Supplementary Information

5,5'-Azoxytetrazolates – A New Nitrogen-rich Dianion and its comparison to 5,5'-Azotetrazolate

Niko Fischer[1], Katharina Hüll[1], Thomas M. Klapötke[1*], Jörg Stierstorfer[1], Gerhard Laus[2], Michael Hummel[2], Carmen Froschauer[2], Klaus Wurst[2] and Herwig Schottenberger[2]

[1] Energetic Materials Research, Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, 81377 Munich, Germany

[2] Faculty of Chemistry and Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria

1. Crystal Structures

1.1 Crystal Structure of barium azoxybistetrazolate pentahydrate (2)

Barium azoxybistetrazolate pentahydrate **(2)** crystallizes in the monoclinic space group $P2_1/m$ with two molecules per unit cell. All bond lengths of the tetrazolyl moiety lie in between the respective single and double bonds. The N5-N5^i bond is slightly longer than a N=N double bond (1.20 Å). Also the N5–O1 bond is quite short (1.183(4) Å). Compared to all other presented azoxystructures, these two bonds are significantly shorter. The zTO ligands are nearly planar.

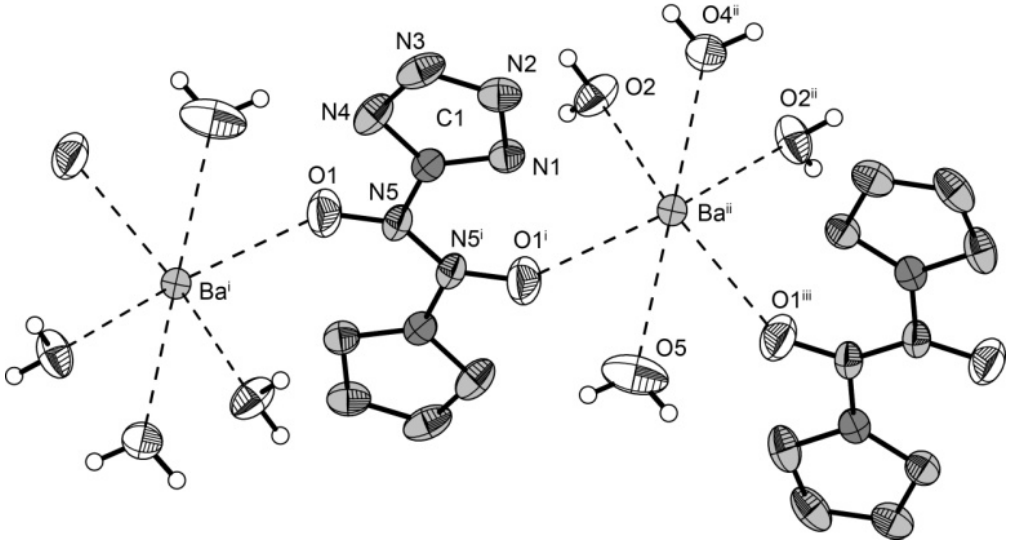

Figure S1. View on the formation of chains in the structure of barium 5,5'-azoxybistetrazolate tetrahydrate (**2**). Thermal ellipsoids represent the 50 % probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry codes: (i) -x, 1-y, -z; (ii) x, 0.5-y, z; (iii) -x, -0.5+y, -z.

The structure of **2** is again disordered (around the azoxy moiety). Every O1 position is half occupied. Due to this structural disorder, the zTO molecule inhabits a centre of inversion in

between N5 and N5^{i}. The space group $P2_1/m$ possesses a mirror plane *m* in the *a*/*c* plane. O3, O4, O5 and Ba1 lie in this plane, while O2 does not. The bolt axis 2_1 is found along *b*, but is not visible directly due to the disorder and the resulting inversion centre. **2** forms chains in two directions. The dianions act as bridging and chelating ligands, coordinating to the barium cations via O1 and N1 (larger distance).

1.2 Diaminoguanidinium azoxybistetrazolate monohydate (5)

Crystals of diaminoguanidinium azoxybistetrazolate monohydrate (**5**), depicted in Figure S2, were gained from the mother liquor. It crystallizes as a monohydrate in the triclinic space group *P*-1 with two molecules in the unit cell. The bond lengths and the geometry of the diaminoguanidinium cations are comparable to those already reported in literature.[1] The bond lengths of the azoxybistetrazolate dianions are listed in Table S1. The dianions form sloped rows in the *c*/*a* plane. The rows are connected via alternating diaminoguanidinium cations.

