Crystal structure of *N,N,N',N'*-tetramethylethylenediammonium bis(nitrilotriacetato)zirconate pentahydrate, $[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2]\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]_2 \cdot 5\text{H}_2\text{O}$

E. Haussühl*

Universität Wien, Institut für Mineralogie und Kristallographie, Althanstr. 14 · Geozentrum, A-1090 Wien, Austria

Received July 10, 2002; accepted and available on-line October 7, 2002; CCDC-No. 1267/910

Abstract

$\text{C}_{18}\text{H}_{40}\text{N}_4\text{O}_{17}\text{Zr}$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.887(2) \text{ \AA}$, $b = 10.149(2) \text{ \AA}$, $c = 23.458(5) \text{ \AA}$, $\beta = 94.38(3)^\circ$, $V = 2821.7 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.022$, $wR_{\text{ref}}(F^2) = 0.055$, $T = 293 \text{ K}$.

Source of material

The raw material was obtained from an aqueous solution by fractional crystallization of the reaction product of *N,N,N',N'*-tetramethylethylenediamine, 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 (001). The first type consists of complex nitrilotriacetato-zirconate anions, in which the zirconium cations are coor-

ordinated by six oxygen and two nitrogen atoms of the nitrilotriacetato groups. The second type is occupied by interstitial water molecules and by *N,N,N',N'*-tetramethylethylenediammonium cations, which are connected by hydrogen bonds to carboxylic groups of the $\text{Zr}[\text{N}(\text{CH}_2\text{COO})_3]_2$ anions. The two types of layers are bound by ionic interactions and by a three-dimensional network of hydrogen bonds which are characterized by donor acceptor distances between 2.74 Å and 3.06 Å and D–H...O angles between 123° and 179°. Split-positions had to be assumed for the carbon atoms of the ethylene group (C33 and C43) of the *N,N,N',N'*-tetramethylethylenediammonium cations which might be a hint at a statistical disorder. The positions of the hydrogen atoms attached to the split carbon atoms were first calculated and included in the least-squares refinement using a rigid-body model of an idealized CH_2 -group with fixed C–H bond distances and tetrahedral bond angles. Then these atoms were included in the refinement procedure with varying positional and isotropic displacement parameters.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.25 × 0.30 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	4.72 cm^{-1}
Diffraction, scan mode:	Nonius Kappa-CCD, φ/ω
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	31042, 8205
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7659
$N(\text{param})_{\text{refined}}$:	558
Programs:	SHELXS-97 [1], SHELXL-97 [2], ATOMS [3]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(11A)	4e		0.190(1)	−0.025(2)	0.3271(7)	0.040(4)
H(11B)	4e		0.137(1)	0.110(2)	0.3416(7)	0.042(4)
H(12A)	4e		0.006(1)	0.171(2)	0.2844(7)	0.041(4)
H(12B)	4e		−0.020(1)	0.045(2)	0.2473(7)	0.047(4)
H(13A)	4e		0.112(1)	−0.080(2)	0.2158(7)	0.045(4)
H(13B)	4e		0.234(2)	−0.076(2)	0.2400(8)	0.055(5)
H(21A)	4e		0.307(1)	0.569(2)	0.3415(7)	0.047(4)
H(21B)	4e		0.364(1)	0.431(2)	0.3538(7)	0.044(4)
H(22A)	4e		0.497(1)	0.405(2)	0.3018(7)	0.048(4)
H(22B)	4e		0.508(1)	0.536(2)	0.2696(7)	0.047(4)
H(23A)	4e		0.363(2)	0.660(2)	0.2392(8)	0.061(5)
H(23B)	4e		0.239(2)	0.627(2)	0.2527(8)	0.062(5)
HN(3A)	4e		0.241(2)	0.724(2)	0.4346(9)	0.062(6)
H(31A)	4e		0.246(2)	0.520(3)	0.461(1)	0.095(8)
H(31B)	4e		0.236(2)	0.571(2)	0.524(1)	0.076(6)
H(31C)	4e		0.340(2)	0.604(3)	0.495(1)	0.101(9)

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

Table 2. Continued.

