Crystal structure of the low temperature phase of bis(butylamine) zirconium bis(nitrilotriacetate) dihydrate, $[\text{NH}_3(\text{CH}_2)_4]_2\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]_2 \cdot 2\text{H}_2\text{O}$

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Abstract

$\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_{14}\text{Zr}$, orthorhombic, $P2_12_12_1$ (No. 19),
 $a = 10.054(2) \text{ \AA}$, $b = 13.010(3) \text{ \AA}$, $c = 20.870(4) \text{ \AA}$,
 $V = 2729.8 \text{ \AA}^3$, $Z = 4$, $\rho_m = 1.511(1) \text{ g}\cdot\text{cm}^{-3}$ (at 293 K),
 $R_{\text{gt}}(F) = 0.023$, $wR(F^2) = 0.047$, $T = 100 \text{ K}$.

Source of material

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

Discussion

From differential scanning calorimetry runs, thermal expansion and elastic behaviour a first-order phase transition at about 188 K was detected. Other distinct anomalies were found in respect to the variation of the thermoelastic constants with temperature and the attenuation of ultrasonic waves [1]. The structures of most zirconium nitrilotriacetates, so far investigated, and also of bis(butylamine) zirconium bis(nitrilotriacetate) dihydrate, are built up from puckered layers of $\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]^{2-}$ anions with intralayer and interlayer Coulomb interactions between anions and cations and in addition strong hydrogen bonds. The anions, which Zr is coordinated by six oxygen and two nitrogen atoms of the nitrilotriacetate group, possess an almost perfectly persistent conformation, which has been thoroughly studied by Howard et al. [2]. In this case the intralayer bonds consist mainly of Coulomb interactions between the anions and the NH_3 groups, further strengthened by hydrogen bonds between the nitrogen atoms of the NH_3 groups and oxygen atoms of the carboxylic groups. The layers are held together by Coulomb interactions between NH_3 groups and anions belonging to adjacent layers. These are reinforced by hydrogen bonds between the water molecules W1, W2 and oxygen atoms of carboxy groups. The hydrogen bonds are characterized by donor acceptor distances between 2.83 Å and 2.95 Å (hydrogen acceptor distances between 1.89 Å and 2.06 Å) and D–H...O angles between 165° and 177°.

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.24 \times 0.25 \times 0.26 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	4.77 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, ψ
$2\theta_{\text{max}}$:	72.62°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13108, 13108
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 12458
$N(\text{param})_{\text{refined}}$:	513
Programs:	SHELXS-97 [3], SHELXL-97 [4], ATOMS [5]

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

Atom	Site	x	y	z	<i>U</i> _{iso}
H(11A)	4a	0.576(2)	−0.225(1)	1.0366(7)	0.017(3)
H(11B)	4a	0.599(2)	−0.109(1)	1.0252(7)	0.016(3)
H(12A)	4a	0.702(2)	−0.100(1)	0.9352(7)	0.018(4)
H(12B)	4a	0.715(1)	−0.212(1)	0.9122(7)	0.018(3)
H(13A)	4a	0.441(2)	−0.309(1)	0.9693(8)	0.031(4)
H(13B)	4a	0.559(2)	−0.325(1)	0.9184(8)	0.025(4)
H(21A)	4a	0.335(2)	0.216(1)	1.0079(7)	0.017(4)
H(21B)	4a	0.326(2)	0.113(1)	1.0443(7)	0.019(4)
H(22A)	4a	0.142(2)	0.045(1)	1.0252(8)	0.029(4)
H(22B)	4a	0.062(2)	0.132(1)	0.9869(7)	0.020(4)
H(23A)	4a	0.153(1)	0.208(1)	0.9032(7)	0.014(3)
H(23B)	4a	0.300(2)	0.232(1)	0.9048(8)	0.024(4)
H(3A)	4a	0.896(2)	−0.159(1)	0.8158(8)	0.026(4)
H(3B)	4a	0.958(2)	−0.253(1)	0.8438(8)	0.030(4)
H(3C)	4a	1.027(2)	−0.150(1)	0.8515(9)	0.034(5)
H(31A)	4a	1.127(2)	−0.254(1)	0.7732(7)	0.021(4)
H(31B)	4a	0.992(2)	−0.234(1)	0.7330(8)	0.025(4)
H(32A)	4a	1.174(2)	−0.077(1)	0.7673(7)	0.021(4)
H(32B)	4a	1.157(2)	−0.117(1)	0.6964(8)	0.032(4)
H(33A)	4a	1.045(2)	0.044(1)	0.7178(8)	0.029(4)

Table 2. Continued.

