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Articles

Preparation, Characterization, X-ray Crystal Structure, and Energetics of Cesium 5-Cyano-1,2,3,4-Tetrazolate: $\mathrm{Cs[NC\overline{CNNNN}]}$

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Cesium 5-cyano-1,2,3,4-tetrazolate, $\mathrm{Cs[NC\overline{CNNNN}]}$ (Cs**1**), was prepared in 100% yield by a 3 + 2 cycloaddition reaction of $\mathrm{CsN_3}$ and $\mathrm{(CN)_2}$ in $\mathrm{SO_2}$. Cs**1** forms monoclinic crystals (a = 8.297(2) Å, b = 11.040(3) Å, c = 6.983(2) Å, β = 120.31(2)°, space group $C2/c$, Z = 4, R1 = 0.048, wR2 = 0.120 for 1217 independent reflections). Cs**1** is best described as a three-dimensional array of cations and anions connected by weak $\mathrm{Cs^+{-}N^{\delta-}}$ contacts. The cations and anions each form a diamond-type lattice (tetrahedral arrangement of ions) with the counterions lying in hexagonal channels running parallel to the c-axis. The anions in the channels form stacks with the CN groups pointing in opposite directions in adjacent layers. The calculated (RB3PW91/6-311+G*) geometry of **1** is in agreement with the X-ray crystal structure, and the calculated vibrational spectrum is in good agreement with the observed FT-IR and FT-Raman spectra. The lattice enthalpies and heats of formation of M**1** (M = Cs, K) as well as the enthalpy of formation from $\mathrm{MN_3(s)}$ and $\mathrm{(CN)_2(g)}$ were estimated. The ^{13}C and ^{14}N NMR spectra of Cs**1** are also reported. The ionization potential (450.7 kJ mol) and electron affinity (427.4 kJ/mol) of **1** were calculated. Attempts to oxidize **1** with $\mathrm{AsF_5}$ led to the formation of Cs**1**·$x\mathrm{AsF_5}$ ($x \approx 2$). The 7π dianion $\mathrm{[NC\overline{CNNNN}]^{\bullet 2-}}$ is calculated to be a stable entity in the gas phase, but $\mathrm{Cs_2}$**1** is estimated to be unstable with respect to dissociation to 2 CsCN and $^3/_2$ $\mathrm{N_2}$ ($\Delta H_{\mathrm{diss}} = -132.4$ kJ/mol). The preparation of the potassium salt of **1** and the corresponding thermodynamic quantities are reported.

Introduction

Tetrazolate salts and substituted tetrazoles are important chemicals with a variety of industrial uses,[1] including pharmaceuticals, explosives, sweeteners, photographic processing chemicals, fuels, and agricultural agents. The most convenient route for their preparation is the 1,3-dipolar cycloaddition reaction of inorganic,[2] organic,[3,4] silyl,[5] and complexed metal azides[6] with nitriles. Reactivity is greatly enhanced by electron-withdrawing groups bonded to the nitrile.[2] Two general mechanisms for the cycloaddition have been discussed in the literature based on experimental[7−13] and theoretical[14] investigations: a concerted mechanism involving one cyclic transition state[10] and a nonconcerted, two-step polar or diradical mechanism,[11,12] the latter favored by theoretical calculations.[14] Although many tetrazolate salts have been characterized by spectroscopic methods and elemental analysis, the number of structurally characterized compounds is small, and they include $\mathrm{[Na(digly)_2][(CF_3\overline{CNNNN})_3Mn_2(CO)_6]}$ (**2**),[15] $\mathrm{[(NC\overline{CNNNN})Co(NH_3)_5][ClO_4]}$ (**3**),[16] 5-[(3-chlorobenzyl)dimethylammonio]tetrazolide (**4**),[17] diethylammonium 5-methoxy-3-(1-methylethoxy)-1-phenyl-*N*-(tetrazol-5-yl)-1*H*-indole-2-carboxamide,[18] bis(1,2,3-triaminoguanadinium)bis(5-aminotetrazolate)monohydrate (**5**),[19] and $\mathrm{[Ph_3PNPPh_3][\overline{NNNNC}\overline{CSNC(CN)N}]}$ (**6**).[20] An X-ray crystal structure of a simple metal or ammonium tetrazolate salt has yet to be determined; however, the gas phase geometry of $\mathrm{[HCNNNN]^-}$ has been calculated at the MP2/6-31G* level of theory.[21]

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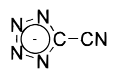

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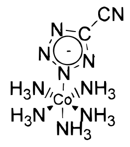

$(ClO_4^-)_2$

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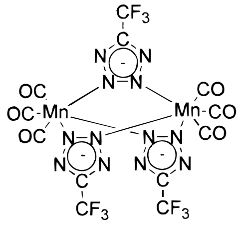
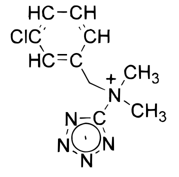


$[Na(diglyme)_2]^+$

2



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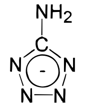

