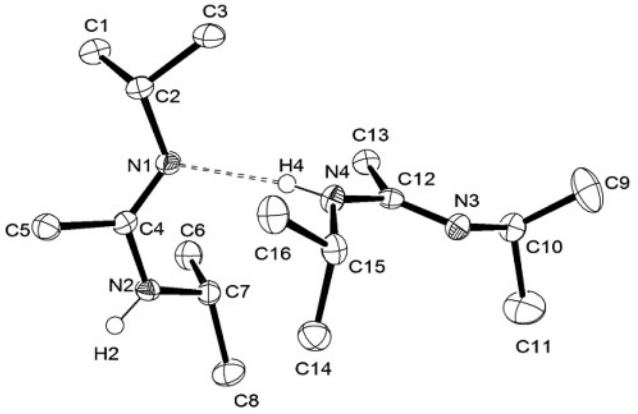
The crystal structure of *N*-(1-(dimethyl-l4-azanylidene)ethyl)propan-2-amine, a *Z'* > 1 structure, $C_8H_{18}N_2$

Gamall Makhloufi, Kai Schütte and Christoph Janiak*

Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl I: Bioanorganische Chemie und Katalyse, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Received September 08, 2014, accepted October 30, 2014, available online November 07, 2014, CCDC no. 1267/4223



Abstract

$C_8H_{18}N_2$, monoclinic, $P2_1/n$ (no. 14), a = 9.708(9) Å, b = 14.988(17) Å, c = 13.207(12) Å, β = 95.92(3)°, V = 1911.4 Å^3, Z = 8, $R_{gt}(F)$ = 0.0369, $wR_{ref}(F^2)$ = 0.0937, T = 100 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.05×0.15×0.20 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	4.51 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa APEX-II CCD, ω
$2\theta_{max}$:	130.37°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13974, 3145
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2628
$N(param)_{refined}$:	199
Programs:	SHELX [1]

Source of material

The synthesis was carried out with standard Schlenk techniques under nitrogen atmosphere since the lithium amidinate is hygroscopic and air sensitive. The solvents (*n*-hexane and tetrahydrofuran) were dried using the MBraun solvent purification system. *N*-(1-(dimethyl-l4-azanylidene)ethyl)propan-2-amine was synthesized by deprotonation and methylation of 1,3-diisopropylcarbo- diimide with methyllithium according to literature procedures [2, 3]. The resulting lithium amidinate was then reacted with a stoichiometric amount of water and purified by sublimation to afford colourless crystals (800 mbar, 25°C).

Experimental details

The two N-bound hydrogen atoms were found in difference Fourier syntheses and were refined freely (H2, H4). The hydrogen atoms of the isopropyl groups were idealized and refined using rigid groups. For the CH_3-groups AFIX 137 (with U_{iso}(H) = 1.5U_{eq}(C)) and for the CH-group AFIX 13 option (U_{iso}(H) = 1.2U_{eq}(C)) of the SHELXL-2013 program was used [1].

