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The Dianion of 5-Cyanoiminotetrazoline: $C_2N_6^{2-}$

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Several salts (alkali, $Pd(NH_3)_3$, and $^iPrNH_2$) of 5-cyanoiminotetrazoline ($C_2N_6^{2-}$, 5-cyanoiminotetrazolinediide, CIT) were investigated. A full characterization by means of X-ray, Raman, NMR techniques, mass spectrometry, and elemental analysis is presented for the $^iPrNH_2$ (**4**), Cs (**5**), and $Pd(NH_3)_3$ (**6**) salts. The CIT dianion represents a nitrogen-rich binary CN dianion, and **5** forms monoclinic crystals ($a = 7.345(2)$ Å, $b = 9.505(2)$ Å, $c = 10.198(2)$ Å, $\beta = 92.12(3)°$, space group $P2_1/n$, $Z = 4$). DSC and in situ temperature-dependent X-ray diffraction measurements of the cesium salt **5** revealed an astonishing thermal stability accompanied by a reversible phase transition from the low-temperature α modification to the metastable β modification at 253 °C. Above the melting point (334 °C), the cesium salt decomposes yielding cesium azide and cesium dicyanamide, which decomposes under further heating under release of nitrogen. The reaction of Cs_2CIT with SO_2 resulted in the surprising formation of a new cesium salt with the 5-cyaniminotetrazoline-1-sulfonate dianion ($Cs_2CITSO_3 \cdot SO_2$ (**7**)). **7** crystallizes in the monoclinic space group $P2_1$ with one SO_2 solvent molecule ($a = 8.0080(2)$ Å, $b = 8.0183(2)$ Å, $c = 9.8986(3)$ Å, $\beta = 108.619(1)°$, $Z = 2$). The structure and bonding of the 10π dianion are discussed on the basis B3LYP/aug-cc-pvTZ computations (MO, NBO), and the three-dimensional array of the cesium salts with respect to the $Cs^{\delta+}$–$N^{\delta-}$ in **5** compared to the $Cs^{\delta+}$–$N^{\delta-}$ and $Cs^{\delta+}$–$O^{\delta-}$ in **7** is discussed. Due to the expected rich bonding modes of the CIT anions, the coordination chemistry with palladium was also studied, yielding monoclinic crystals of $[Pd(CIT)(NH_3)_3] \cdot H_2O$ (**6**, $a = 7.988(2)$ Å, $b = 8.375(2)$ Å, $c = 13.541(3)$ Å, $\beta = 104.56°$, space group $P2_1/n$, $Z = 4$). In the solid state, the complex is composed of dimers, showing two agostic interactions and an unusual close interplanar π–π stacking of the tetrazole moiety of the CIT ligand.

Introduction

The most prominent binary carbon−nitrogen anion is the cyanide anion (CN^-). The salts of hydrogen cyanide belong to the most important chemicals used in industrial and pharmaceutical as well as agricultural processes.[1] Among the binary carbon and nitrogen anions which have been reported, relatively few have alternating carbon−nitrogen connectivity,[2] although such structures are highly stable. Due to the expected alternating connectivity in β-carbon nitride (C_3N_4), alternating binary carbon−nitrogen anions may qualify as precursors for the synthesis of β-C_3N_4, a material predicted to be harder than diamond.[3] Moreover, nonalternating carbon−nitrogen anions obtained from the family of polycyanocarbons have been examined as coordination ligands to metals and as the basis for supramolecular frameworks.[4] The interest for practical applications of polycyanocarbons as electron acceptors or anions was also aroused for use as deeply colored dyes,[5] catalysts,[6] and

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† X-ray structure analysis.

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nonlinear optical materials.[7] Among them, formation of highly conductive charge transfer (CT) complexes and ferro- or antiferromagnetic CT complexes[8] has been most intensively investigated with respect to their properties as electron acceptors or anions by both chemists and physicists.[9]

Besides the carbon−nitrogen connectivity, there are other ways to systematically divide CN anions such as the charge [singly charged ions, e.g. dicyanamide (DCA), $NC{-}N{-}CN^-$;[10] doubly charged ions, e.g. cyanamide (CA), NCN^{2-},[11] *N*,*N*′,*N*″-tricyanoguanidinate (TCG), $C_4N_6^{2-}$;[2a] triply charged ions, e.g. tricyanomelaminate (TCMA),[12] $(NC{-}NCN)_3^-$] or the carbon−nitrogen stoichiometry. Using the carbon−nitrogen stoichiometry as criterion, CN anions may be grouped into three classes: (i) nitrogen-rich (e.g. $NC{-}N{-}CN^-$, NCN^{2-}); (ii) carbon-rich CN anions (e.g. tricyanomethanide (TCM),[13] $C(CN)_3^-$); (iii) CN anions with the same number of carbon and nitrogen atoms (e.g. cyanide, CN^-). Most of the nitrogen-rich CN anions are based on the tetrazole ring such as azidotetrazolate (AzT), CN_7^-,[14] cyanotetrazolate (CT),[15] $C_2N_5^-$, 5,5′-bis(tetrazolate) (BT), $C_2N_8^{2-}$,[16] 5,5′-azotetrazolate (ZT), $C_2N_{10}^{2-}$,[17] and 3,6-bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazinediide (BTT), $C_4N_{12}^{2-}$.[18] The nitrogen-rich anions are of special interest, as they are salts with high nitrogen content, having high heats of formation and showing in the most cases remarkable insensitivities to friction, electrostatic discharge, and shock.[17c−h,19] The carbon-rich CN anions are mainly based on cyano and polycyano groups. A compendium of selected anions is depicted in Scheme 1.

Examples for polycyano organic anions are the tetracyano-2-azapropenide (TCAP), $C_6N_5^-$, pentacyanopropenide (PCP), $C_8N_5^-$,[20] pentacyanocyclopentadienide (PCCP), $C_{10}N_5^-$,[21a] hexacyanotrimethylenemethanediide (PCA), $C_{10}N_6^{2-}$,[21b,c] hexacyano-3,4-diazahexadienediide (HCDAH), $C_{10}N_8^{2-}$,[22] tetracyano-1,1′,3,3′-tetraazafulvalenediide (TCTAF), $C_{10}N_8^{2-}$,[23] 2-dicyanomethyl-1,1,3,4,5,5-hexacyanopentadienediide (DHCP), $C_{14}N_8^{2-}$,[24] and tris(dicyanomethylene)cyclopropanediide (HCP), $C_{12}N_6^{2-}$.[21a]

A long forgotten and poorly characterized nitrogen-rich anion of this class is represented by 5-cyaniminotetrazolinediide (**3**), $C_2N_6^{2-}$, CIT,[25] which can be obtained by the reaction of aminotetrazole (**1**) with cyanogen bromide under base condition (Scheme 2). Azido-*N*-cyanoformamidine (cyanoguanyl azide) (**2**) is formed as intermediate and could be isolated when **1** was reacted with 1 equiv of base and cyanogen bromide. Additional base leads to the deprotonation of **2** and ring-closure to form the dianion **3**. In general, the tetrazole ring may exist in equilibrium with the acyclic imidoyl azide form, and depending of the subsitiuent at the imidoyl fragment present, both isomers can be observed. Electron-withdrawing groups such as CN or NO_2 favor the open azide chain isomer, imidoyl azide, whereas electron-donating groups (e.g. alkyl) or bases are required for effecting the cyclization to the isomeric tetrazole.[25−27]