$[C(N_2H_3)_3]^+$

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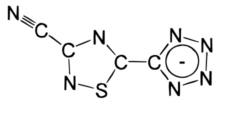

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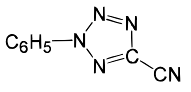

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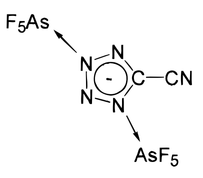

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The $[NC\overline{CNNNN}]^-$ anion (**1**) was first prepared in 1913 by Olivery-Mandana and Passalaqua[22] by the reaction of HN_3 and $(CN)_2$ followed by neutralization of the 1*H*-tetrazole with NaOH. More recently the anion has been isolated and characterized crystallographically as part of the transition metal complex $[(NC\overline{CNNNN})Co(NH_3)_5][ClO_4]$[16] and been prepared directly as $[Ph_3PNPPh_3][NC\overline{CNNNN}]$[20] although the structure was not determined. We report below the synthesis, characterization, vibrational spectrum, X-ray crystal structure, and energetics of the preparation of Cs**1**. In addition, we report theoretical (B3PW91/6-311+G*) and experimental investigations of the redox chemistry of **1** as well as the preparation of K**1**.

Experimental Section

Materials. $(CN)_2$ (Matheson, 98%) was distilled directly from the cylinder into a leak-tight, flame-dried Monel vessel prior to use. CsN_3 (Eastman-Kodak) was stored under an atmosphere of dry nitrogen in the drybox (see above). SO_2 (Liquid Air, 100%) was distilled onto CaH_2 and stored for at least 24 h prior to use.

General Procedures. All reactions were performed in two-bulb, two-valve Pyrex vessels incorporating 25 mL bulbs using techniques that have been described previously.[23] Solid reagents and crystals were manipulated in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train (HE-493) and 1 kg of 3 Å molecular sieves contained in an internal circulating drying unit. ^{13}C and ^{14}N NMR spectra were obtained at 298 K on a Varian XL400 spectrometer. FT-IR spectra of Nujol mulls between CsI disks were recorded at 293 K on a Bruker IFS66 FT-IR. Gas phase IR spectra were obtained on a Perkin-Elmer 683 spectrometer using a custom-made Monel cell (path length 10 cm) incorporating AgCl plates and using a polystyrene film as standard. FT-Raman spectra were recorded at 293 K on a Bruker IFS66 FT-IR equipped with a Bruker FRA106 FT-Raman accessory using a Nd:YAG laser (emission wavelength, 1064 nm; maximum laser power, 3009 mW; used laser power, 5.5%). Samples were sealed in melting point capillaries, and data was collected in the backscattering mode (180° excitation; resolution 4.0 cm^{-1}). Chemical analysis was carried out by Bellor Mikroanalytisches Laboratorium, Göttingen, Germany.

The structures of anionic, dianionic, and neutral $[NC\overline{CNNNN}]$ species were optimized at the B3PW91 level of theory employing the 6-311+G* basis set using either the Gaussian94W[24] or Gaussian98W[24] suite of programs. Their nature as a stationary point on the hypersurface was proven by a subsequent frequency analysis at the given level of theory. Calculated vibrational frequencies were animated and assigned using Hyperchem.[25] The starting geometry for optimizations of the neutral, anionic, and dianionic $[NC\overline{CNNNN}]$ species was the solid state structure of the anion in Cs**1**. N_3^- and $(CN)_2$ were optimized at the same level of theory.

Synthesis and Characterization of Cs1. SO_2 (9.946 g) and $(CN)_2$ (1.520 g/29.210 mmol) were condensed successively onto cooled (−196 °C) CsN_3 (5.040 g/28.812 mmol), giving a bright yellow solution over a white insoluble solid at room temperature. Within minutes, the solution became a much paler yellow and colorless crystals formed on the glass surface. Crystals continued to grow for approximately 1 h. After 1 day the solution was filtered and the volatiles [gas phase IR: SO_2, $(CN)_2$] were removed by dynamic vacuum for 2 h, giving a constant weight of 6.633 g (101% yield of Cs**1** based on eq 1 and weight of CsN_3 used). The colorless solid (solubles) and colorless crystals (insolubles) gave identical IR and FT-Raman spectra.

Elemental anal. for Cs**1**, obsd (calcd): Cs 58.20 (58.56), C 10.38 (10.58), N 30.51 (30.86). ^{13}C NMR (0.132 g of Cs**1** in 10.485 g of H_2O, 298 K): $\delta = 138.1$ ppm (C3, tetrazolate ring), −111.7 ppm (C2, cyano group). Assignments are based on reported chemical shifts for neutral tetrazoles[1] (C3, 146.5 to 166.9 ppm) and nitriles[26] (C2, ∼−110 ppm). ^{14}N NMR (0.132 g of Cs**1** in 10.485 g of H_2O, 298 K): $\delta = 1.9$ ppm (N5/N5a, tetrazolate ring), −57.1 ppm (N4/N4a, tetrazolate ring), −121.1 ppm (N1, cyano group). Assignments are based on reported chemical shifts for $Na[F_2NCF_2\overline{CNNNN}]$[27] in $CDCl_3$/THF (N4/N4a, −65.21 ppm, N5/N5a, −39.73 ppm) and nitriles[39] (N1, ∼−150 ppm). FT-IR (Figure 1a) and FT-Raman (Figure 1b) frequencies of Cs**1** are listed in Table 1 along with the IR frequencies of $Na[CF_3\overline{CNNNN}]$[28]

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[25] Hyperchem: Release 3 for Windows, Copyright 1993 Hypercube, Inc. and Autodesk, Inc.; Developed by Hypercube, Inc.

