Supplementary Information

Metal Salts and Complexes of 1,1'-Dinitramino-5,5'-bitetrazole

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1. X-ray Diffraction

For all compounds (except for **4**, **15** and **16**), an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-*K*α radiation (λ = 0.71073 Å). By using the CRYSALISPRO software[S2] the data collection and reduction were performed. The structures were solved by direct methods (SIR-92, [S3] SIR-97[S4] or SHELXS-97[S5]) and refined by full-matrix least-squares on F^2 (SHELXL [S5]) and finally checked using the PLATON software [S6] integrated in the WinGX software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multiscan method.[S7]. All DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii. The crystal structures of compounds **4**, **15** and **16** were determined at 100 K on a Bruker D8 Venture TXS diffractometer equipped with a multilayer monochromator, a Photon 2 detector, and a rotating-anode generator (MoKα radiation). The SADABS program embedded in the Bruker APEX3 software has been used for multi-scan absorption corrections in all structures.[S8]

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Table S1. Crystallographic data and refinement parameters of compound **2**, **6**, **7a** and**7b**.

	2	**6**	**7a**	**7b**
Formula	$C_6H_8N_{10}O_4$	$CH_2LiN_4O_4$	$C_2H_4N_{12}Na_2O_6$	$C_2H_4N_{12}Na_2O_6$
FW [g mol^{-1}]	284.22	306.06	338.08	338.08
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	*P*−1 (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
Color / Habit	Colorless block	Colorless block	Colorless block	Colorless block
Size [mm]	0.01 x 0.03 x 0.10	0.15 x 0.34 x 0.39	0.08 x 0.15 x 0.28	0.29 x 0.45 x 0.56
a [Å]	4.1866(7)	8.2760(9)	8.8347(5)	6.2136(3)
b [Å]	7.2348(10)	10.8140(8)	9.4711(5)	10.9858(6)
c [Å]	10.3368(13)	6.0650(4)	7.2402(4)	16.9609(8)
α [°]	81.092(5)	90	90	90
β [°]	83.309(6)	106.073(10)	105.804(5)	90
γ [°]	75.044(6)	90	90	90
V [Å^3]	297.88(8)	521.58(8)	582.92(6)	1157.77(10)
Z	1	2	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.584	1.949	1.927	1.940
μ [mm^{-1}]	0.134	0.176	0.236	0.238
F(000)	146	308	340	680
$\lambda_{MoK\alpha}$[Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	123
ϑ min-max [°]	3.3, 26.0	4.2, 26.7	4.3, 26.0	4.4, 26.0
Dataset h; k; l	−5:4; −8:8; −12:12	−5:10; −13:13; −7:7	−10:10; −11:11; −6:8	−7:6; −13:13; −20:20
Reflect. coll.	3156	3905	2933	8554
Independ. refl.	1159	1105	1136	1132
R_{int}	0.039	0.032	0.027	0.022
Reflection obs.	880	893	956	1059
No. parameters	96	108	108	108
R_1 (obs)	0.0481	0.0334	0.0305	0.0277
wR_2 (all data)	0.1184	0.0805	0.0812	0.0791
S	1.08	1.08	1.11	1.09
Resd. Dens.[e Å^{-3}]	−0.22, 0.22	−0.28, 0.26	−0.26, 0.26	−0.21, 0.37
Device type	Bruker D8 Venture	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3
	rotating anode	CCD	CCD	CCD
Solution	SIR-92	SIR-92	SIR-92	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	1502966	1500005	1500002	1500003

Table S2. Crystallographic data and refinement parameters of compound **8**–**11**.