Discussion

Metal amidinates are investigated and widely used as precursors for thin metal films in low pressure chemical vapor deposition (CVD) or atomic layer deposition (ALD) [2–5]. They also can be used as precursors for mono- and bimetallic nanoparticle synthesis [6]. Here we show that hydrolytic decomposition of metal amidinates like $[Me(C(N^iPr)_2)]_2Zn$ or $\{[Me(C(N^iPr)_2)]Li\}_2$ yields the free N-(1-(dimethyl-l4-azanylidene)ethyl)propan-2-amine molecule. Two crystallographically independent molecules (Z' = 2) are connected through the N4–H4···N1 hydrogen bond to form the asymmetric unit (*cf.* Fig.). Z' is the number of formula units in the unit cell divided by the number of independent general positions [7, 8]. There is an ongoing discussion on the origin of so-called Z' > 1 structures. Different ideas have been put forward to rationalize this phenomenon [9]: A "fossil relic" of a more stable form [10], a crystal "on the way" [11, 12] or strong and special supramolecular interactions between the two (or more) symmetry-independent units [13–15]. A high Z' is also obtained when the molecule has different equi-energetic conformations, with these conformations co-existing in the crystal [16]. An overlay of the two symmetry-independent molecules of the title structure shows a small difference in C–N–C(^iPr)–C(^iPr) torsion angles. Hence, we trace the co-existence of two crystallographically independent molecules to the presence of the hydrogen bond. The di-molecular unit is part of a supramolecular hydrogen-bridged chain structure which extends along the *ac*-diagonal. Neighboring chains are arranged in parallel through van der Waals contacts.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.2072	0.5430	1.0191	0.041
H(1B)	4*e*	0.0957	0.5935	1.0795	0.041
H(1C)	4*e*	0.2530	0.6271	1.0893	0.041
H(2A)	4*e*	0.1159	0.7232	0.9767	0.025
H(3A)	4*e*	0.0016	0.6649	0.8235	0.046
H(3B)	4*e*	–0.0562	0.6156	0.9179	0.046
H(3C)	4*e*	0.0535	0.5664	0.8546	0.046
H(5A)	4*e*	0.2586	0.8412	0.9857	0.034
H(5B)	4*e*	0.4234	0.8447	1.0104	0.034
H(5C)	4*e*	0.3342	0.7769	1.0708	0.034
H(2)	4*e*	0.540(2)	0.777(1)	0.907(1)	0.030(4)
H(6A)	4*e*	0.6502	0.6003	0.9242	0.041
H(6B)	4*e*	0.5917	0.5390	0.8303	0.041
H(6C)	4*e*	0.4927	0.5672	0.9145	0.041
H(7)	4*e*	0.4467	0.6539	0.7627	0.024
H(8A)	4*e*	0.6116	0.7576	0.7173	0.046

* Correspondence author (e-mail: janiak@hhu.de)

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8B)	4*e*	0.6748	0.6591	0.7145	0.046
H(8C)	4*e*	0.7207	0.7238	0.8083	0.046
H(9A)	4*e*	0.1101	0.5857	0.3154	0.063
H(9B)	4*e*	0.0489	0.5159	0.3908	0.063
H(9C)	4*e*	0.1609	0.4840	0.3176	0.063
H(10)	4*e*	0.2677	0.5031	0.4854	0.027
H(11A)	4*e*	0.4527	0.5949	0.4495	0.069
H(11B)	4*e*	0.3609	0.6379	0.3543	0.069
H(11C)	4*e*	0.4066	0.5354	0.3512	0.069
H(13A)	4*e*	0.3526	0.5200	0.6491	0.033

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(13B)	4*e*	0.1951	0.4868	0.6362	0.033
H(13C)	4*e*	0.2515	0.5452	0.7331	0.033
H(4)	4*e*	0.200(2)	0.681(1)	0.730(1)	0.038(4)
H(14A)	4*e*	0.3649	0.7903	0.5793	0.044
H(14B)	4*e*	0.3634	0.8261	0.6934	0.044
H(14C)	4*e*	0.3013	0.8864	0.5996	0.044
H(15)	4*e*	0.1190	0.7841	0.5609	0.026
H(16A)	4*e*	0.1336	0.8317	0.7719	0.044
H(16B)	4*e*	–0.0059	0.8077	0.7018	0.044
H(16C)	4*e*	0.0776	0.8967	0.6807	0.044