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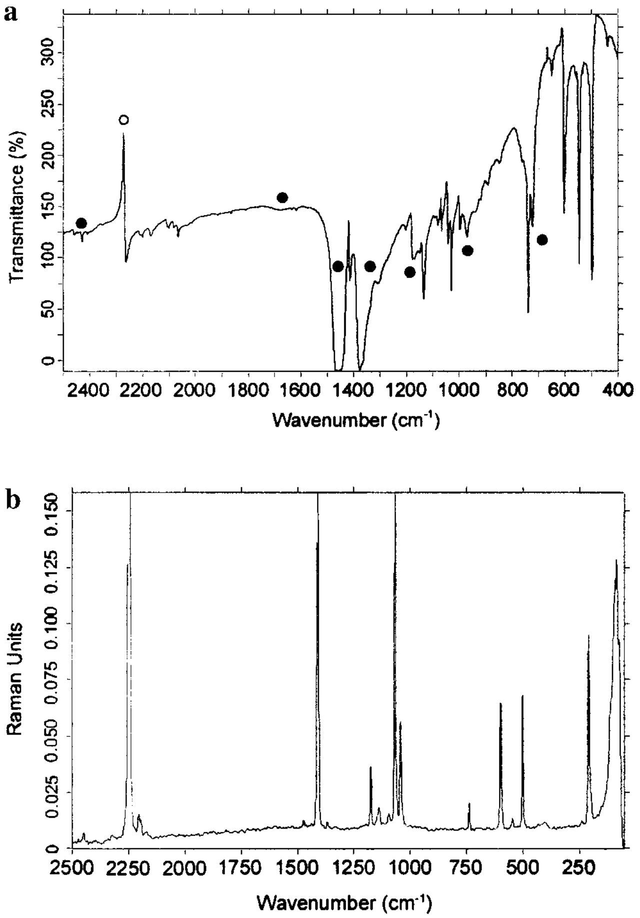


Figure 1. (a) FT-IR spectrum (128 scans, resolution 2 cm^{-1}) of Cs**1**. Peaks marked with a ● are due to Nujol, and the negative peak marked with a ○ is a result of subtracting the background spectrum from the sample spectrum. (b) FT-Raman spectrum (3072 scans, resolution 4 cm^{-1}) of Cs**1**.

and calculated frequencies (RB3PW91/6-311+G*) and assignments. Cs**1** is a colorless solid which is indefinitely stable under an atmosphere of dry nitrogen at room temperature. It is sparingly soluble in SO$_2$ but is very soluble in water, in which it is stable and from which it can be recovered (^{1}H NMR, infrared). The stability of the tetrazolate anion in water has also been observed for Na[CF$_3$CNNNN].[28] Cs**1** showed no signs of instability on grinding or striking with a pestle and is thermally stable at temperatures up to at least 400 °C (FT-Raman), at which point the salt still had not melted.

K**1** was also prepared from KN$_3$ (4.126 g/50.857 mmol) and (CN)$_2$ (5.504 g/105.765 mmol, 108% excess) in SO$_2$ (16.217 g) at room temperature in quantitative yield (6.728 g) in a manner identical to the preparation of Cs**1**. The FT-IR spectrum of K**1** is essentially identical to that of Cs**1** and is included in the Supporting Information.

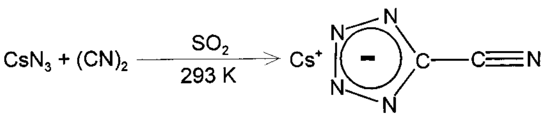
Attempted Preparation of Cs$_2$[NNNNCCNNNN]. (CN)$_2$ (0.343 g/6.591 mmol) and SO$_2$ (17.378 g) were successively condensed onto CsN$_3$ (2.296 g/13.127 mmol) in an attempt to prepare Cs$_2$[NNNNCCNNNN]. The reaction proceeded similarly to the 1:1 reaction, but insoluble white solid remained in the reaction bulb and the solution was a darker yellow. The reaction refluxed at 60 °C for 1 week with no change observed. The volatiles (gas phase IR: SO$_2$) were removed by dynamic vacuum, giving a constant weight of 2.643 g of colorless material in the reaction bulb (total mass of initial materials = 2.639 g), shown to be Cs**1** and unreacted CsN$_3$ (FT-Raman). The FT-Raman spectrum of CsN$_3$ is included in the Supporting Information.