	8	**9**	**10**	**11**
Formula	$C_2N_{12}O_4Rb_2$	$C_2N_{12}O_4Cs_2$	$C_2Ag_2N_{12}O_4$	$C_2H_{18}N_{18}O_4Ni$
FW [g mol^{-1}]	427.08	521.96	471.88	417.05
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	*P*−*1* (No. 2)	$P2_1/c$ (No. 14)	$P2/c$ (No. 13)	$P2_1/c$ (No. 14)
Color / Habit	Colorless needle	Colorless needle	Colorless plate	Purple cylinder
Size [mm]	0.03 x 0.05 x 0.44	0.04 x 0.09 x 0.37	0.02 x 0.10 x 0.12	0.09 x 0.13 x 0.26
a [Å]	5.3034(5)	5.5885(2)	6.7520(4)	13.5062(12)
b [Å]	7.0632(6)	12.4847(4)	5.0649(4)	11.5426(8)
c [Å]	8.5675(7)	8.7893(3)	14.1529(9)	10.4455(7)
α [°]	66.821(8)	90	90	90
β [°]	86.667(7)	92.250(3)	92.180(6)	95.176(7)
γ [°]	70.964(8)	90	90	90
V [Å^3]	277.98(5)	612.76(4)	483.65(6)	1621.8(2)
Z	1	2	2	4
$\rho_{calc.}$ [g cm^{-3}]	2.551	2.829	3.240	1.708
μ [mm^{-1}]	8.845	5.989	4.097	1.255
F(000)	202	476	444	864
$\lambda_{MoK\alpha}$[Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
ϑ min-max [°]	4.3, 26.0	4.6, 26.0	4.3, 26.0	4.1, 25.0
Dataset h; k; l	−6:6; −8:8; −10:10	−6:6; −15:15; −10:10	−7:8; −5:6; −17:17	−10:16; −13:13; −12: 12
Reflect. coll.	3969	8446	2377	7466
Independ. refl.	1096	1195	955	2837
R_{int}	0.041	0.034	0.029	0.063
Reflection obs.	1000	1061	761	1838
No. parameters	91	91	93	232
R_1 (obs)	0.0242	0.0172	0.0333	0.0503
wR_2 (all data)	0.0509	0.0386	0.0779	0.0992
S	1.04	1.08	1.05	0.97
Resd. Dens.[e Å^{-3}]	−0.47, 0.49	−0.37, 0.77	−1.43, 0.85	−0.53, 0.81
Device type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Bruker D8 Venture rotating anode
Solution	SIR-92	SIR-92	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	1500001	1500004	1524647	1524646

Table S3. Crystallographic data and refinement parameters of compound **12**, **13**, **15** and **16**.

	12	**13**	**15**	**16**
Formula	$C_2H_{14}CuN_{16}O_5$	$C_2H_{12}N_{16}O_4Zn$	$C_2H_8N_{12}O_8Ba$	$C_2H_{12}N_{12}O_{10}Ba$
FW [g mol^{-1}]	405.83	389.65	415.82	501.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Color / Habit	Blue block	Colorless block	Colorless block	Colorless block
Size [mm]	0.05 x 0.11 x 0.23	0.10 x 0.13 x 0.20	0.03 x 0.07 x 0.10	0.03 x 0.06 x 0.09
a [Å]	11.4131(5)	10.2414(3)	10.7948(3)	8.9593(3)
b [Å]	7.4648(3)	10.6483(3)	15.0619(4)	9.5952(3)
c [Å]	17.2079(8)	13.1297(4)	9.3539(2)	17.9981(6)
α [°]	90	90	90	90
β [°]	98.739(5)	94.149(3)	110.333(1)	92.798(1)
γ [°]	90	90	90	90
V [Å^3]	1449.03(11)	1428.09(7)	1426.09(6)	1545.39(9)
Z	4	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.860	1.812	1.937	2.156
μ [mm^{-1}]	1.570	1.774	3.849	2.651
F(000)	828	792	824	976
$\lambda_{MoK\alpha}$[Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	173	100	173
ϑ min-max [°]	4.2, 26.0	4.1, 26.0	2.8, 27.5	2.3, 26.0
Dataset h; k; l	−13:14; −9:9; −21:21	−12:12; −13:8; −16:14	−14:14; −19:19; −12:12	−11:11; −11:11; −22:22
Reflect. coll.	5250	10947	23112	49826
Independ. refl.	1422	2785	3271	3024
R_{int}	0.040	0.030	0.029	0.030
Reflection obs.	1205	2310	2910	2875
No. parameters	117	256	240	246
R_1 (obs)	0.0300	0.0257	0.0202	0.0162
wR_2 (all data)	0.0695	0.0675	0.0501	0.0868
S	1.08	1.03	1.07	1.43
Resd. Dens.[e Å^{-3}]	−0.31, 0.27	−0.37, 0.58	−0.29, 0.86	−1.12, 0.80
Device type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD
Solution	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	1502968	1510459	1510459	1510459