Atom	Site	Occ.	x	y	z	<i>U</i> _{iso}
H(32A)	4e		0.076(2)	0.610(2)	0.431(1)	0.078(7)
H(32B)	4e		0.054(2)	0.759(3)	0.436(1)	0.105(9)
H(32C)	4e		0.057(2)	0.662(2)	0.489(1)	0.086(7)
H(33A)	4e	0.646	0.208(3)	0.794(2)	0.543(1)	0.041(7)
H(33B)	4e	0.646	0.321(3)	0.800(3)	0.522(1)	0.047(8)
H(33C)	4e	0.354	0.118(7)	0.899(9)	0.477(3)	0.08(2)
H(33D)	4e	0.354	0.150(4)	0.819(4)	0.532(2)	0.03(1)
HN(4A)	4e		0.226(2)	1.027(2)	0.5603(9)	0.066(6)
H(41A)	4e		0.235(2)	1.193(2)	0.474(1)	0.082(7)
H(41B)	4e		0.214(3)	1.234(3)	0.536(1)	0.11(1)
H(41C)	4e		0.124(3)	1.149(3)	0.497(1)	0.12(1)
H(42A)	4e		0.411(2)	1.104(2)	0.512(1)	0.089(8)
H(42B)	4e		0.383(3)	1.149(3)	0.573(1)	0.13(1)
H(42C)	4e		0.416(2)	1.002(3)	0.560(1)	0.11(1)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	<i>U</i> _{iso}
H(43A)	4e	0.646	0.264(3)	0.964(3)	0.450(1)	0.044(8)
H(43B)	4e	0.646	0.148(4)	0.953(4)	0.473(2)	0.07(1)
H(43C)	4e	0.354	0.311(4)	0.958(5)	0.459(2)	0.04(1)
H(43D)	4e	0.354	0.349(4)	0.858(6)	0.512(2)	0.05(1)
HW(1A)	4e		0.031(2)	0.563(2)	0.0949(9)	0.074(7)
HW(1B)	4e		0.051(2)	0.446(2)	0.117(1)	0.093(8)
HW(2A)	4e		0.455(2)	0.001(3)	0.081(1)	0.11(1)
HW(2B)	4e		0.394(2)	0.098(3)	0.105(1)	0.093(8)
HW(3A)	4e		0.086(2)	0.803(2)	0.115(1)	0.083(7)
HW(3B)	4e		-0.023(2)	0.801(2)	0.1118(9)	0.071(7)
HW(4A)	4e		0.520(2)	0.736(2)	0.102(1)	0.083(8)
HW(4B)	4e		0.410(2)	0.758(3)	0.112(1)	0.091(8)
HW(5A)	4e		0.386(2)	0.803(2)	0.371(1)	0.080(7)
HW(5B)	4e		0.434(2)	0.712(2)	0.4066(9)	0.063(6)