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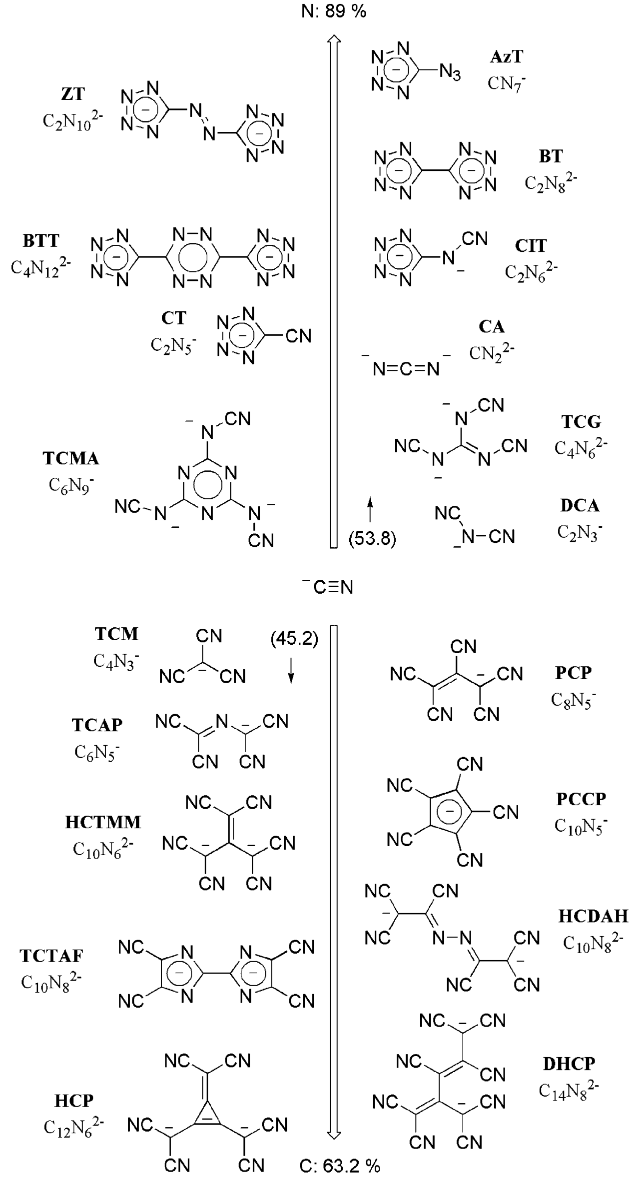
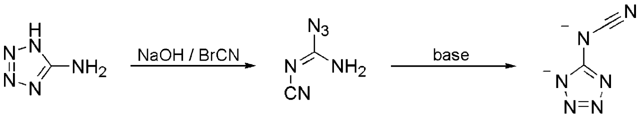
Scheme 1. Selected Carbon−Nitrogen Anions



Scheme 2. Synthesis of 5-Cyaniminotetrazolinediide Salts



1 **2** **3**

Here we wish to report a modified synthesis and full characterization of the new bis(isopropylammonium) (**4**), cesium (**5**), and triaminepalladium(II) (**6**) CIT salts, an interesting class of salts with surprising thermal stability and properties. Moreover, the recrystallization of dicesium 5-cyaniminotetrazolinediide (**5**) in liquid sulfur dioxide resulted in an unexpected redox reaction which finally gave the new dicesium 5-cyaniminotetrazoline-1-sulfonatediide$\cdot SO_2$ (**7**) containing the new 5-cyaniminotetrazoline-1-sulfonatediide anion ($CITSO_3$). Especially the latter dianion might qualify as a new building block in materials science for supramolecular frameworks e.g. in charge transfer (CT) complexes or in nonlinear optical materials as it meets the requirements of the commonly used sulfonate as well cyano anions in combination with organic radical cations.[9]

Experimental Section

Materials. All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich Fine Chemicals Inc. and used as supplied. Et_2O, MeOH, and EtOH were dried according established procedures, freshly distilled, and stored under nitrogen.

General Procedure. All reactions in liquid SO_2 were performed in two-bulb, two-valve Pyrex vessels incorporating 10 mL bulbs using techniques that have been described previously.[28] Solid reagents and crystals were manipulated in a Brown drybox containing an internal circulating drying unit. The ^1H, ^{13}C, and $^{14}N/^{15}N$ NMR spectra were recorded on a JEOL Eclipse 400 instrument. The spectra were measured in DMSO-d_6 at 25 °C. The chemical shifts are given relative to tetramethylsilane (^1H, ^{13}C) or nitromethane ($^{14}N/^{15}N$) as external standards. Coupling constants are given in Hz. Infrared (IR) spectra were recorded on a Perkin-Elmer Spektrum One FT-IR instrument as KBr pellets at 20 °C. Raman spectra were recorded on a Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported in percent relative to the most intense peak and given in parentheses. Elemental analyses were performed with a Netsch Simultanous Thermal Analyzer STA 429. Melting points were determined by differential scanning calorimeter (Perkin-Elmer Pyris 6 DSC, calibrated by standard pure indium and zinc). Measurements were performed at a heating rate of $\beta = 10$ °C in closed Al containers with a hole (1 μm) on the top for gas release, and a $0.003 \times 3/16$-in. disk was used to optimize good thermal contact between the sample and the container with a nitrogen flow of 20 mL/min. The reference sample was an Al container with air.

Synthesis of Azido-*N*-cyanoformamidine (Cyanoguanyl Azide) (2). 5-Amino-1*H*-tetrazole monohydrate (25.95 g, 0.25 mol), a suspension in 40 mL of water, was brought in solution and neutralized by adding a concentrated solution of sodium hydroxide (phenolphthalein as indicator). To the cooled solution (0 °C) 75 mL of acetone and cyanogen bromide (27.0 g, 0.25 mol) were added in small portions while agitating. The reaction mixture was stirred for 3 h at 0 °C and 2 h at RT (room temperature). After that, the solution was extracted with Et_2O (4×250 mL) and the ether solution was dried with anhydrous magnesium sulfate. Pure **2** (19.94 g, 72.5%) was obtained after evaporation and recrystallization from Et_2O. Mp: 145 °C (dec). IR (KBr, cm^{-1}): $\tilde{\nu} = 3355$ (s), 3172 (s), 2707 (vw), 2659 (vw), 2456 (vw), 2187 (vs), 2161 (vs), 2131 (m, sh), 1646 (vs), 1562 (vs), 1497 (w), 1433 (vs), 1369 (m), 1243 (s), 1210 (s), 1191 (s), 1031 (m), 888 (m), 718 (w), 705 (w), 635 (m), 603 (m), 539 (w), 445 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 3289$ (2), 3178 (6), 2187 (100), 2166 (35), 2127 (10), 1673 (4), 1575 (15), 1564 (22), 1415 (40), 1373 (6), 1245 (9), 1191 (6), 1120 (2), 1027 (8), 894 (4), 720 (6), 609 (35), 561 (2), 485 (5), 442 (28), 227 (75), 191 (20), 159 (81), 115 (16). ^1H NMR (DMSO-d_6, 25 °C): δ 8.53 (s, NH), 8.79 (s, NH). ^{13}C NMR (DMSO-d_6, 25 °C): δ 114.2 (*C*N), 163.3 (C). ^{15}N NMR (DMSO-d_6, 25 °C): δ −141.6 (*N*-NH_2), −147.5 (C*N*), −176.1 (N_β),[29] −267.8 (N_γ), −278.0 (N_α), −280.2 (N1-*N*H_2, $^1J_{NH} = 91.1$ Hz). MS (DEI, 70 eV, >5%; *m/z* (%)): 110 (48) [M^+], 81 (38), 68 (10), 67 (6), 66 (6), 54 (12), 53 (32), 52 (5), 42 (100), 41 (23), 40 (10), 38 (6), 30 (55), 29 (21), 28 (36), 27 (18), 26 (7). Anal. Calcd for $C_2H_2N_6$ (M_r = 110.08): C, 22.34; H, 2.07; N, 75.50. Found: C, 22.37; H, 2.05; N, 75.54.

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(29) Connectivity for the azide group: $R{-}N_\alpha N_\beta N_\gamma$.