Atom	Site	x	y	z	<i>U</i> _{iso}
H(33B)	4a	0.948(1)	−0.007(1)	0.7647(7)	0.012(3)
H(34A)	4a	0.853(2)	−0.112(1)	0.6813(8)	0.034(4)
H(34B)	4a	0.841(2)	0.009(1)	0.6627(8)	0.034(5)
H(34C)	4a	0.959(2)	−0.060(1)	0.6289(8)	0.032(4)
H(4A)	4a	0.607(2)	−0.046(1)	0.7148(8)	0.036(5)
H(4B)	4a	0.601(2)	−0.063(1)	0.6450(8)	0.034(4)
H(4C)	4a	0.486(2)	−0.015(1)	0.6808(8)	0.030(4)
H(41A)	4a	0.449(2)	−0.157(1)	0.7385(8)	0.024(4)
H(41B)	4a	0.576(2)	−0.211(1)	0.7073(7)	0.021(4)
H(42A)	4a	0.332(1)	−0.156(1)	0.6401(7)	0.015(3)
H(42B)	4a	0.454(2)	−0.215(1)	0.6049(7)	0.022(4)
H(43A)	4a	0.318(1)	−0.301(1)	0.7179(7)	0.016(4)
H(43B)	4a	0.416(2)	−0.364(1)	0.6721(7)	0.024(4)
H(44A)	4a	0.153(2)	−0.297(1)	0.6288(7)	0.028(4)
H(44B)	4a	0.256(2)	−0.357(1)	0.5867(8)	0.032(4)
H(44C)	4a	0.191(2)	−0.412(1)	0.6462(8)	0.031(4)
HW(1A)	4a	0.698(2)	−0.401(2)	0.786(1)	0.052(6)
HW(1B)	4a	0.735(2)	−0.412(1)	0.8485(8)	0.030(4)
HW(2A)	4a	0.749(2)	0.105(1)	1.0417(8)	0.030(4)
HW(2B)	4a	0.857(2)	0.043(1)	1.0255(9)	0.042(5)