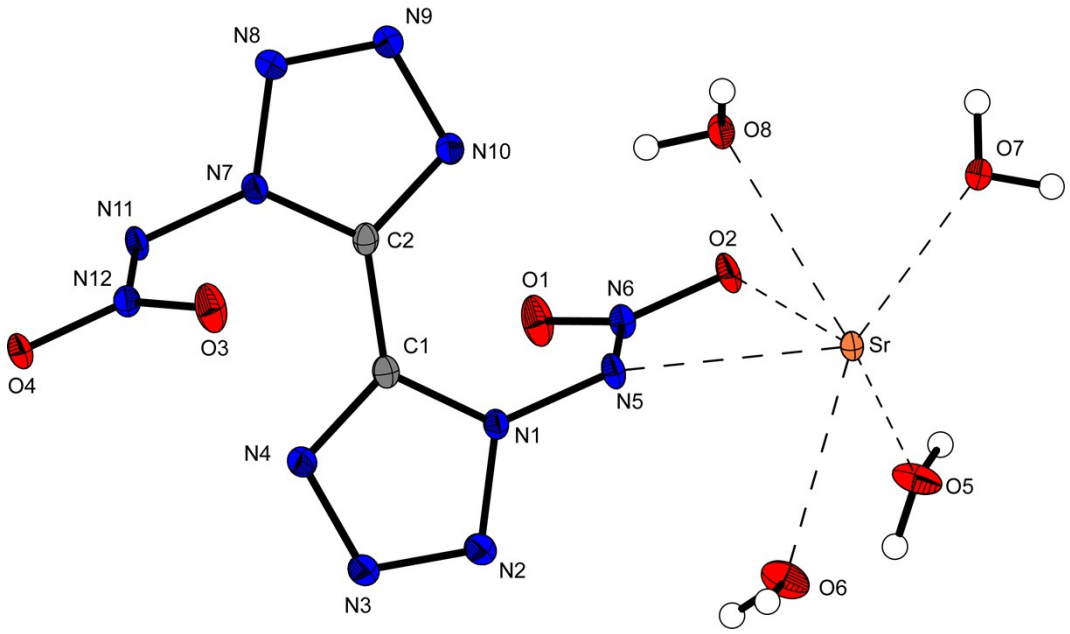


Figure S1 Molecular structure of **15** showing the atom-labelling scheme. Thermal ellipsoids represent the 50% probability level.