Isopropylammonium Salt of 5-Cyaniminotetrazoline, $(^i\mathrm{PrNH_3})_2$-CIT·MeOH (4). To a slurry of **2** (11,01 g, 0,1 mol) in 60 mL of EtOH was added isopropylamine (12.41 g, 0.21 mol) at once, and the solution was allowed to warm spontaneously. The azide dissolves with immediate precipitation of the salt **4**. The slurry was stirred for further 20 min, and Et_2O (150 mL) was added. The white, hygroscopic powder was separated by filtration, washed with ether, and dried. Yield: 22.0 g (96%) of **4**. X-ray-quality crystals of **4**·MeOH were grown from concentrated MeOH solution at RT in the course of 3 days. IR (KBr, cm^{-1}): $\tilde{\nu} = 3041$ (m), 2990 (s), 2941 (s), 2832 (s), 2750 (s), 2655 (m), 2559 (m), 2554 (m), 2149 (vs), 1640 (m), 1532 (m), 1490 (vs), 1394 (m), 1383 (w), 1358 (m), 1244 (m), 1224 (m), 1199 (m), 1164 (m), 1130 (m), 1055 (w), 1038 (m), 954 (vw), 938 (vw), 801 (w), 760 (w), 571 (w), 478 (m). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2984$ (96), 2949 (95), 2933 (100), 2888 (69), 2749 (27), 2691 (16), 2562 (11), 2257 (7), 2148 (85), 1624 (9), 1501 (98), 1466 (49), 1400 (11), 1373 (19), 1360 (31), 1228 (30), 1201 (32), 1168 (16), 1132 (53), 1058 (82), 1019 (24), 957 (12), 940 (22), 804 (62), 763 (6), 570 (40), 482 (24), 442 (74), 426 (38), 378 (13), 349 (17), 208 (45), 171 (34), 136 (34). ^{1}H NMR (DMSO-d_6, 25 °C): δ 1.09 (d, 6H, $^3J = 6.4$ Hz), 3.17 (hept, 1H, $^3J = 6.4$ Hz), 6.82 (s, 3H). ^{13}C NMR (DMSO-d_6, 25 °C): δ 23.2 (CH_3), 43.1 (CH), 124.0 (CN), 163.2 (C). m/z (FAB$^-$, xenon, 6 keV, glycerine matrix): 109, $[C_2N_6 + H]^-$; 219, $[2(C_2N_6 + H) + H]^-$. Anal. Calcd for $C_8H_{20}N_8$ ($M_r = 228.30$): C, 42.09; H, 8.83; N, 49.08. Found: C, 41.86; H, 8.92; N, 49.13.

Cesium Salt of 5-Cyaniminotetrazoline, Cs_2CIT (5). **2** (6.85 g, 30 mmol) was dissolved in 80 mL of MeOH, and a solution of $CsOH{\cdot}H_2O$ (10.08 g, 60 mmol) in 40 mL was added. The volatiles were removed under reduced pressure leaving a powdery white residue. The residue was recrystallized from MeOH/Et_2O (10.9 g, 97%). Mp: 335 °C. IR (KBr, cm^{-1}): $\tilde{\nu} = 2379$ (w), 2136 (vs), 1714 (w), 1639 (w), 1590 (w), 1526 (s), 1495 (vs), 1364 (s), 1261 (vw), 1217 (w), 1201 (w), 1190 (w), 1158 (vw), 1117 (w), 1042 (vw), 1003 (w), 791 (w), 763 (m), 704 (w), 626 (vw), 579 (m). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2123$ (38), 2115 (61), 1570 (7), 1521 (6), 1480 (26), 1469 (100), 1448 (8), 1358 (22), 1218 (12), 1183 (30), 1154 (8), 1104 (27), 1035 (68), 997 (7), 785 (13), 761 (7), 567 (25), 441 (33), 348 (19), 187 (39), 161 (10), 143 (7). ^{13}C NMR (DMSO-d_6, 25 °C): δ 128.1 (CN), 166.6 (C). m/z (FAB$^-$, xenon, 6 keV, NBA matrix): 109, $[C_2N_6 + H]^-$. Anal. Calcd for $C_2Cs_2N_6$ ($M_r = 373.87$): C, 6.43; Cs, 71.10; N, 22.48. Found: C, 6.56; N, 22.23.

Triammine(5-cyanoiminotetrazolinediide)palladium(II) Monohydrate $[Pd(C_2N_6)(NH_3)_3]{\cdot}H_2O$ (6). To a solution of **2** (220 mg, 2 mmol) in 5 mL of water and 2 mL of concentrated NH_3 was added a solution of tetramminepalladium(II) chloride[30] (490.9 mg, 2 mmol) in 5 mL of H_2O, and the new solution was heated for 10 min to 75 °C. Pale yellow plates of **6** (406 mg, 72%) crystallized after 1 week from the pale yellow solution. IR (KBr, cm^{-1}): $\tilde{\nu} = 3444$ (s), 3278 (s), 3164 (s), 3058 (s), 2923 (m), 285 (w), 2128 (vs), 1637 (w), 1577 (w), 1518 (s), 1380 (m), 1325 (vw), 1281 (m), 1265 (m), 1230 (m), 1115 (m), 861 (w), 837 (w), 786 (w), 748 (w), 569 (w), 501 (w), 478 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 3279$ (9), 3193 (10), 2123 (64), 1575 (5), 1514 (27), 1422 (3), 1377 (8), 1318 (10), 1297 (15), 1266 (22), 1230 (14), 1151 (5), 1116 (25), 1097 (28), 1003 (16), 851 (5), 788 (13), 751 (9), 573 (32), 509 (100), 487 (57), 364 (8), 257 (25), 219 (25), 154 (28). Anal. Calcd for $C_2H_{11}N_9OPd$ ($M_r = 283.59$): C, 8.47; H, 3.91; N, 44.45. Found: C, 8.53; H, 3.82; N, 44.20.

Dicesium 5-Cyaniminotetrazoline-1-sulfonatediide·SO_2, Cs_2-CITSO$_3$·SO_2 (7). SO_2 (~10 mL) was condensed onto cooled (−196 °C) **5** (560 mg, 1.5 mmol), giving a bright yellow solution, which turned deep yellow, red, and then brown after warming to RT. The reaction mixture was stirred for 1 day, and a clear, pale yellow solution containing a gummy residue was obtained. The solution was separated from the residue by filtration and reduced to half of its volume. After 1 week pale yellow crystals of **7** (312 mg, 40%) were obtained. IR (KBr, cm^{-1}): $\tilde{\nu} = 2342$ (vw), 2153 (s), 1642 (sh, m), 1588 (sh, m), 1556 (vs), 1529 (vs), 1378 (m), 1358 (s), 1292 (vs), 1265 (vs), 1215 (sh, m), 1142 (m), 1125 (m), 1087 (s), 1042 (s), 742 (w), 629 (s), 608 (s), 559 (m), 476 (w). Raman (200 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2166$ (23), 1546 (13), 1477 (3), 1355 (4), 1303 (26), 1227 (13), 1144 (100), 1117 (8), 1086 (16), 1046 (47), 987 (7), 886 (3), 793 (10), 621 (6), 601 (7), 545 (17), 531 (7), 480 (20), 398 (7), 338 (24), 297 (30), 208 (25), 135 (20). ^{13}C NMR (DMSO-d_6, 25 °C): δ 136.0 (CN), 164.1 (C). Anal. Calcd for $C_2Cs_2N_6SO_3{\cdot}xSO_2$ ($x = 1$, $M_r = 373.87$): C, 4.64; S, 12.38; N, 16.22. Found: C, 5.66; S, 9.30; N, 19.53.

Attempted Direct Synthesis of $Cs_2CITSO_3.SO_2$ (7). To prepare **7** in a direct synthesis, SO_2 (~10 mL) was condensed at −196 °C onto freshly prepared CsN_3 (525 mg, 3 mmol)[31] and $CsN(CN)_2$ (597 mg, 3 mmol), giving a bright yellow solution at room temperature. Within minutes, the solution became orange/red and a dark red oil started to separate. The reaction mixture was stirred at room temperature for 1 day, and the obtained clear yellow solution separated from the formed red residue by filtration. Concentration of the yellow solution by dynamic vacuum (gas-phase IR: SO_2) yielded 0.135 g of a pale yellow product, soluble in MeOH. The Raman spectrum of the pale yellow solid as well as of the red residue did not show any characteristic bands which could be assigned to CIT, $CITSO_3$, CsN_3, or $CsN(CN)_2$. The red residue (1.245 g) dissolves in water under release of SO_2, yielding a yellow solution. Both products are still under investigation.