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

Atom	Site	x	y	z	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Zr(1)	4a	0.356687(8)	−0.054974(6)	0.907108(4)	0.00714(3)	0.00743(3)	0.00785(3)	0.00051	−0.00016(3)	−0.00107(3)
N(1)	4a	0.52864(8)	−0.17550(7)	0.94585(4)	0.0108(3)	0.0123(3)	0.0101(3)	0.0004(3)	0.0006(3)	0.0003(3)
N(2)	4a	0.25277(8)	0.10139(6)	0.95403(4)	0.0089(3)	0.0116(3)	0.0109(3)	−0.0012(3)	0.0005(3)	−0.0028(3)
N(3)	4a	0.97748(9)	−0.19019(7)	0.82359(4)	0.0119(3)	0.0148(4)	0.0131(4)	−0.0019(3)	0.0001(3)	0.0015(3)
N(4)	4a	0.55303(9)	−0.06285(8)	0.68286(4)	0.0155(4)	0.0157(4)	0.0163(4)	−0.0015(3)	−0.0023(3)	0.0008(3)
C(11)	4a	0.5408(1)	−0.16257(8)	1.01601(5)	0.0109(4)	0.0176(4)	0.0109(4)	0.0023(3)	−0.0003(3)	0.0006(3)
C(12)	4a	0.65569(9)	−0.15261(8)	0.91262(5)	0.0086(3)	0.0185(4)	0.0135(4)	0.0017(3)	0.0010(3)	0.0018(3)
C(13)	4a	0.4806(1)	−0.28134(8)	0.93040(5)	0.0166(4)	0.0095(4)	0.0172(4)	0.0020(3)	−0.0003(4)	0.0009(3)
C(14)	4a	0.4066(1)	−0.13377(7)	1.04459(5)	0.0127(4)	0.0104(4)	0.0116(4)	−0.0002(3)	0.0006(3)	0.0008(3)
C(15)	4a	0.6303(1)	−0.10838(7)	0.84641(4)	0.0107(4)	0.0112(4)	0.0116(4)	−0.0002(3)	0.0014(3)	−0.0023(3)
C(16)	4a	0.3749(1)	−0.28488(7)	0.87807(5)	0.0134(4)	0.0106(4)	0.0187(4)	0.0003(3)	0.0016(3)	−0.0016(3)
C(21)	4a	0.3439(1)	0.14399(8)	1.00312(5)	0.0113(4)	0.0166(4)	0.0135(4)	−0.0001(3)	−0.0014(3)	−0.0065(3)
C(22)	4a	0.12348(9)	0.07249(7)	0.98263(5)	0.0108(4)	0.0139(4)	0.0146(4)	−0.0007(3)	0.0037(3)	−0.0036(3)
C(23)	4a	0.2331(1)	0.17668(7)	0.90096(5)	0.0173(4)	0.0098(4)	0.0156(4)	0.0026(3)	0.0018(4)	−0.0006(3)
C(24)	4a	0.4879(1)	0.11732(7)	0.98817(5)	0.0120(4)	0.0109(4)	0.0109(4)	−0.0002(3)	−0.0004(3)	−0.0009(3)
C(25)	4a	0.05942(9)	−0.01514(7)	0.94609(5)	0.0099(4)	0.0117(4)	0.0114(4)	0.0009(3)	−0.0005(3)	0.0011(3)
C(26)	4a	0.2509(1)	0.13179(7)	0.83434(5)	0.0100(4)	0.0108(4)	0.0139(4)	0.0004(3)	−0.0002(3)	−0.0003(3)
C(31)	4a	1.0521(1)	−0.20512(8)	0.76227(5)	0.0132(4)	0.0178(4)	0.0147(4)	−0.0005(3)	0.0015(3)	−0.0017(4)
C(32)	4a	1.1050(1)	−0.10305(9)	0.73784(5)	0.0122(4)	0.0222(5)	0.0147(4)	−0.0043(3)	0.0006(3)	0.0001(4)
C(33)	4a	0.9998(1)	−0.02081(9)	0.72540(5)	0.0182(5)	0.0164(4)	0.0171(5)	−0.0033(4)	0.0027(4)	0.0008(4)
C(34)	4a	0.9047(1)	−0.0482(1)	0.67116(6)	0.0193(5)	0.0289(6)	0.0257(5)	−0.0017(5)	−0.0066(4)	0.0049(5)
C(41)	4a	0.4975(1)	−0.16590(8)	0.69932(5)	0.0183(4)	0.0131(4)	0.0144(4)	−0.0008(3)	−0.0026(4)	0.0009(3)
C(42)	4a	0.4056(1)	−0.20854(8)	0.64821(5)	0.0143(4)	0.0148(4)	0.0121(4)	−0.0003(3)	0.0000(3)	−0.0009(3)
C(43)	4a	0.3452(1)	−0.31061(8)	0.67112(5)	0.0161(4)	0.0152(4)	0.0147(4)	−0.0010(4)	0.0008(4)	−0.0002(3)
C(44)	4a	0.2287(1)	−0.34672(9)	0.63040(6)	0.0200(5)	0.0172(5)	0.0204(5)	−0.0041(4)	0.0008(4)	−0.0012(4)
O(14A)	4a	0.38826(7)	−0.14178(6)	1.10299(3)	0.0189(3)	0.0179(3)	0.0097(3)	0.0032(3)	0.0020(2)	0.0013(2)
O(14B)	4a	0.31899(7)	−0.09855(6)	1.00547(3)	0.0107(3)	0.0158(3)	0.0113(3)	0.0014(2)	0.0006(2)	0.0018(3)
O(15A)	4a	0.71983(7)	−0.10561(6)	0.80581(4)	0.0120(3)	0.0206(4)	0.0137(3)	0.0007(3)	0.0039(3)	0.0001(3)
O(15B)	4a	0.51359(7)	−0.07160(6)	0.83710(3)	0.0116(3)	0.0154(3)	0.0109(3)	0.0040(2)	0.0013(2)	−0.0007(2)
O(16A)	4a	0.3547(1)	−0.36347(6)	0.84829(5)	0.0247(4)	0.0132(3)	0.0384(5)	0.0025(3)	−0.0075(4)	−0.0110(3)
O(16B)	4a	0.30618(7)	−0.20056(6)	0.87170(4)	0.0139(3)	0.0102(3)	0.0208(4)	0.0020(2)	−0.0034(3)	−0.0035(3)
O(24A)	4a	0.57786(8)	0.16422(6)	1.01539(4)	0.0133(3)	0.0172(3)	0.0188(3)	−0.0017(3)	−0.0036(3)	−0.0060(3)
O(24B)	4a	0.50582(7)	0.04157(5)	0.94901(3)	0.0105(3)	0.0121(3)	0.0130(3)	−0.0003(2)	0.0006(2)	−0.0040(2)
O(25A)	4a	−0.05807(7)	−0.03752(6)	0.95570(4)	0.0095(3)	0.0181(4)	0.0185(3)	−0.0013(2)	0.0020(3)	−0.0017(3)
O(25B)	4a	0.13666(6)	−0.06447(5)	0.90744(3)	0.0092(2)	0.0136(3)	0.0141(3)	0.0009(2)	−0.0003(3)	−0.0037(3)
O(26A)	4a	0.21449(8)	0.18048(6)	0.78721(4)	0.0241(4)	0.0161(4)	0.0163(3)	0.0062(3)	−0.0037(3)	0.0025(3)
O(26B)	4a	0.31328(7)	0.04523(6)	0.83119(3)	0.0153(3)	0.0115(3)	0.0116(3)	0.0039(2)	0.0002(2)	−0.0001(3)
OW(1)	4a	0.67070(8)	−0.42979(7)	0.82355(4)	0.0172(4)	0.0334(5)	0.0170(4)	−0.0071(3)	0.0010(3)	−0.0011(3)
OW(2)	4a	0.82919(8)	0.08416(7)	1.05418(4)	0.0151(4)	0.0249(4)	0.0173(3)	0.0049(3)	−0.0005(3)	−0.0038(3)

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