Attempted Oxidation of Cs1. SO$_2$ (10.748 g) and AsF$_5$ (0.291 g/1.713 mmol) were successively condensed at −196 °C onto Cs**1** (0.186 g/0.820 mmol) giving a pale yellow solution over a small amount of insoluble white solid at room temperature. Over a period of 6 h the solid dissolved and the solution became amber colored. After 1 day the volatiles were condensed into the second bulb, leaving an amorphous-looking amber-colored solid that was soluble even in traces of solvent. Repeated attempts to grow crystals failed. The volatiles (gas phase IR: SO$_2$) were removed by dynamic vacuum, leaving 0.481 g of solid orange product (total mass of Cs**1** and AsF$_5$ = 0.477 g), implying some retention of SO$_2$. Spectral data for orange product: FT-Raman (cm^{-1}) ν = 2279.0 vs (**1**), 1486.0 ms (**1**), 1193.6 w (**1**), 1151.7 m (**1**), 1088.8 m (**1**), 1034.2 m (**1**), 735.9 msh (ν AsF$_{ax}$), 724.6 mbr (ν AsF$_{ax}$), 684.5 s (ν AsF$_{4eq}$), 664.0 s (ν AsF$_{4eq}$), 601.0 mw (**1**), 544.5 mw (**1**), 489.5 mw (**1**), 476.1 mw, 409.6 w, 385.2 msh (F$_{ax}$AsF$_{eq}$ wag), 374.1 ms (F$_{ax}$AsF$_{eq}$ wag), 346.8 w, 262.6 w (ν N−As), 217.8 w (ν N−As), 170.9 w, 160.6 wsh, 138.1 m, 121.4 wsh.

X-ray Crystal Structure Determination of Cs1. Several of the colorless crystals of Cs**1** were placed in thin-walled Pyrex glass capillaries, flame sealed, under nitrogen and mounted on an Enraf Nonius CAD4 diffractometer. The unit cell was determined by centering of 25 reflections (12° ≤ θ ≤ 15°). Data were collected at 293 K and corrected for Lorentz and polarization effects. Sample decomposition during data collection was not observed; 4306 reflections were collected to a maximum of 2θ of 70°, and a semiempirical absorption correction[29] was performed [μ(Mo Kα) = 6.593 mm^{-1}, I_{max}/I_{min} = 0.6235/0.1156]. Of those, 1217 independent reflections (R_{int} = 13.4%) were used for structure solution and refinement. The structure was solved using Patterson methods, and all missing atoms were found during the refinement of the subsequent difference Fourier maps. All atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 gave R1 = 0.0475, wR2 = 0.1201, GOF = 1.094. Crystal data are given in Table 2.

Results and Discussion

Synthesis of Cs1. CsN$_3$ and (CN)$_2$ reacted quantitatively at room temperature in liquid sulfur dioxide solution to give Cs**1** as shown in eq 1. Cs**1** was characterized by elemental analysis,



(1)

IR and FT-Raman spectroscopy, and X-ray crystal structure determination. The K**1** salt was prepared similarly with uptake of 1 equiv of (CN)$_2$ for one KN$_3$. The infrared spectrum is identical to that of Cs**1**, implying a similar structure.

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(31) $\Delta H_{elec} = E([\mathrm{NCCNNNN}]^-) - [E(\mathrm{C_2N_2}) + E(\mathrm{N_3}^-)] = -349.92556$ au + [−185.62067 au + (−164.21458)] = −0.09031 au = −237.1 kJ/mol.

(32) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609−3620.

(33) $\Delta H_{react(s)} = U(\mathrm{CsN_3}) + \Delta H_{react(g)} - U(\mathrm{Cs}\mathbf{1}) = 655.3 - 237.1 - 556.6 = -138.4$ kJ/mol.

(34) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press Inc.: Boca Raton, 1991; 5-7 to 15 and 12-12 to 26.

(35) $\Delta H_f°(\mathrm{Cs}\mathbf{1}) = \Delta H_{react} + \Delta H_f°(\mathrm{C_2N_2})^{34} + \Delta H_f°(\mathrm{CsN_3})^{34} = -138.4 + 306.7 - 19.7 = +148.6$ kJ/mol.

(36) $\Delta H_{react(s)} = U(\mathrm{KN_3}) + \Delta H_{react(g)} - U(\mathrm{K}\mathbf{1}) = 678.7 + (-237.1) - 566.8 = -125.2$ kJ/mol.

(37) $\Delta H_f°(\mathrm{K}\mathbf{1}) = \Delta H_{react} + \Delta H_f°(\mathrm{C_2N_2})^{34} + \Delta H_f°(\mathrm{KN_3})^{34} = -125.2 + 306.7 + 43.9 = +225.4$ kJ/mol.

(38) Donation from the HOMO of N$_3^-$ (E = −0.00028 au) to the LUMO of [NCCNNNN] (E = +0.11760 au). HOMO−LUMO gap = 0.11788 au = +309.4 kJ/mol.