X-ray Analyses. X-ray-quality crystals of **4** and **6** were mounted in a Pyrex capillary and the X-ray crystallographic data collected on a Nonius Mach3 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The X-ray crystallographic data for **5** and **7** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Unit cell parameters of **4** and **6** were obtained from setting angles of a minimum of 25 carefully centered reflections having $2\theta > 20°$; the choice of the space groups was based on systematically absent reflections and confirmed by the successful solution and refinements of the structures. The structures were solved by direct methods (SHELXS-86 (**4**, **6**), SHELXS-97 (**5**), SIR97 (**7**))[32] and refined by means of full-matrix least-squares procedures using SHELXL-93 and SHELXL-97. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are available in Table 2, and the numbering and the molecular model of the C_2N_6 frame in 5-cyaniminotetrazolinediide are shown in Figure 1. All non-hydrogen atoms were refined anisotropically. In the case of **4** and **6** the hydrogen atoms were included at geometrically idealized positions and refined. They were assigned fixed isotropic temperature factors with the value of $-1.2B_{eq}$ of the atom to which they were bonded. Further information on the crystal-structure determinations (excluding structure factors) has

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(32) (a) Sheldrick, G. M. *SHELXL-86, Program for Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986. (b) Sheldrick, G. M. *SHELXL-97, Program for Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Details of the Structure Determination for **4**−**7**

cryst data	**4**	**5**	**6**	**7**
formula	$C_9H_{24}N_8O$	$C_2Cs_2N_6$	$C_2H_{11}N_9OPd$	$C_2Cs_2N_6O_5S_2$
fw	260.36	373.90	283.60	518.02
cryst system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1$
a, Å	7.141(2)	7.345(2)	7.988(2)	8.0080(2)
b, Å	9.539(2)	9.505(2)	8.375(2)	8.0183(2)
c, Å	12.817(4)	10.198(2)	13.541(3)	9.8986(3)
α, deg	72.51(2)	90.0	90.0	90.0
β, deg	85.21(2)	93.12(3))	104.56(3)	108.619(1)
γ, deg	67.39(2)	90.0	90.0	90.0
V, Å^3	768.3(3)	710.9(2)	876.8(3)	602.33(3)
Z	2	4	4	2
ρ_{calcd}, g/cm^{-3}	1.125	3.493	2.148	2.856
μ, mm^{-1}	0.080	10.185	2.098	6.417
$\lambda_{Mo\ K\alpha}$, Å	0.710 73	0.710 73	0.710 73	0.710 73
T, K	295(2)	200(2)	295(2)	200(2)
reflcns collcd	2520	11869	1846	7607
indpndt reflcns	2396	1612	1719	2752
R_{int}	0.0080	0.0430	0.0079	0.069
obsd reflcns	1977	1524	1668	2583
F(000)	284	656	560	472
$R_1{}^a$ (obs)	0.0529	0.0175	0.0195	0.0287
$wR_2{}^b$ (all data)	0.1104	0.0405	0.0533	0.0605
weighting scheme^b	0.0545, 0.2685	0.0107, 0.4285	0.0286, 0.9463	0.0206, 0.000
GooF	0.995	1.224	1.157	1.019
no. of params	170	91	119	154
CCDC	267216	267201	267217	267200

[a] $R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(F_o{}^2 - F_c{}^2)/\Sigma w(F_o)^2]^{1/2}$, $w = [\sigma_c{}^2(F_o{}^2) + (xP)^2 + yP]^{-1}$, $P = (F_o{}^2 - 2F_c{}^2)/3$.

Table 2. Comparison of Selected Interatomic Distances (Å) and Bond Angles (deg) of the C_2N_6 Frame in **4**−**7**[a]

	4	**6**	**5**	**7**	CIT[b]	CITSO$_3$[b]
			Bond Lengths			
C1−N1	1.337(2)	1.344(3)	1.338(4)	1.359(6)	1.358	1.352
N1−N2	1.348(2)	1.357(3)	1.362(4)	1.379(5)	1.355	1.359
N2−N3	1.301(2)	1.298(3)	1.309(4)	1.274(6)	1.321	1.294
N3−N4	1.348(2)	1.358(3)	1.357(4)	1.362(6)	1.358	1.366
C1−N4	1.331(2)	1.335(3)	1.337(4)	1.330(7)	1.357	1.379
C1−N5	1.368(2)	1.364(3)	1.388(4)	1.342(7)	1.387	1.344
C2−N5	1.301(2)	1.299(3)	1.302(4)	1.318(7)	1.293	1.306
C2−N6	1.159(2)	1.157(3)	1.174(4)	1.147(7)	1.197	1.186
			Bond Angles			
N1−C1−N4	111.2(1)	109.8(2)	112.6(3)	106.9(5)	110.9	106.7
C1−N1−N2	104.8(1)	106.3(2)	104.0(2)	108.6(4)	104.9	106.4
N1−N2−N3	109.5(1)	108.2(2)	109.5(2)	105.8(4)	109.7	112.0
N2−N3−N4	109.6(1)	110.3(2)	109.8(2)	111.9(4)	109.7	106.5
N3−N4−C1	104.9(1)	105.4(2)	104.1(2)	106.8(4)	104.8	108.5
C1−N5−C2	116.1(1)	119.0(2)	116.8(3)	117.4(5)	123.6	121.0
N5−C2−N6	175.9(2)	173.3(2)	174.0(3)	173.2(7)	171.6	172.2

[a] For numbering, see Figure 1. [b] Theoretical gas-phase data: B3LYP/aug-cc-pvTZ.

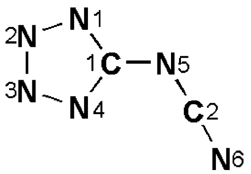

Figure 1. Molecular model and numbering scheme of the C_2N_6 frame in 5-cyaniminotetrazolinediide.

been deposit with the Cambridge Crystallographic Data Centre as supplementary publication nos. 267216(**4**), 267217(**6**), 267200(**7**), and 267201(**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Properties of CIT Salts. Our two-step synthesis of 5-cyaniminotetrazoline salts (CIT) starts from amino-1*H*-tetrazolium monohydrate which after neutralization with sodium hydroxide was reacted with cyanogen bromide to give azido-*N*-cyanoformamidine (**2**). **2** represents an easily accessible source for an NCN−N_3 unit. Treating a methanolic or ethanolic solution of **2** with bases (e.g. MOH (M = Li, Na, K, Cs), amines), immediate deprotonation, and cyclization of **2** can be observed resulting in the formation of the stable 5-cyaniminotetrazolinediide salts (Scheme 2). Especially Raman and IR spectroscopy are suitable to identify CIT salts very rapidly with the help of the CN stretching mode at ca. 2150 and the missing N_3 stretching at 2190 cm^{-1} (for approximate assignment of all normal modes on the basis of DFT calculation, see Supporting Information Table S2).

Pure alkali metal and ammonium CIT salts are stable at ambient temperature and are neither heat nor shock sensitive. To determine the thermal properties of cesium CIT salt (**5**), combined IR and DSC experiments were carried out. DSC experiments of the cesium CIT salt (**5**) revealed three interesting features: (i) an endothermic reversible change of the modification at ca. 253 °C (ΔH = 34.8 J/g for $\alpha \rightarrow \beta$ modification; see Supporting Information, Figure S2), which was supported by powder diffraction studies (see Supporting Information, Figure S3); (ii) melting at 335 °C (onset); (iii) the decomposition of Cs_2CIT after melting in cesium azide and cesium dicyanamide. It is assumed that the presence of an over the entire dianion delocalized π-system probably accounts for the remarkable kinetic and thermodynamic stability of CIT salts (see below).