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

Atom	Site	Occ.	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)	4e		0.249613(8)	0.282978(9)	0.221725(4)	0.02169(6)	0.02041(5)	0.02020(5)	-0.00305(3)	0.00236(3)	-0.00113(3)
N(1)	4e		0.14802(7)	0.09204(9)	0.25710(4)	0.0250(4)	0.0245(4)	0.0279(4)	-0.0029(3)	0.0050(3)	-0.0021(3)
N(2)	4e		0.34537(8)	0.47305(9)	0.26966(4)	0.0253(4)	0.0250(4)	0.0289(4)	-0.0022(3)	0.0037(3)	-0.0038(3)
N(3)	4e		0.2068(1)	0.7082(1)	0.46563(5)	0.086(1)	0.0428(6)	0.0296(5)	-0.0095(6)	0.0241(6)	-0.0048(5)
N(4)	4e		0.2577(1)	1.0493(1)	0.52912(6)	0.0655(8)	0.0434(6)	0.0431(6)	-0.0145(6)	0.0182(6)	-0.0049(5)
C(11)	4e		0.1881(1)	0.0680(1)	0.31780(5)	0.0353(6)	0.0336(5)	0.0269(5)	-0.0057(4)	0.0068(4)	0.0036(4)
C(12)	4e		0.02568(9)	0.1233(1)	0.25083(6)	0.0237(5)	0.0338(6)	0.0448(7)	-0.0049(4)	0.0075(5)	0.0003(5)
C(13)	4e		0.1733(1)	-0.0227(1)	0.22084(5)	0.0407(6)	0.0231(5)	0.0372(6)	-0.0030(4)	0.0062(5)	-0.0047(4)
C(14)	4e		0.3032(1)	0.1278(1)	0.33233(5)	0.0342(6)	0.0275(5)	0.0278(5)	0.0010(4)	0.0041(4)	0.0009(4)
C(15)	4e		-0.0041(1)	0.2127(1)	0.20005(5)	0.0261(5)	0.0322(5)	0.0392(6)	-0.0016(4)	0.0026(4)	-0.0062(4)
C(16)	4e		0.2120(1)	0.0173(1)	0.16346(6)	0.0360(6)	0.0328(6)	0.0405(6)	-0.0083(5)	0.0131(5)	-0.0139(5)
C(21)	4e		0.3101(1)	0.4807(1)	0.32880(5)	0.0338(6)	0.0397(6)	0.0303(5)	-0.0059(5)	0.0059(4)	-0.0130(5)
C(22)	4e		0.46885(9)	0.4543(1)	0.26895(5)	0.0235(5)	0.0378(6)	0.0357(6)	-0.0049(4)	0.0019(4)	-0.0086(5)
C(23)	4e		0.3084(1)	0.5921(1)	0.23673(6)	0.0431(7)	0.0216(5)	0.0516(7)	-0.0018(5)	0.0035(6)	0.0008(5)
C(24)	4e		0.1960(1)	0.4175(1)	0.33273(5)	0.0340(6)	0.0290(5)	0.0333(5)	-0.0005(4)	0.0080(4)	-0.0073(4)
C(25)	4e		0.49798(9)	0.3743(1)	0.21778(5)	0.0259(5)	0.0252(5)	0.0293(5)	-0.0013(4)	0.0041(4)	0.0027(4)
C(26)	4e		0.2779(1)	0.5612(1)	0.17455(6)	0.0300(5)	0.0316(5)	0.0473(7)	-0.0016(4)	-0.0002(5)	0.0133(5)
C(31)	4e		0.2652(2)	0.5901(3)	0.48975(8)	0.067(1)	0.094(2)	0.0380(8)	-0.006(1)	-0.0009(8)	0.0158(9)
C(32)	4e		0.0859(2)	0.6812(3)	0.4530(1)	0.078(1)	0.081(1)	0.055(1)	0.027(1)	0.006(1)	-0.008(1)
C(33)	4e	0.646(6)	0.2476(2)	0.8115(2)	0.50983(9)	0.044(2)	0.039(1)	0.028(1)	0.0013(9)	0.0001(9)	-0.0010(7)
C(33A)	4e	0.354	0.1753(4)	0.8468(4)	0.4914(2)	0.045(3)	0.038(2)	0.042(2)	0.002(2)	0.010(2)	-0.008(2)
C(41)	4e		0.2012(2)	1.1695(3)	0.5061(1)	0.071(2)	0.079(2)	0.088(2)	0.013(1)	0.021(1)	0.011(1)
C(42)	4e		0.3772(2)	1.0767(3)	0.5456(1)	0.065(1)	0.095(2)	0.081(2)	-0.003(1)	-0.001(1)	0.007(1)
C(43)	4e	0.646	0.2217(3)	0.9467(2)	0.4848(1)	0.043(2)	0.040(1)	0.038(1)	0.002(1)	-0.000(1)	0.0011(8)