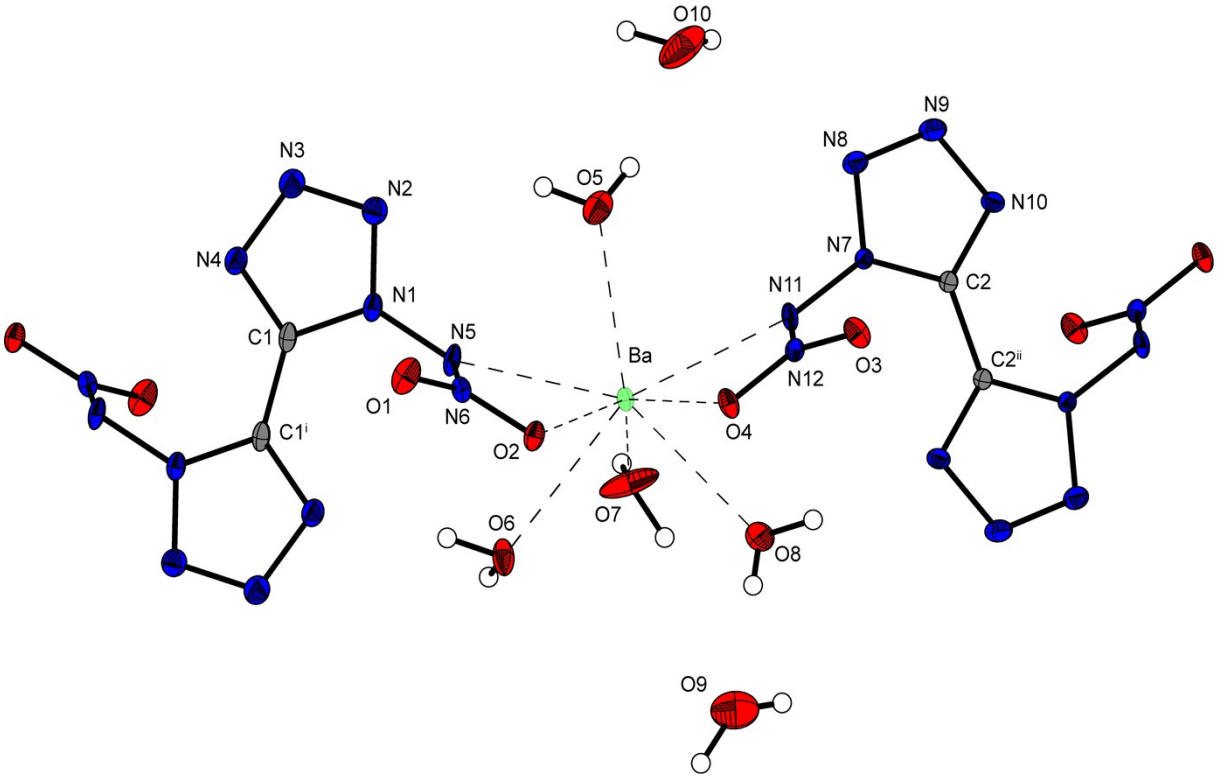


Figure S2 Extended molecular structure of **16** showing the atom-labelling scheme. Thermal ellipsoids represent the 50% probability level. Symmetry codes: (i) −x, −y, 2−z; (ii) 1−x, −y, 1−z.

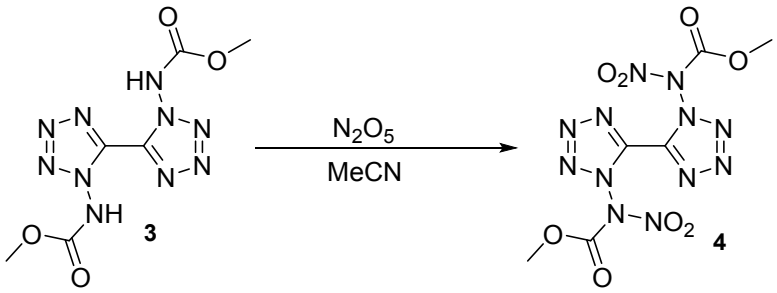
2. Experimental Part

General Procedures

Differential Scanning Calorimetry (DSC) was performed on a LINSEIS DSC PT10 with about 1 mg substance in a perforated aluminum vessel with a heating rate of 5 K·min^{-1} and a nitrogen flow of 5 dm^3·h^{-1}. Differential Thermal Analysis (DTA) measurements were carried out in glass tubes on an OZM DTA 552-Ex device with a heating rate of 5 K·min^{-1}. Thermal gravimetric analysis (TGA) measurements were performed on a Perkin Elmer TGA4000 with a heating rate of 5 K min^{-1} in Al_2O_3 crucibles. The NMR spectra were recorded with a 400 MHz instrument (^{1}H 399.8 MHz, ^{13}C 100.5 MHz, ^{14}N 28.9 MHz, and ^{15}N 40.6 MHz). Chemical shifts are given in parts per million relative to tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N, ^{15}N). Infrared spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), and "weak" (w). Raman spectra were recorded using a Bruker MultiRAM FT-Raman instrument fitted with a liquid-nitrogen cooled germanium detector and a Nd:YAG laser (λ = 1064 nm). The intensities are quoted as percentages of the most intense peak and are given in parentheses. Low-resolution mass spectra were recorded with a JEOL MStation JMS 700 (DEI+ / FAB+/−). Elemental analysis was carried out using a Vario Micro from the Elementar Company.