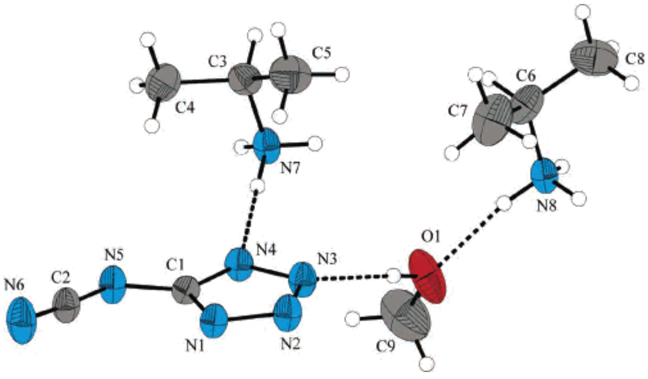

Figure 2. Formula unit and labeling scheme for **4** (ORTEP plot, thermal ellipsoid represents 50% probability).

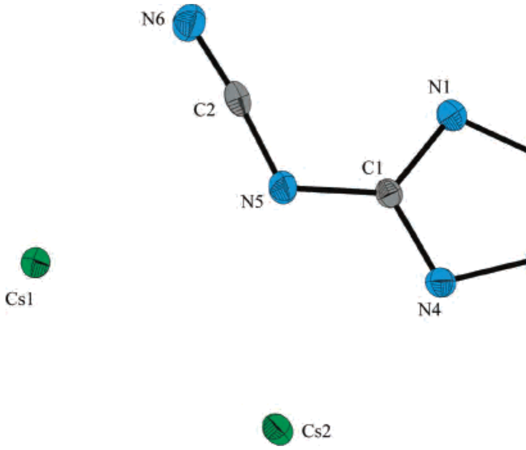

Figure 3. Formula unit and labeling scheme for **5** (ORTEP plot, thermal ellipsoid represents 50% probability).

X-ray Crystal Structures of (^{i}PrNH$_3$)$_2$CIT•MeOH (4) and Cs$_2$CIT (5). Figures 2 and 3 show the molecular units with the atom labeling scheme of **4** and **5**, respectively. Selected bond lengths and angles are presented in Table 2. **4** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the cell, and **5** in the monoclinic space group $P2_1/n$ with 4 units in the cell.

As shown in Figure 2, there are only small cation−anion interactions (hydrogen bridges) in the solid-state structure of **4** (the bond distances and angles in the isopropylammonium and MeOH are as observed for many other salts with isopropylamine or MeOH as cosolvent, and therefore, we abstain from a discussion),[33] in contrast to the very complex bonding situation between anions and cations in **5**. The structure of **5** consists of an infinite three-dimensional network of repeating Cs$_2$CIT units. Each anion is bonded to 12 cesium cations while each Cs$^+$ has contacts to 9 N$^{\delta-}$ atoms in six different CIT anions (Figure 4 with Cs−N bond distances of 3.131(2)−3.586(3) Å. All Coulombic interactions (listed in Table 3) are either larger than the sum of the ionic radii of Cs$^+$ (1.92 Å, CN = 9) and N^{3-} (1.32 Å)[34] or in the range, indicating that the structure is predominantly ionic. The sum of the calculated valency units for Cs1$^+$ and Cs2$^+$ accounts for 1.026 and 1.051, respectively, consistent with a single positive charge on both Cs$^+$ and a doubly negatively charged CIT ion (Table 3).

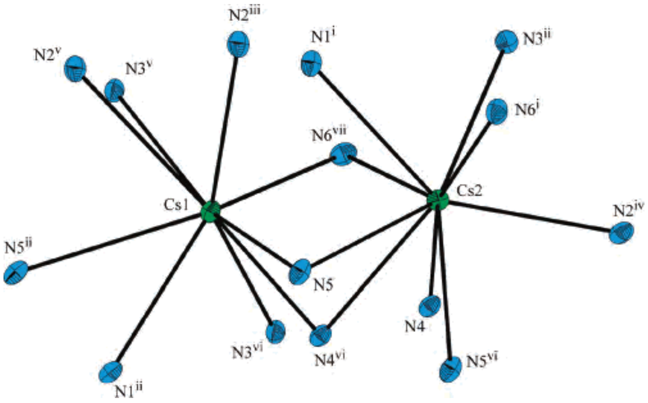

Figure 4. View of cesium coordination environment in Cs$_2$CIT.

Table 3. Observed Cs−N Contacts and Calculated Vaelency Units in Cs$_2$CIT

contact^{a,b}	dist (Å)	valency units^c	contact^{a,b}	dist (Å)	valency units^c
Cs1−N1^{ii}	3.403(3)	0.0969	Cs2−N1^{i}	3.481(3)	0.0836
Cs1−N2^{iii}	3.290(3)	0.1213	Cs2−N2^{iv}	3.302(3)	0.1184
Cs1−N2^{v}	3.505(3)	0.0799	Cs2−N3^{ii}	3.324(3)	0.1136
Cs1−N3^{vi}	3.320(3)	0.1143	Cs2−N4	3.178(3)	0.1525
Cs1−N3^{v}	3.233(3)	0.1362	Cs2−N4^{vi}	3.586(3)	0.0687
Cs1−N4^{vi}	3.131(2)	0.1679	Cs2−N5	3.483(3)	0.0832
Cs1−N5	3.330(3)	0.1120	Cs2−N5^{vi}	3.265(3)	0.1276
Cs1−N5^{ii}	3.571(3)	0.0706	Cs2−N6^{i}	3.154(3)	0.1606
Cs1−N6^{vii}	3.266(3)	0.1273	Cs2−N6^{vii}	3.208(3)	0.1433
sum of valency units		1.0264			1.0515

^{a} Locations of contacts are shown in Figure 4. ^{b} Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $0.5-x, 0.5+y, 0.5-z$; (iii) $1-x, 1-y, -z$; (iv) $-0.5+x, 0.5-y, -0.5+z$; (v) $x, 1+y, z$; (vi) $-x, 1-y, -z$; (vii) $-0.5+x, 1.5-y, -0.5+z$. ^{c} Valency units were calculated using Brown's expression $s = (R/R_0)^{-N}$, where R is the observed contact distance; R_0 is the distance corresponding to a valency unit of 1, and N is a fitted constant. Values of R_0 for contacts to N and O differ by an average of 0.10−0.15 Å for other nuclei; R_0 for Cs−O is reported to be 2.24 Å. As no Cs−N contacts are given, R_0 was set to 2.39 Å. The value of N for Cs−O contacts is 6.6, and this value was used for the Cs−N contacts.

Structure and Bonding of the CIT Dianion. In agreement with DFT calculations, the CIT anion is almost planar in the solid state. The tetrazole ring in **4** and **5** is planar with the attached exocyclic nitrogen atom of the NCN moiety lying within the tetrazole plane (e.g. with a maximal deviation of 0.0034 Å in **4**). The cyanoimino moiety is slightly outside of the tetrazole plane (<N4−C1−C2−N6: **4**, 9.4(4)°; **5**, 5.4(5)°). Similar to the situation found in covalent bound azides,[35] a trans bent geometry is found for the NCN group (<NCN: **4**, 175.9(2)°; **5**, 174.0(3)°). Actually, the CIT dianion is isoelectronic to the related azidotetrazolate monoanion (replacement of the middle N atom of the azido group by C$^-$); hence, the hitherto unknown structure of azidotetrazolate can be expected to have similar features such as those of CIT. As displayed in Table 2, the distances and angles of CIT in different salts are not significantly different. Thus, it can be assumed that the geometry of the C$_2$N$_6$ dianion is little affected by coordina-

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(35) Schulz, A.; Klapötke, T. M. *Inorg. Chem.* **1996**, *35*, 4791.