(39) Kloptman equation: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons: New York, 1976.

Table 1. Infrared and FT-Raman Spectra of Cs[NCCNNNN]

FT-Raman (cm^{-1})	infrared (cm^{-1})	infrared of $[CF_3CNNNN]^-$ (cm^{-1})[e]	calcd for $[NCCNNNN]^-$ (cm^{-1}), RB3PW91/6-311+G* (int IR/Raman)	assignment[a]
2248.9 (100.0)	2263.7 ms		2278.2 (100.0/100.0)	N1≡C2 str
2204.2 (0.5)	2200.8 w			isotopomer[d] ^{15}N on N1
2194.9 (1.0)	2196.3 w			isotopomer[d] ^{13}C on C2
		1644		
		1510		
1410.4 (16.8)	1414.6 m	1420	1403.5 (0.7/17.7)	$C3(N4)_2$ asym str
1369.5 (<0.1)	1330 msh		1362.6 (28.3/0.0)	$C3(N4)_2$ sym str
		1232		
	1202.9 w	1183	1200.2 (5.8/1.8)	N5/N5a str
1174.8 (0.4)	1176.4 m	1168	1172.9 (1.5/4.8)	2 (N4/N5) asym str
1137.1 (0.1)	1134.7 ms	1141		combination band IR (603.0 + 545.7) R (598.4 + 546.9)
1067.3 (5.5)	1067.6 w		1059.4 (1.5/4.2)	2(N4/N5) sym str
			1051.4 (1.0/0.1)	ip ring def
1043.3 (1.7)	1042.6 w	1037	1042.6 (7.5/25.1)	ip ring def
		775		
			739.0 (0.0/0.0)	oop ring def
737.7 (0.2)	738.0 vs	720	735.1 (0.6/0.8)	C2−C3=N4 bend (oop)
	724.0 s			isotopomer ^{13}C on C3
653.4 (0.1)	649.9 mw			unassigned
598.4 (3.9)	603.0 vs		592.1 (3.8/0.9)	N1≡C2−C3 bend (ip)
546.9 (0.1)	545.7 vs		568.4 (5.8/1.8)	C2−C3 stretch
501.6 (3.9)	497.6 vs		529.2 (2.1/1.5)	N1≡C2−C3 bend (oop)
434.4 (0.1)	439.0 w			unassigned
236.2 (2.6)	*c*		235.1 (3.5/0.8)[b]	N1≡C2−C3 wag
209.4 (5.6)	*c*		217.4 (4.2/0.1)[b]	C2−C3=N4 wag
112.5 (sh)	*c*			lattice vibration?
97.6 (sh)	*c*			lattice vibration?
85.1 (sh)	*c*			lattice vibration?
72.1 (sh)	*c*			lattice vibration?

[a] sym = symmetric, asym = asymmetric, str = stretch, ip = in-plane, oop = out-of-plane, def = deformation. [b] The wagging modes were scaled by a factor of 1.20. [c] Spectrum cutoff is at 250 cm^{-1}. [d] Isotopomer frequencies were determined by specifying the relevant isotope for each atom position (one isotope at a time at each position) and using freqchk.exe (included in the G98W suite) to generate the frequency output. [e] Intensities not given.

Addition of a another 1 equiv of CsN_3 to Cs**1** did not lead to Cs_2[NNNNCCNNNN] (refluxing SO_2, 60 °C, 1 week), in agreement with earlier unsuccessful attempts by W. Beck et al.[6] to synthesize similar bis(tetrazolate) dianions by reaction of $NCCH_2CN$ with complexed metal azides. Neutral covalent azides cycloadd across both C≡N bonds of $(CN)_2$ to form neutral bis-tetrazoles at 105 °C and 10 kbar pressure.[30]

Kinetic and Thermodynamic Considerations. The azide anion and cyanogen react via a reverse electron demand [HOMO of N_3^- donates to the LUMO of $(CN)_2$] 3 + 2 cycloaddition. The HOMO−LUMO gap was calculated (RB3PW91/6-311+G*) to be −275.8 kJ/mol, indicating that the activation energy for the reaction is very low or zero and consistent with the observation that the reaction proceeds quickly at room temperature. The gas phase enthalpy of the reaction of $(CN)_2$(g) and N_3^-(g) was calculated at the same level to be −237.1 kJ/mol.[31] The molecular volume of Cs**1**(s) (unit cell volume/Z = 555.2/4 = 138.8 Å^3) was used to estimate its lattice enthalpy (556.6 kJ/mol) from the empirical relationship between the lattice enthalpy of an AB salt and the thermochemical volume of the salt[32] given in eq 2. For AB salts α = 2345 kJ/mol and β = 103.7 kJ/mol. The lattice enthalpy of CsN_3(s) was similarly determined to be 655.3 kJ/mol by summing the thermochemical volumes of Cs^+ (18.82 Å^3)[32] and N_3^- (58.0 Å^3).[32] The enthalpy of reaction of reaction 1 was determined to be −138.4 kJ/mol[33] (see the Born−Haber cycle in Figure 2a). Using the heats of formation of $(CN)_2$(g) (+306.7 kJ/mol)[34] and CsN_3(s) (−19.7 kJ/mol),[34] and the enthalpy of reaction calculated above, the heat of formation of Cs**1**(s) is estimated to be +148.6 kJ/mol.[35] Similarly, the lattice enthalpies of K**1**(s) (566.8 kJ/mol) and KN_3(s) (678.7 kJ/mol) were estimated using the thermochemical volume of K^+ (9.86 Å^3).[32] The enthalpy of formation of K**1**(s) from KN_3(s) and $(CN)_2$(g) and the heat of formation of K**1**(s) were then estimated to be −125.2 kJ/mol[36] and +225.4 kJ/mol,[37] respectively.