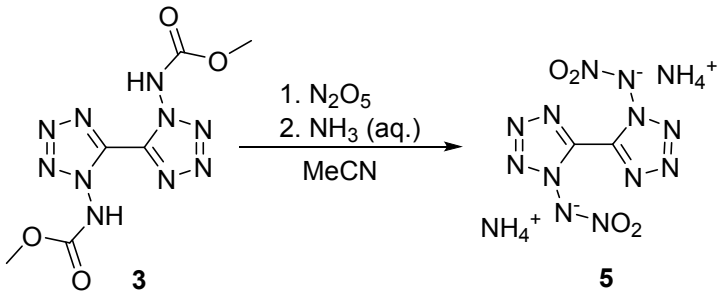
The impact sensitivity tests were carried out according to STANAG 4489[S9] modified instruction[S10] using a Bundesanstalt für Materialforschung (BAM) drophammer.[S11] The friction sensitivity tests were carried out according to STANAG 4487[S12] modified instruction[S13] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[S14] All compounds were tested upon the sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.[S15]

***1N,1N'*-Dimethylnitrocarbamate-*5,5'*-bitetrazole (4)**



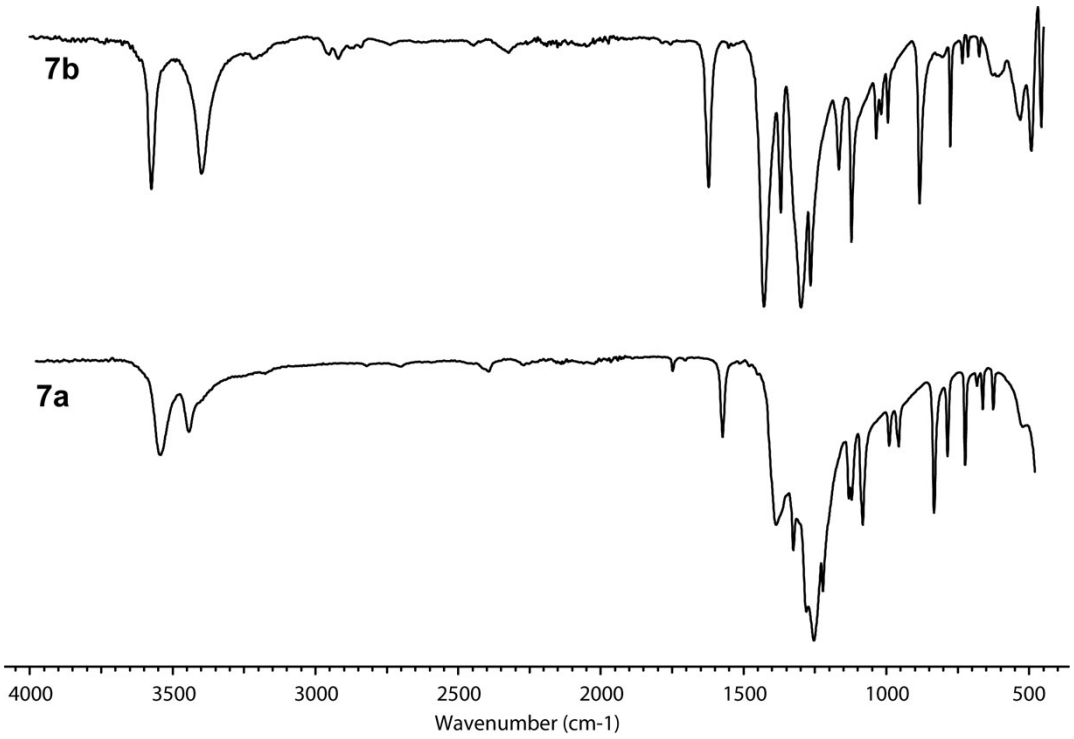
0.45 g (4.17 mmol) N_2O_5 was dissolved in 50 mL MeCN at −5°C and 0.3 g **3**[S1] (1.05 mmol) was added portion wise. The mixture was stirred for 2.5 h at −5 °C and finally quenched by adding the mixture to 50 g of ice-water. The precipitate was filtered off giving **4** (355 mg, 0.95 mmol, 90 %). **DTA** (5 °C min^{-1}): 102 °C (dec.); **IR** (atr, cm^{-1}) $\tilde{\nu}$ = 3223 (w), 2969 (w), 1794 (m), 1658 (m), 1438 (w), 1408 (w), 1322 (m), 1220 (s), 1180 (m), 1103 (w), 1041 (w), 990 (w), 936 (w), 864 (w), 818 (m), 769 (s), 732 (m), 666 (m), 590 (w); **^{1}H NMR** (dmso-d_6, 25 °C, ppm): δ: 3.85 (s, 6H, CH_3); **^{13}C{^{1}H} NMR** (dmso-d_6, 25 °C, ppm) δ: 48.7 (CH_3), 124.3 (C_Q), 141.0 (C=O); **^{14}N NMR** (dmso-d_6, 25 °C, ppm): δ = −66; **MS** *m/z* (FAB$^+$): 375.4 ($C_6H_7N_{12}O_8^+$); **EA** ($C_6H_6N_{12}O_8$, 374.19): calc.: C 19.26, H 1.62; N 44.92; found: C 20.31, H 1.90, N 44.73 %; **BAM drophammer**: 1 J, **friction tester**: <5 N, **ESD**: 3 mJ.