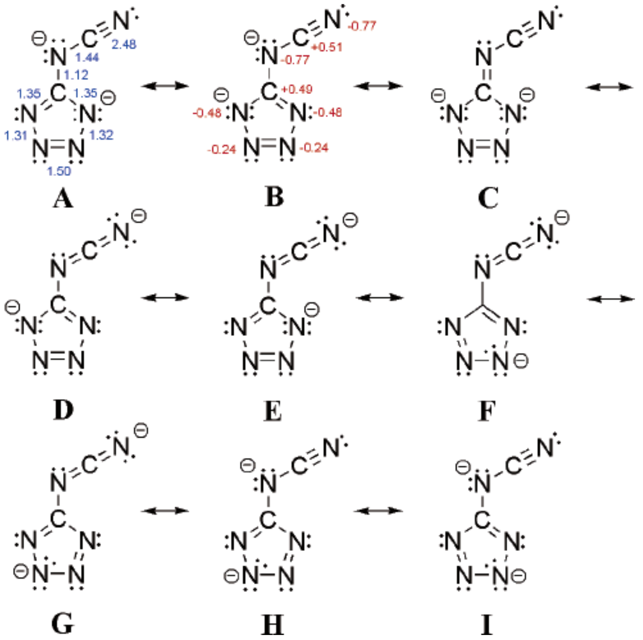

Figure 5. Nine possible Lewis representations according to NBO analysis along with WBI (blue color) and NPA charges (red color).

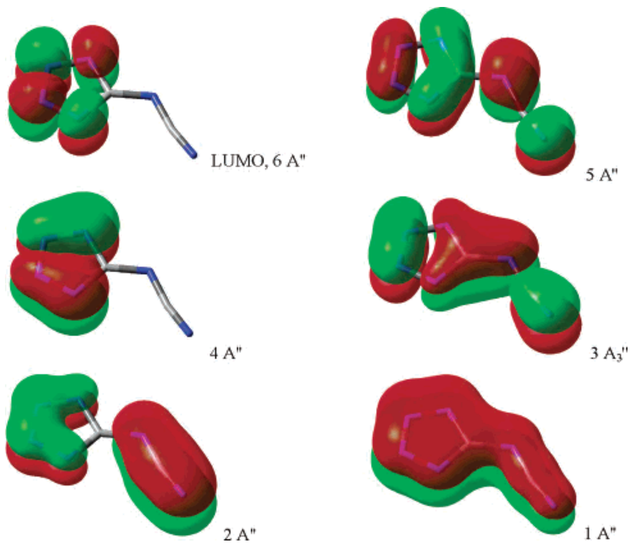

Figure 6. π-type MOs (B3LYP/aug-cc-pvTZ) of CIT displaying the $10\pi-8c$ bond.

Table 4. Selected Structural Parameters (Å, deg) of **6**

Pd−N1	2.008(2)	Pd−N8	2.043(2)
Pd−N7	2.046(2)	Pd−N9	2.043(2)
N1−Pd−N7	90.22(9)	N1−Pd−N8	176.90(8)
N7−Pd−N8	89.82(9)	N7−Pd−N9	179.67(9)
N8−Pd−N9	90.37(9)	Pd−N1−C1	132.5(2)
N9−Pd−N1	89.57(9)	Pd−N1−N2	120.9(2)

tion to a metal (see X-ray data for **6**) or substitution at a ring nitrogen (see X-ray data for **7**). The calculated gas-phase geometry of CIT at the B3LYP/aug-cc-pvTZ level of theory is similar to that found in the solid state and is given in Table 2.

As expected, for all CIT salts the N2−N3 bonds are significantly shorter than the N1−N2 and C1−N1 bonds (Figure 1; e.g. **6**: 1.298(3), 1.357(3), and 1.335(3) Å), which is comparable to the situation found in the structure of the cyanotetrazolate.[15] The C2−N6 bond length is significantly smaller than all other C−N or N−N bond lengths indicating a stronger π-interaction along the cyano group of the NCN unit. The bond length found for the cyano group lies in a normal range (e.g.: **4**, 1.159(2) Å, and **5**, 1.174(4) Å, for C2−N6; Table 2).[36] These relatively short NN and CN bond lengths, together with the planarity, indicate the presence of delocalization of π-bonds over the whole anionic species. MO and NBO calculations displayed the existence of a 10π-electron, 8-center bond unit (Figures 5 and 6).[37] In Figure 5, **A** and **B** are the energetically preferred Lewis representations of NNCM according to NBO analysis which is in agreement with the calculated Wiberg bond indices[38] (WBI) and the calculated partial charges (Figure 5). Investigation of the intramolecular donor−acceptor interactions utilizing the NBO partitioning scheme clearly indicates a highly delocalized 10π-system according to resonance between Lewis representations **A**−**I**.

The calculated WBI's indicate a stronger π-bond along the NCN moiety and the N_3-N_4 unit. The largest negative NPA net charge (NPA, natural population analysis) is found on the two N atoms of NCN unit. Summing the net charges of the NCN and the tetrazole moiety reveals for both units a negative charge close to −1 (NCN, −1.04; N_4C, −0.96 e).

Transition Metal CIT Complexes: Crystal Structure of [Pd(C_2N_6)(NH_3)$_3$]•H_2O (6). Complexes of CN species with transition metals are well-known and often exhibit interesting magnetic properties.[39] Due to the potential of being polydentate, we have synthesized several transition metal salts of CIT (M(CIT)(NH_3)$_3$; M = Cu, Ni, Pd) of which we only want to introduce the palladium complex here. These complexes are easily obtained from the reaction of the according transition metal(II) chlorides and **2** in ammonia solution.

The pale yellow palladium complex crystallizes in the monoclinic space group $P2_1/n$ with 4 units/cell. The structural data for **6** are presented in Tables 2 and 4, and the numbering

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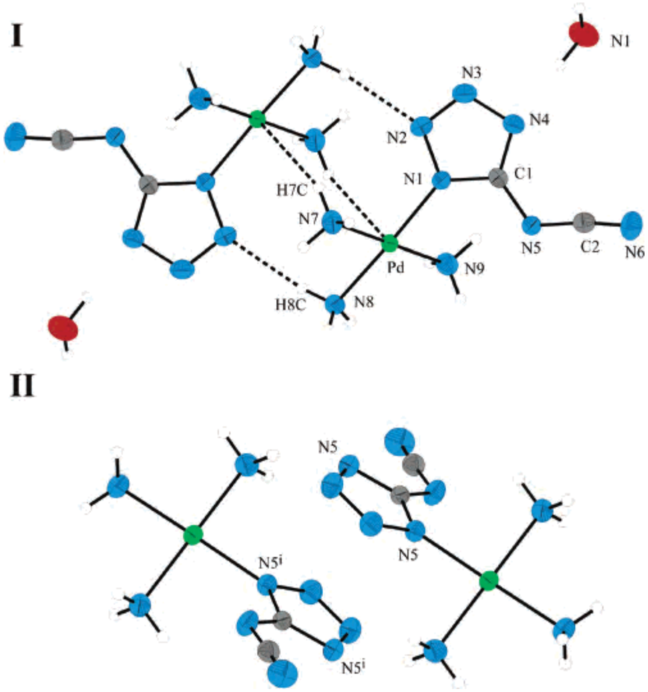


Figure 7. (I) Dimer [Pd(C_2N_6)(NH_3)$_3$]·H_2O (**6**), showing the atom-numbering scheme and displacement ellipsoid at the 50% probability level. (II) Part of the crystal structure of **6**, showing the $\pi-\pi$-stacking interaction which links the dimers to chains along the [010] axis. Atoms marked with superscript i are at the symmetry position $-x$, $-y$, $-z$.

scheme is depicted in Figure 7. The Pd atom lies in the center of a slightly distorted square-planar arrangement composed of three NH_3 ligands and one CIT ligand (coordination via N1 of the tetrazole ring), with N−Pd−N angles ranging from 89.58(9) to 90.22(9)° (mean deviation from the square plane is 0.0707 Å). All Pd−N distances are in the range of 2.008(2)−2.046 (2) Å (Table 4) and lie well within the range of distances recorded previously.[40] The CIT ligand is not part of the square plane as the tetrazole ring is twisted by 31.1° (N7−N9−N1−C1). The molecular parameters are comparable with those found in **4** and **5** (Table 2). It is interesting to note that the cyanoimino group is not involved in any bonding to the Pd metal.