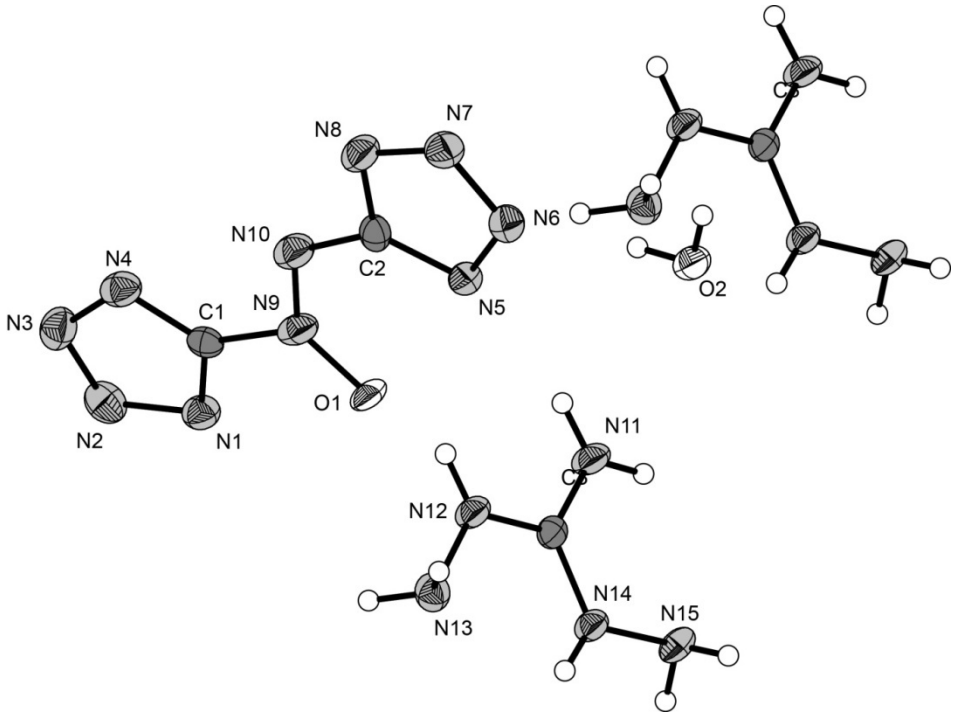

Figure S2. Molecular structure of bis(diaminoguanidinium) 5,5'-azoxybistetrazolate monohydrate (**5**). atom-labelling scheme and bond-distances (Å) with standard deviations. Thermal ellipsoids represent the 50 % probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

[1] T. M. Klapötke, P.Mayer and J. Stierstorfer, *Phosphorus, Sulfur and Silicon* 2009, **184**, 2399.

1.3 Selected bond lengths

Table S1. Selected bond lengths [Å] of compounds **1**, **3**–**5**, and **7**.

atoms A–B	**1**	**3**	**4**	**5**	**7 (a)**	**7 (b)**
N1–C1	1.331(3)	1.303(5)	1.319(3)	1.323(2)	1.326(3)	1.325(3)
N1–N2	1.332(3)	1.325(4)	1.340(2)	1.355(2)	1.346(3)	1.345(2)
N2–N3	1.315(3)	1.315(3)	1.324(3)	1.323(2)	1.326(3)	1.328(2)
N3–N4	1.339(3)	1.328(4)	1.342(3)	1.345(2)	1.345(2)	1.347(2)
N4–C1	1.335(3)	1.325(4)	1.318(3)	1.318(2	1.332(3)	1.330(3)
N5–C2	1.312(3)	1.303(5)	1.337(3)	1.341(2)	1.328(3)	1.330(3)
N5–N6	1.332(3)	1.325(4)	1.346(2)	1.344(2)	1.352(3)	1.347(3)
N6–N7	1.346(4)	1.315(3)	1.316(3)	1.317(2)	1.305(3)	1.305(3)
N7–N8	1.318(3)	1.328(4)	1.334(2)	1.326(2)	1.343(3)	1.345(3)
N8–C2	1.328(3)	1.325(4)	1.340(3)	1.343(2)	1.347(3)	1.343(3)
N9–C1	1.416(3)	1.439(8)	1.440(3)	1.466(2)	1.436(3)	1.437(3)
N9–N10	1.251(3)	1.274(10)	1.273(2)	1.259(2)	1.283(2)	1.284(2)
N10–C2	1.451(3)	1.439(8)	1.396(3)	1.398(2)	1.383(3)	1.385(3)
O1–N9	1.273(3)	1.316(8)	1.253(2)	1.2692(19)	1.251(2)	1.251(2)

