2)	0.110(2)	-0.005(1)	0.022(2)	0.005(2)
OW(3)	2a	-0.3118(3)	0.3198(3)	-0.1384(3)	0.094(2)	0.052(2)	0.060(2)	0.019(2)	0.029(1)	0.002(1)
OW(4)	2a	-0.3076(3)	0.2953(4)	0.4094(3)	0.080(2)	0.069(2)	0.070(2)	-0.022(2)	0.042(1)	-0.019(2)

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