In the solid state the complex is composed of dimers where the two complexes are related via an inversion center. The long Pd−Pd^{i} distance of 4.2743(2) Å in the dimer excludes the possibility of the existence of a metal−metal interaction. A closer inspection of the molecular structure as shown in Figure 7 reveals two agostic interactions (N7−H7C····Pd1^{i}; $d(\mathrm{Pd}\cdots\mathrm{N7})^{i} = 3.536(3)$ Å; symmetry code (i) $-x$, $1 - y$, $-z$) between the two Pd complex fragments forming the dimer. Apparently, these two interactions together with an intermolecular hydrogen bond (N8−H8C····N2^{i}) can be regarded as the driving force for the dimerization.

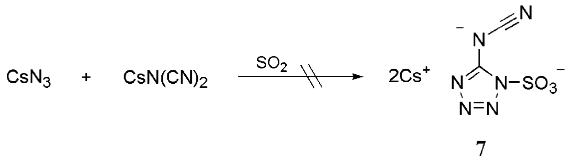
Moreover, the dimers are linked by $\pi-\pi$-stacking interactions to chains along the [010] axis. The parallel tetrazole rings of the CIT ligands at (x, y, z) and ($-x$, $-y$, $-z$) have an interplanar stacking spacing of 3.307(2) Å. Additionally, several hydrogen bonds including the water molecule are found linking the dimers to a three-dimensional network (Table 5).

Table 5. Hydrogen Bond Geometry (Å, deg) of **6**

D−H···A	D−H	H···A	D···A	D−H···A
O1−H1A···N6^{i}	0.948(2)	2.072(3)	2.994(3)	164.0(2)
O1−H1B···N4	0.947(3)	2.037(4)	2.966(4)	166.3(2)
N7−H7A···O1^{ii}	0.89(2)	2.11(1)	2.989(3)	172.4(9)
N7−H7B···N4^{iii}	0.891(1)	2.154(6)	3.031(4)	157.4(5)
N8−H8B···N5^{iv}	0.891(1)	2.16(1)	3.031(4)	167.4(9)
N8−H8C···N2^{v}	0.890(9)	2.187(1)	3.066(3)	169.1(7)
N9−H9B···N6^{vi}	0.890(8)	2.302(6)	3.151(4)	159.4(5)

Symmetry codes: (i) $-0.5 + x$, $-0.5 - y$, $-0.5 + z$; (ii) $-0.5 + x$, $0.5 - y$, $0.5 + z$; (iii) $-x$, $-y$, $-z$; (iv) $0.5 - x$, $0.5 + y$, $0.5 - z$; (v) $-x$, $1 - y$, $-z$; (vi) x, $1 + y$, z.

Scheme 3. Attempted Synthesis of **7**



Reaction of Cs_2CIT with SO_2. A frozen mixture of $Cs_2C_2N_6$ and SO_2 reacts on thawing under formation of a bright yellow solution which turns into a deep red solution within a few minutes. From this solution a gummy residue separates within 20 min from which a pale yellow solution was separated after 1 day. From this pale yellow solution, **7** crystallized as pale yellow plates in an overall yield of 40% according eq 1. Interestingly, the pale yellow crystals of **7** contain one SO_2 molecule (solvent) per formula unit and are surprisingly stable at room temperature even without SO_2 atmosphere. The loss of SO_2 starts only slowly from the surface of the crystals. It can be assumed that in the first reaction step SO_2 is attached to the N1 atom of the tetrazole ring followed by oxidation to SO_3 by SO_2 yielding the total reaction

$$2Cs_2C_2N_6 + 3SO_2 \xrightarrow{SO_2} 2Cs_2C_2N_6SO_3 + 1/8S_8 \qquad (1)$$

This reaction represents a typical disproportionation reaction ($3SO_2 \rightarrow 2SO_3 + 1/8S_8$). The reaction of Cs_2CIT/SO_2 system is related to the known reaction of CsF with SO_2 resulting in $CsSO_3F$ and S_8.[41] Two more things are worth mentioning: (i) In contrast to the CsF/SO_2 reaction, no ultrasonic activation is needed for the spontaneous reaction of Cs_2CIT with SO_2.[41] (ii) The related cesium cyanotetrazolate was prepared in SO_2 without any reaction with the solvent SO_2.[15]

Unfortunately, the direct synthesis of **7** from CsN_3 and $CsN(CN)_2$ in SO_2 according Scheme 3 did not yield the sulfonate **7**.

It is known that neutral as well ionic azide can undergo cycloaddition with cyano groups, and Beck and Fehlhammer succeeded in the synthesis of bis(tetrazolate) dianions with

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Table 6. Selected Geometric Parameters (Å, deg) of **7**

N1−S1	1.738(4)	S1−O3	1.425(4)
S1−O1	1.434(4)	S2−O4	1.423(5)
S1−O2	1.437(4)	S2−O5	1.423(5)
O1−S1−O2	115.2(2)	N1−S1−O2	103.6(2)
O1−S1−O3	116.5(3)	N1−S1−O3	102.7(2)
O2−S1−O3	113.0(3)	O4−S2−O5	117.3(2)
N1−S1−O1	103.6(2)		

complex metal azides.[42] Also the reaction of sodium dicyanamide with sodium azide under acid-catalyzed condition yield the corresponding bis(tetrazolate)amine.[25] It is also known that the reactivity of the 1,3-dipolar cycloaddition reaction of organic,[43] inorganic,[44] silyl,[45] and complexed as well as alkali metal azides with nitriles is greatly enhanced by electron-withdrawing groups bonded to the nitrile and therefore there might be a chance for this reaction. Raman investigation of the obtained products (see Experimental Section) strongly supports the assumption that a cyclo addition reaction took place as no evidence for starting material (CsN_3 and $CsC(CN)_2$) was found. Unfortunately, also no evidence for the formation of the cesium CIT or $CITSO_3$ was found. The reaction that took place is still not understood and under further investigation.

Crystal Structure of $Cs_2CITSO_3{\bullet}SO_2$ (7). The crystal data are summerized in Table 1. To ensure that the crystal was representative of the whole sample, its Raman spectrum was recorded and no difference from the crushed sample was found. **7** crystallizes in the monoclinic space group $P2_1$ with 2 formula units in the unit cell. Bond lengths and angles are summarized in Tables 2 and 6. A view of the molecular arrangement can be depicted from Figure 8. Formally, **7** can be regarded as a donor−acceptor complex of CIT ($C_2N_6^{2-}$) and SO_3. However, upon "SO_3 complexation" the structural parameters of the CIT frame are not much affected (Table 2). The largest deviations are found for the N2−N3 distance (**7**, 1.274(6) Å, vs **5**, 1.309(4) Å) and the C2−N6 (CN group, **7**, 1.147(7) Å, vs **5**, 1.174(4) Å) indicating a stronger localization of the π bonds in **7** along the N2−N3 and C2−N6 units. The S−N distance of 1.738(4) Å represents a typical single bond (cf. 1.791 Å in $SO_3(N_2O_2)^{2-}$ [46] and $\Sigma r_{cov}(SN) = 1.74$ Å).[34] The lengths of the sulfonate S−O bonds are in good agreement with those of known sulfonate salts,[46,47] and the sulfonate O atoms are approximately staggered with respect to the substituents on N1. The O−S−O angle in the sulfonate groups are increased due to the no longer balanced repulsion of the lone pairs, giving an O−S−O angle greater than the tetrahedral angle of 109.47°. The SO_2 solvent molecule has regular bond lengths, and the O−S−O angle is comparable to those of the gas-phase structure and therefore is not affected by the crystal lattice.[41,48]

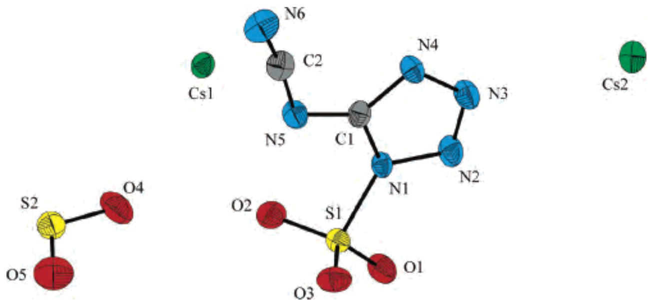

Figure 8. Formula unit and labeling scheme for **7** (ORTEP plot, thermal ellipsoids represent 50% probability).