$$U_{\mathrm{pot.}} = (\alpha)(V^{-1/3}) + \beta \qquad (2)$$

The cycloaddition of N_3^- with the nitrile in **1** (see eq 3) is also reverse electron demand (the HOMO of N_3^- donates to the LUMO of **1**). The HOMO−LUMO gap is calculated (B3PW91/6-311+G*) to be +309.4 kJ/mol,[38] indicating a high activation energy which is increased by the electrostatic repulsion between N_3^- and **1**.[39] This is consistent with the

$$\mathrm{CsN_3 + Cs[NCCNNNN] \rightarrow Cs_2[NNNNCCNNNN]} \qquad (3)$$

Table 2. Crystal and Data Collection Parameters for Cs[NCCNNNN]

formula	CsC_2N_5
M (g/mol)	226.98
space group	*C*2/*c*
a (Å)	8.297(2)
b (Å)	11.040(3)
c (Å)	6.983(2)
β (deg)	120.31(2)
V (Å^3)	552.2(2)
d_c (g/cm^3)	2.730
Z	4
F(000)	408
cryst size (mm)	0.53 × 0.53 × 0.92
radiation	Mo Kα (λ = 0.71073)
temp (K)	293
index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-11 \le l \le 11$
scan type	$\theta-2\theta$
scan speed (deg/min)	variable; max speed 5.49
θ_{max} (deg)	69.94
no. of reflns collected	4306
no. of indep reflns	1217
abs correction	μ(Mo Kα) = 6.593 mm^{-1}
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0475^a wR2 = 0.120^b
GOF	1.094

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $(\sum[w(F_o^2 - F_c^2)^2/\sum[wF_o^4])^{1/2}$.

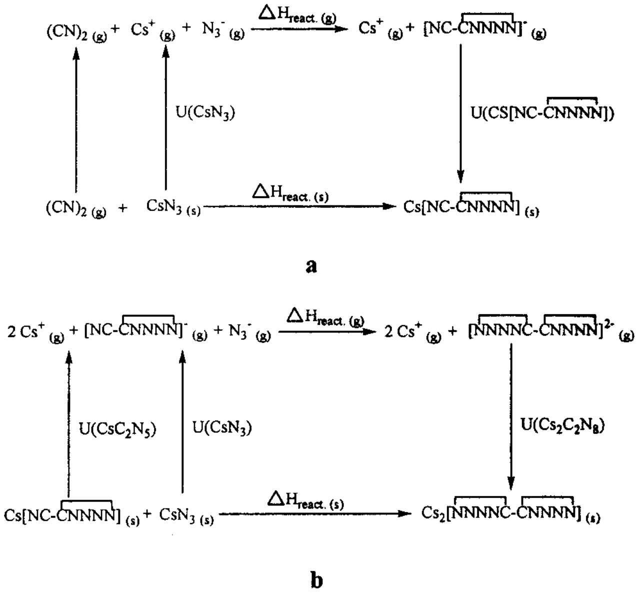

Figure 2. Born–Haber cycles for the reaction between (a) $(CN)_2$ and CsN_3 to form Cs**1** and (b) Cs**1** and CsN_3 to form Cs_2[NNNNC-CNNNN]. Lattice enthalpies (*U*) were estimated using the relation between thermochemical volumes and lattice enthalpy.[32] Enthalpies of formation were taken from the literature.[34]

observation that this cycloaddition did not proceed under the conditions we employed (60 °C in SO_2). The gas phase enthalpy of reaction for this reaction was calculated to be +167.6 kJ/mol,[40] but the lattice enthalpy of Cs_2[NNNNCCNNNN](s) (+1502.0 kJ/mol[41]) is larger than the sum of the lattice energies of CsN_3(s) (655.3 kJ/mol) and Cs**1**(s) (556.6 kJ/mol). An estimated enthalpy of reaction of −122.5 kJ/mol[42] for the reaction of CsN_3(s) and Cs**1**(s) is obtained using the Born–Haber cycle shown in Figure 2b, and the standard enthalpy of formation of Cs_2[NNNNCCNNNN](s) is estimated to be +6.4 kJ/mol.[43] This indicates that Cs_2[NNNNCCNNNN](s) may be preparable, but it may be unstable with respect to dissociation to 2 CsCN(s) and 3 N_2 (ΔH_{diss} = −221.4 kJ/mol[44]).