Diammonium 1,1'-dinitramino-5,5'-bitetrazolate (5)



1.00 g (3.52 mmol) of **3**[S1] was suspended in 50 mL dry acetonitrile and cooled to −10°C. 1.5 g of dinitrogen pentoxide (13.9 mmol) was added all at once and the reaction mixture was stirred for 2 h at the initial temperature. An excess of concentrated ammonia solution (3 mL) was added to the obtained solution and the suspension was stirred for 20 minutes. The pH-value was checked to be above 9 and the colorless precipitate was collected by suction filtration and washed with ice-cold water (1 mL) and ethanol to give **5** (0.89 g, 3.06 mmol, 87 %). **IR** (atr, cm^{-1}) $\tilde{\nu}$ = 3177 (w), 3050 (w), 1395 (s), 1368 (s), 1280 (s), 1259 (s), 1179 (w), 1126 (m), 1036 (w), 1009 (w), 995 (w), 875 (s), 778 (m), 772 (w); **^{1}H NMR** (dmso-d_6, 25 °C, ppm): δ: 7.07 (s, 8H, NH_4^+); **^{13}C{^{1}H} NMR** (dmso-d_6, 25 °C, ppm) δ: 140.4 (C_Q); **^{14}N NMR** (dmso-d_6, 25 °C, ppm): δ = −359.

3. IR spectroscopy of 7a and 7b



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[S6] A. L. Spek, *PLATON*, *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 1999.

[S7] *SCALE3 ABSPACK – An Oxford Diffraction program* (1.0.4, gui: 1.0.3), Oxford Diffraction Ltd., 2005.

[S8] *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.

[S9] NATO standardization agreement (STANAG) on explosives, *impact sensitivity tests*, no. 4489, 1st ed., Sept. 17, 1999.

[S10] WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, 2002.

[S11] http://www.bam.de

[S12] NATO standardization agreement (STANAG) on explosive, *friction sensitivity tests*, no. 4487, 1st ed., Aug. 22, 2002.

[S13] WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, 2002.

[S14] Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N, According to: *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 4th edition, United Nations, New York-Geneva, 1999.

[S15] http://www.ozm.cz