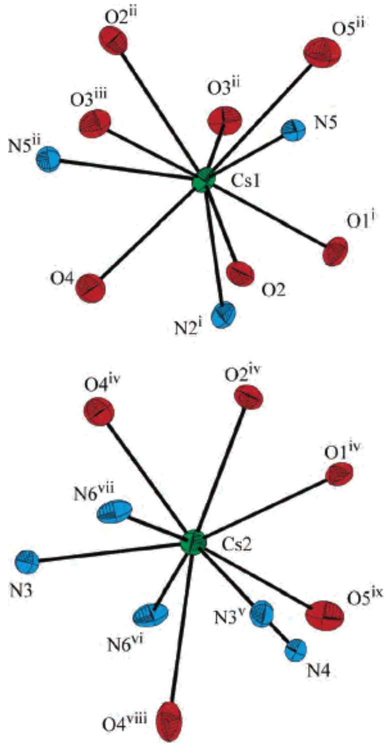

Figure 9. View of cesium coordination environment in $Cs_2CITSO_3{\cdot}SO_2$ (**7**).

Both Cs^+ cations possess a coordination number of 10, which is quite common for cesium salts. Cs1 has contacts to seven oxygen and three nitrogen atoms resulting from four dianions and two SO_2 molecules.[49] Cs2 has contacts to five oxygen and five nitrogen atoms resulting from five dianions and three SO_2 molecules (Figure 9 and Table 7; see Supporting Information Figure S1). The SO_2 solvent molecule always coordinates to five different Cs cations. As shown by the investigation of the valency units, the Cs−N and Cs−O interactions are essentially ionic. The sum of the valency units to Cs^+ and the dianion is 1.9803, consistent with a single positive charge on each Cs cation and two negative charges on the $CITSO_3$ anion (Table 7).

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Table 7. Interionic Distances (Å) for **7**

contact[a,b]	dist (Å)	valency units[c]	contact[a,b]	dist (Å)	valency units[c]
Cs1−O1^{i}	3.034(4)	0.1350	Cs2−O1^{iv}	3.390(4)	0.0649
Cs1−O2	3.146 (4)	0.1061	Cs2−O2^{iv}	3.147(3)	0.1061
Cs1−O2^{ii}	3.328(4)	0.0733	Cs2−O4^{iv}(SO_2)	3.277(5)	0.0812
Cs1−O3^{iii}	3.054(4)	0.1293	Cs2−O4^{viii} (SO_2)	3.743(5)	0.0337
Cs1−O3^{ii}	3.181(5)	0.0988	Cs2−O5^{ix} (SO_2)	3.406(5)	0.0629
Cs1−O4 (SO_2)	3.336(4)	0.0722	Cs2−N3	3.335(5)	0.1109
Cs1−O5^{ii} (SO_2)	3.537(4)	0.0491	Cs2−N3^{v}	3.435(5)	0.0913
Cs1−N2^{i}	3.306(4)	0.1175	Cs2−N4	3.503(5)	0.0802
Cs1−N5^{ii}	3.287(5)	0.1221	Cs2−N6^{vi}	3.127(5)	0.1697
Cs1−N5	3.315(5)	0.1154	Cs2−N6^{vii}	3.153(6)	0.1606
sum of valency units		1.0188			0.9615

[a] Locations of contacts are shown in Figure 9. [b] Symmetry codes for **7**: (i) $-x, -0.5 + y, -z$; (ii) $1 - x, -0.5 + y, -z$; (iii) $x, -1 + y, z$; (iv) $x, y, 1 + z$; (v) $-x, 0.5 + y, 1 - z$; (vi) $-1 + x, y, z$; (vii) $1 - x, 0.5 + y, 1 - z$; (viii) $-x, 0.5 + y, -z$; (ix) $1 - x, y, z + 1$. [c] Valency units were calculated using Brown's expression $s = (R/R_0)^{-N}$, where R is the observed contact distance; R_0 is the distance corresponding to a valency unit of 1, and N is a fitted constant. Values of R_0 for contacts to N and O differ by an average of 0.10−0.15 Å for other nuclei; R_0 for Cs−O is reported to be 2.24 Å. As no Cs−N contacts are given, R_0 was set to 2.39 Å. The value of N for Cs−O contacts is 6.6, and this value was used for the Cs−N contacts.

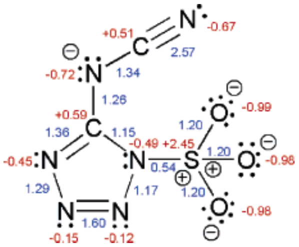

Figure 10. Best Lewis representation of $CITSO_3$ according to NBO analysis along with WBI (blue color) and NPA charges (red color).

CIT versus $CITSO_3$. The best Lewis representation according to the NBO analysis along with the WBI's and partial charges is displayed in Figure 10. The bond situation of the CIT subunit in $CITSO_3$ corresponds to the best representation found for the CIT anion. Investigation of the donor−acceptor interaction displays similar delocalization effects as found for CIT; hence, a similar resonance scheme as found for CIT (Figure 5) can be expected for $CITSO_3$. Interestingly, the C2−N6 distance of the NCN and the N2−N4 distance decrease upon addition of SO_3, indicating a better localization of the triple bond along the CN group (WBI, **5**, 2.46 Å, vs **7**, 2.57 Å) and a double bond along N2−N3 (WBI, **5**, 1.50 Å, vs **7**, 1.60 Å). The S−N bond as well as all S−O bonds is highly polarized resulting in a large positive charge at S (+2.45 e). Similar to the situation in the CIT anion, both N atoms attached to a carbon in the $CITSO_3$ anion possess the largest negative charge, and for both species the most negatively charged N atom is the amido nitrogen followed by the terminal N atom of the NCN group. Upon addition a considerable charge transfer occurs (q_{CT} = 0.49 e). The tetrazole ring transfers 0.33 e and the NCN moiety 0.16 e, respectively, resulting in an overall negative charge for the CIT subunit of only 1.51 e.

Conclusions. We have reported an improved synthesis of CIT (CIT = $C_2N_6^{2-}$) salts and have fully characterized a series of different CIT salts and complexes for the first time. The CIT dianion represents a nitrogen-rich binary CN anion with surprising high thermal stability which decomposes in the case of the cesium salt (**5**) above 395 °C into cesium azide and cesium dicyanamide. The crystal structures of several CIT salts reveal the large coordination potential for CIT as a ligand utilizing several mono- and bidentate modes. Surprisingly, Cs_2CIT reacts with liquid SO_2 in a disproportionation reaction yielding a new anion, $C_2N_6SO_3^{2-}$ ($CITSO_3$). The easy access of CIT salts may qualify them as a useful educts for the preparation of new charge-transfer, ferro- or antiferrormagnetic complexes as well as the basis for supramolecular frameworks, for contacting organic radical cation salts, and in material science as precursors for novel ternary $M_xC_yN_z$ or binary C_xN_y systems.

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Supporting Information Available: Coordination environment of **7** (Figure S1 and S2), experimental details and results of the difference scanning calorimetry (Figure S2) and temperature-dependent X-ray diffraction measurement (Figure S3) of **5**, and computational details, frequency data, and NPA charges of the investigated species (Tables S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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