Table S2. X-ray data and parameters of **1**–**5** and **7**.

	1	**2**	**3**	**4**	**5**	**7**
Formula	$C_2H_{10}N_{10}Na_2O_6$	$C_2H_{10}BaN_{10}O_6$	$C_2H_8N_{12}O$	$C_2H_{12}N_{12}O_5$	$C_4H_{18}N_{20}O_2$	$C_5H_{18}N_{24}O_7$
FW [g mol^{-1}]	316.18	407.53	216.20	284.24	378.38	526.43
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space Group	*P*-1 (No. 2)	$P2_1/m$	*P*-1 (No. 2)	$P2_1/c$ (No. 14)	*P*-1 (No. 2)	$P2_1/c$ (No. 14)
Color / Habit	yellow needle	yellow plate	Yellow plate	Yellow rod	Yellow plate	Yellow plate
Size [mm]	0.40×0.15×0.08	0.20×0.15×0.05	0.04x0.12x0.39	0.10x0.11x0.28	0.10x0.35x0.40	0.02x0.18x0.19
a [Å]	7.2189(6)	5.7898(3)	4.708(1)	8.0709(6)	6.6702(5)	13.0674(10)
b [Å]	7.6977(5)	14.9314(7)	7.429(1)	22.2329(15)	10.0880(8)	6.8891(7)
c [Å]	11.9774(9)	7.0531(3)	7.483(1)	6.7382(6)	12.7314(11)	24.3334(18)
α [°]	82.844(5)	90	102.21(1)	90	68.218(8)	90
β [°]	81.990(4)	101.949(3)	107.68(1)	102.014(7)	84.845(7)	104.661(7)
γ [°]	68.294(4)	90	106.78(1)	90	76.760(7)	90
V [Å^3]	610.41(8)	596.53(5)	225.54(7)	1182.62(16)	774.36(12)	2119.2(3)
Z	2	2	1	4	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.720	2.269	1.592	1.596	1.623	1.650
μ [mm^{-1}]	0.214	3.376	0.131	0.145	0.133	0.145
F(000)	324	392	0.71073	592	396	1088
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	173	0.71073	0.71073	0.71073
T [K]	233	233	233	173	173	173
θ Min–Max [°]	2.86, 24.99	2.7, 26.0	3.0, 24.9	4.5, 25.7	4.2, 26.3	4.2, 25.8
Dataset	-8:6;-9:8; -14:13	-6:7; -17:18; -8:7	-5:5; -8:8; -8:8	-8:9; -27:21; -8:8	-8:8; -12:12; -15:15	-14:15; -8:7; -29:29
Reflections collected	3373	3780	1285	5933	11855	10384
Independent refl.	2100	1212	755	2257	3123	4026
R_{int}	0.0202	0.029	0.029	0.057	0.029	0.041
Observed reflections	1916	1177	687	1262	2649	2898
Parameters	231	117	100	221	307	397
R_1 (obs)	0.0474	0.0169	0.0476	0.0386	0.0427	0.0409
wR_2 (all data)	0.1149	0.0395	0.1240	0.0738	0.1075	0.0936
S[c]	1.081	1.12	1.07	0.81	1.06	1.02
Resd. Dens. [e Å^{-3}]	-0.248, 0.888	-0.61, 0.31	-0.18, 0.21	-0.20, 0.40	-0.33, 0.99	-0.25, 0.22
Device type	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SHELXS-97	SHELXS-97	SIR-92	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	none	none	none	multi-scan	multi-scan	multi-scan
CCDC	881228	881227	881229	881230	881231	881233