C(43A)	4e	0.354	0.2839(5)	0.9230(4)	0.4949(2)	0.041(3)	0.040(2)	0.040(2)	-0.002(2)	0.007(2)	-0.006(2)
O(14A)	4e		0.34875(9)	0.1161(1)	0.38073(4)	0.0526(6)	0.0548(6)	0.0292(4)	-0.0078(5)	-0.0044(4)	0.0078(4)
O(14B)	4e		0.34510(7)	0.19547(8)	0.29214(3)	0.0271(4)	0.0291(4)	0.0302(4)	-0.0015(3)	0.0010(3)	0.0050(3)
O(15A)	4e		-0.10294(8)	0.2256(1)	0.18223(5)	0.0256(4)	0.0586(6)	0.0703(7)	0.0005(4)	-0.0015(4)	0.0079(5)
O(15B)	4e		0.07962(7)	0.27413(9)	0.18000(4)	0.0284(4)	0.0413(5)	0.0338(4)	-0.0073(3)	-0.0032(3)	0.0036(3)
O(16A)	4e		0.1954(1)	-0.0539(1)	0.12193(5)	0.100(1)	0.0626(7)	0.0555(7)	-0.0458(7)	0.0388(7)	-0.0365(6)
O(16B)	4e		0.26930(8)	0.12554(9)	0.16333(4)	0.0402(5)	0.0353(4)	0.0378(4)	-0.0141(4)	0.0160(4)	-0.0141(3)
O(24A)	4e		0.15248(9)	0.4175(1)	0.37836(4)	0.0573(6)	0.0639(7)	0.0393(5)	-0.0185(5)	0.0220(5)	-0.0184(5)
O(24B)	4e		0.15189(6)	0.36252(8)	0.28667(3)	0.0259(4)	0.0297(4)	0.0331(4)	-0.0013(3)	0.0053(3)	-0.0076(3)
O(25A)	4e		0.59517(7)	0.37748(9)	0.20327(4)	0.0266(4)	0.0449(5)	0.0492(5)	-0.0059(4)	0.0115(4)	-0.0072(4)
O(25B)	4e		0.41934(7)	0.30238(8)	0.19397(4)	0.0298(4)	0.0352(4)	0.0329(4)	-0.0096(3)	0.0103(3)	-0.0079(3)
O(26A)	4e		0.2909(1)	0.6419(1)	0.13681(5)	0.0657(7)	0.0512(6)	0.0643(7)	-0.0139(5)	-0.0034(6)	0.0315(6)
O(26B)	4e		0.23306(8)	0.44762(9)	0.16474(4)	0.0477(5)	0.0349(4)	0.0372(5)	-0.0113(4)	-0.0100(4)	0.0113(4)
OW(1)	4e		0.0357(1)	0.4867(1)	0.08541(5)	0.0585(7)	0.0516(6)	0.0421(6)	0.0005(5)	-0.0096(5)	-0.0031(5)
OW(2)	4e		0.4452(1)	0.0795(2)	0.08448(6)	0.0531(7)	0.0619(8)	0.0657(8)	-0.0091(6)	0.0211(6)	-0.0048(6)
OW(3)	4e		0.0299(1)	0.7539(1)	0.10741(7)	0.0485(7)	0.0464(6)	0.097(1)	-0.0067(6)	0.0228(7)	-0.0222(6)
OW(4)	4e		0.4677(1)	0.7927(1)	0.09564(6)	0.0472(7)	0.0575(7)	0.0734(8)	-0.0068(6)	-0.0082(6)	0.0151(6)
OW(5)	4e		0.3813(1)	0.7660(1)	0.40162(5)	0.0546(7)	0.0500(6)	0.0489(6)	0.0059(5)	0.0228(5)	0.0067(5)

Acknowledgments. The author is gratefully indebted to the Austrian Fonds zur Förderung der wissenschaftlichen Forschung FWF (P14125-GEO) and the International Centre for Diffraction Data for financial support of this work (Grant 90-03 ET).

References

- Sheldrick, G. M.: SHELXS-97. Program for the solution of crystal structures. University of Göttingen, Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Program for Refinement of Crystal Structures. University of Göttingen, Göttingen, Germany 1997.
- Dowty, E.: ATOMS 5.0. A Complete Program for Displaying Atomic Structures. Shape software, 521 Hidden Valley Road, Kingsport, TN 37663, USA 1999.