Vibrational Spectrum of Cs1. The symmetry of **1** in the gas phase and the solid state is C_{2v}, and 15 vibrations ($3n - 6$ where *n* is the number of atoms in the molecule, 6 A_1, 1 A_2, 5 B_1, 3 B_2)[45] are expected, all of which are both IR and Raman active. Of the 15 vibrations, 11 are observed in the FT-Raman spectrum (Figure 1b) and 13 in the FT-IR spectrum (Figure 1a). The peak positions are in good agreement with the spectrum calculated by ab initio methods (RB3PW91/6-311+G*), and the IR frequencies are similar to those reported for the anion in Na[CF_3CNNNN][28] (see Table 1). The four missing FT-Raman vibrations are calculated to be very weak in intensity, and the two missing IR vibrations occur below the cutoff of the spectrometer. Peaks at 649.9 and 439.0 cm^{-1} in the FT-IR which have corresponding peaks in the FT-Raman at 654.7 and 434.4 cm^{-1} could not be assigned. All other peaks which are not assigned either are attributed to the mulling agent (Nujol, see FT-IR, Figure 1a) or are very weak in intensity, less than the least intense peaks reported in Table 1.

X-ray Crystal Structure. The *C*2/*c* monoclinic unit cell contains eight halves of Cs$^+$ cations and [NCCNNNN]$^-$ anions so that *Z* = 4. All of these lie on 2-fold axes parallel to the unique *b*-axis which bisect the anions along the linear C−C≡N bonds (see Figure 3). The CNNNN ring of the anion is tilted 16.1° with respect to the *ab*-plane, and along the *c*-axis the anions are separated by *c*/2 (3.49 Å, see Figure 4). A thermal ellipsoid plot (ORTEP) of **1** including bond distances, corresponding Pauling bond orders,[46] and angles is given in Figure 5a, and the distances and angles compared with those of other CNNNN-containing molecules are given in Table 3. The distances and angles are not significantly different; thus the geometry of the ring is little affected by coordination to a metal center or substitution at a ring nitrogen. The calculated geometry of **1** (RB3PW91/6-311+G*) is similar to that for the ring in [HCNNNN]$^-$ obtained at the MP2/6-31G* level of theory[21] and

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(40) $\Delta H_{react(g)} = E(C_2N_8^{2-}) - [E(N_3^-) + E(C_2N_5^-)] = -514.07630 - [(-164.21458) + (-349.92556)] = +0.06384$ au = +167.6 kJ/mol.

(41) The volume of C_6H_5 is half the molecular volume of biphenyl (215.885 Å^3/2 = 107.943 Å^3).[66] The volume of a CN group is the molecular volume of benzonitrile less the volume of C_6H_5 (144.05 Å^3 − 107.943 Å^3 = 36.11 Å^3).[68] The volume of the [CNNNN]$^-$ ring in **1** is the molecular volume of **1** less the volume of CN (120.0 Å^3 − 36.11 Å^3 = 83.9 Å^3). The volume of [NNNNCCNNNN]$^{2-}$ is double the volume of [CNNNN]$^-$ (83.9 Å^3 × 2 = 167.8 Å^3). The volume of Cs_2[NNNNCCNNNN], obtained from twice the thermochemical volume of Cs plus the volume of [NNNNCCNNNN], is 205.4 Å^3 (2 × 18.82 Å^3 + 167.8 Å^3). Applying eq 2 (α = 9918 kJ/mol and β = −179.0 kJ/mol), we estimate a lattice energy of +1502.0 kJ/mol for Cs_2[NNNNCCNNNN].

(42) $\Delta H_{react(s)} = U(CsN_3) + U(CsC_2N_5) + \Delta H_{react(g)} - U(Cs_2C_4N_8) = 556.6 + 655.3 + 167.6 - 1502.0 = -122.5$ kJ/mol.

(43) $\Delta H_f°(Cs_2[NNNNCCNNNN]) = \Delta H_{react} + \Delta H_f°(Cs\mathbf{1}) + \Delta H_f°(CsN_3)^{34} = -122.5 + 148.6 - 19.7 = +6.4$ kJ/mol.

(44) $\Delta H_{diss} = 2\Delta H_f°(CsCN)^{34} + 3\Delta H_f°(N_2) - \Delta H_f°(Cs[NNNNCCNNNN]) = 2(-107.5) + 3(0) - (+6.4) = -221.4$ kJ/mol.

(45) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience (John Wiley & Sons): Toronto, 1986.