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}
C(1)	4*e*	0.1780(1)	0.60113(9)	1.0432(1)	0.0245(6)	0.0293(8)	0.0287(7)	–0.0009(5)	0.0069(6)	0.0046(6)
C(2)	4*e*	0.1438(1)	0.66340(9)	0.95202(9)	0.0175(6)	0.0221(7)	0.0227(7)	0.0000(5)	0.0062(5)	0.0014(5)
C(3)	4*e*	0.0250(1)	0.6241(1)	0.8806(1)	0.0192(6)	0.0426(9)	0.0307(8)	–0.0079(6)	0.0056(6)	0.0013(6)
N(1)	4*e*	0.2671(1)	0.67322(7)	0.89644(8)	0.0154(5)	0.0232(6)	0.0196(6)	–0.0003(4)	0.0032(4)	0.0000(4)
C(4)	4*e*	0.3569(1)	0.73488(8)	0.92476(9)	0.0157(6)	0.0189(7)	0.0166(6)	0.0027(5)	0.0016(5)	0.0039(5)
C(5)	4*e*	0.3419(1)	0.80569(8)	1.0051(1)	0.0210(6)	0.0213(7)	0.0273(7)	0.0000(5)	0.0054(6)	–0.0023(6)
N(2)	4*e*	0.4772(1)	0.74168(7)	0.87907(8)	0.0156(5)	0.0202(6)	0.0210(6)	–0.0020(4)	0.0030(5)	–0.0007(5)
C(6)	4*e*	0.5689(1)	0.58669(9)	0.8765(1)	0.0291(7)	0.0237(7)	0.0288(7)	0.0036(6)	0.0038(6)	–0.0026(6)
C(7)	4*e*	0.5249(1)	0.67039(8)	0.81458(9)	0.0166(6)	0.0250(7)	0.0190(6)	0.0000(5)	0.0022(5)	–0.0022(5)
C(8)	4*e*	0.6436(1)	0.7059(1)	0.7587(1)	0.0256(7)	0.0332(8)	0.0359(8)	0.0025(6)	0.0139(6)	0.0000(6)
C(9)	4*e*	0.1315(2)	0.5335(1)	0.3589(1)	0.0387(8)	0.0386(9)	0.0453(9)	0.0105(7)	–0.0089(8)	–0.0219(7)
C(10)	4*e*	0.2472(1)	0.55655(9)	0.4410(1)	0.0233(6)	0.0214(7)	0.0240(7)	0.0054(5)	0.0046(6)	–0.0023(5)
C(11)	4*e*	0.3785(2)	0.5836(1)	0.3949(1)	0.0364(8)	0.046(1)	0.060(1)	0.0027(7)	0.0261(8)	–0.0143(8)
N(3)	4*e*	0.2052(1)	0.63099(7)	0.50410(8)	0.0193(5)	0.0198(6)	0.0200(6)	0.0031(4)	0.0047(5)	–0.0017(4)
C(12)	4*e*	0.2146(1)	0.62066(8)	0.60188(9)	0.0103(5)	0.0198(7)	0.0234(7)	0.0000(5)	0.0037(5)	0.0006(5)
C(13)	4*e*	0.2572(1)	0.53557(8)	0.6603(1)	0.0203(6)	0.0215(7)	0.0243(7)	0.0018(5)	0.0030(6)	0.0013(5)
N(4)	4*e*	0.1831(1)	0.68941(7)	0.66430(9)	0.0224(5)	0.0195(6)	0.0171(6)	0.0034(4)	0.0024(5)	0.0005(4)
C(14)	4*e*	0.3128(1)	0.82520(9)	0.6252(1)	0.0311(7)	0.0245(7)	0.0311(8)	–0.0024(6)	0.0011(6)	0.0041(6)
C(15)	4*e*	0.1704(1)	0.78279(8)	0.6305(1)	0.0243(6)	0.0194(7)	0.0198(7)	0.0038(5)	–0.0018(6)	–0.0001(5)
C(16)	4*e*	0.0864(2)	0.83431(9)	0.7027(1)	0.0341(7)	0.0238(7)	0.0297(8)	0.0072(6)	0.0011(6)	–0.0044(6)

Acknowledgments. I acknowledge support for the publication fee by the Deutsche Forschungsgemeinschaft (DFG) and the open access publication fund of the Heinrich-Heine-Universität Düsseldorf.

References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64**(2008) 112–122.
2. Lim, B.S.; Rahtu, A.; Park, J.-S.; Gordon, R. G.: Synthesis and Characterization of Volatile, Thermally Stable, Reactive Transition Metal Amidinates. Inorg. Chem. **42** (2003) 7951–7958.
3. Schmidt, S.; Schulz, S.; Blaeser, D.; Boese, R.; Bolte, M.: Synthesis and Structural Characterization of New Zinc Amidinate Complexes. Organometallics **29** (2010) 6097–6103.
4. Krisyuk, V.; Aloui, L.; Prud'homme, N.; Sysoev, S.; Senocq, F.; Samelor, D.; Vahlas, C.: CVD of Pure Copper Films from Amidinate Precursor Electrochemical/Chemical Deposition and Etching. Electrochem. Solid State Lett. **14** (2011) D26–D29.
5. Bahlawane, N.; Kohse-Hoinghaus, K.; Premkumar, P. A.; Lenoble, D.: Advances in the deposition chemistry of metal-containing thin films using gas phase processes. Chem. Sci. **3** (2012) 929–941.
6. Schütte, K.; Meyer, H.; Gemel, C.; Barthel, J.; Fischer, R. A.; Janiak, C.: Synthesis of Cu, Zn and Cu/Zn brass alloy nanoparticles from metal amidinate precursors in ionic liquids or propylene carbonate with relevance to methanol synthesis. Nanoscale **6** (2014) 3116–3126.
7. Ruiz, J.; Rodriuez, V.; Cutillas, N.; Hoffmann, A.; Chamayou, A.-C.; Kazmierczak; K.; Janiak, C.: Structure-solid-state CPMAS ^{13}C NMR correlation in palladacycle solvates (pseudo-polymorphs) with a transformation from Z' = 1 to Z' = 2. CrystEngComm. **10** (2008) 1928–1938.
8. Chamayou, A.-C.; Biswas, C.; Ghosh, A.; Janiak, C.: (Acetato-κ*O*)aqua(1*H*-imidazole-κN^3)(picolinato-κ^2*N*,*O*) copper(II) 0.87-hydrate: a *Z′* > 1 structure. Acta Cryst. **C65** (2009) m311–m313.
9. Gavezotti, A.: Structure and energy in organic crystals with two molecules in the asymmetric unit: causality or chance?. CrystEngComm. **10** (2008) 389–398.
10. Nichol, G. S.; Clegg, W.: Further thoughts on crystal structures with Z' > 1: analysis of single-crystal structures determined using X-ray synchrotron and neutron radiation in the Cambridge Structural Database. CrystEngComm. **9** (2007) 959–960.
11. Steed, J. W.: Should solid-state molecular packing have to obey the rules of crystallographic symmetry?. CrystEngComm. **5** (2003) 169–179.
12. Desiraju, G. R.: On the presence of multiple molecules in the crystal asymmetric unit (*Z′* > 1). CrystEngComm. **9** (2007) 91–92.
13. Althoff, G.; Ruiz, J.; Rodríguez, V.; López, G.; Pérez, J.; Janiak, C.: Can a single C–H···F–C hydrogen bond make a difference? Assessing the H···F bond strength from 2-D ^{1}H-^{19}F CP/MAS NMR. CrystEngComm. **8** (2006) 662–665.
14. Hao, X.; Parkin, S.; Brock, C. P.: The unusual phases of anhydrous and hydrated pinacol. Acta Crystallogr. **B61** (2005) 689–699.
15. Babu, N. J.; Nangia, A.: High *Z′* polymorphs have shorter C–H···O interactions and O–H···O hydrogen bonds. CrystEngComm. **9** (2007) 980–983.
16. Roy, S.; Banerjee, R.; Nangia, A.; Kruger, G. J.: Conformational, Concomitant Polymorphs of 4,4-Diphenyl-2,5-cyclohexadienone: Conformation and Lattice Energy Compensation in the Kinetic and Thermodynamic Forms. Chem. Eur. J. **12** (2006) 3777–3788.