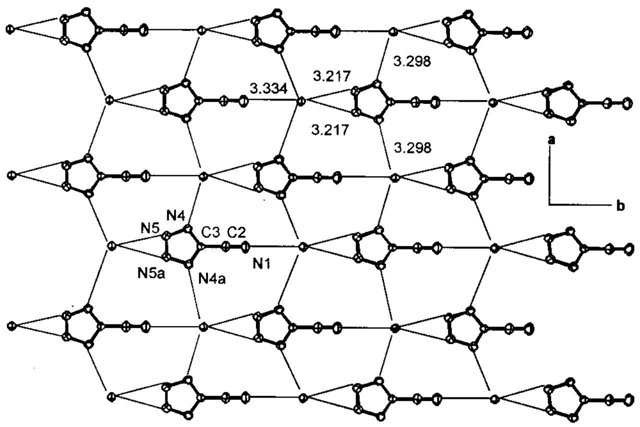

Figure 3. Interactions between cations and anions in Cs**1** giving sheets parallel to the *ab*-plane. ORTEP[64] thermal ellipsoids represent 25% probability surfaces.

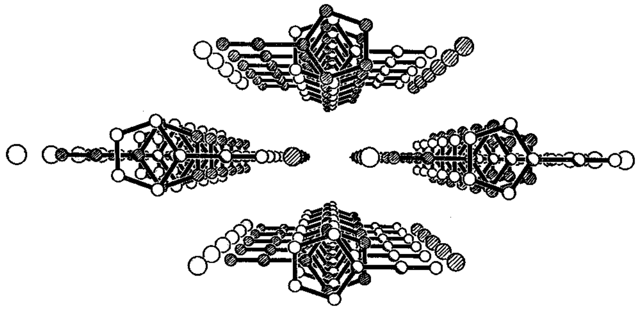

Figure 4. SHELXL[65] diagram showing the packing of Cs**1** with stacks of anions and channels of cations running parallel to the *c*-axis. Clear and shaded anions are in alternating sheets parallel to the *ab*-plane and are oriented in opposite directions parallel to the *b*-axis.

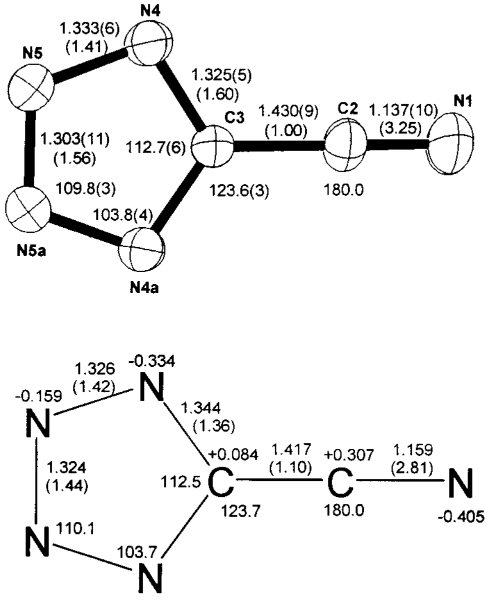

Figure 5. Structure of the $[\mathrm{NC\overline{CNNNN}}]^-$ anion in Cs**1** showing (a) diagram of the X-ray determined bond lengths and angles and Pauling bond orders (in parentheses) and (b) RB3PW91/6-311+G* calculated bond lengths and angles and Wiberg bond orders (in parentheses). ORTEP[64] thermal ellipsoids represent 25% probability surfaces.

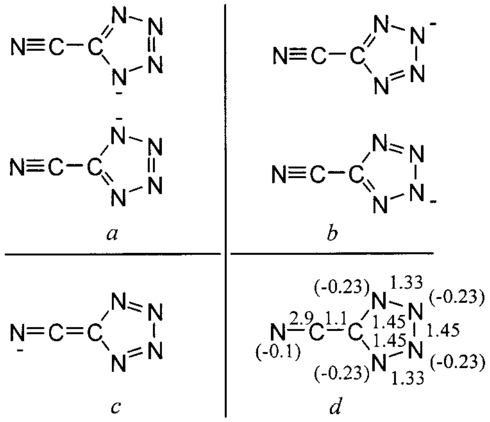

Figure 6. Five possible resonance structures of **1** leading to bond orders (overall charges) assuming 45% of *a*, 45% of *b*, and 10% of *c*, shown in *d*.

Table 3. Comparison of the Bond Distances and Angles of **1** with Those of $[(\mathrm{NC\overline{CNNNN}})\mathrm{Co(NH_3)_5}][\mathrm{ClO_4}]$ (**3**), $[(\mathrm{N_2H_3})_3\mathrm{C}][\mathrm{NH_2\overline{CNNNN}}]$ (**5**), and $\mathrm{NC\overline{CNN(C_6H_5)NN}}$ (**7**)[62]

	1	**3**	**6**	**8**
	Bonds (Å)			
N1−C2	1.137(10)	1.12(2)		1.135(8)
C2−C3	1.430(9)	1.48(2)		1.429(8)
C3−N4	1.325(5)	1.37(2)	1.331(3)	1.342(6)
C3−N4a	1.325(5)	1.37(2)	1.323(3)	1.316(6)
N4−N5	1.333(6)	1.30(2)	1.360(3)	1.323(6)
N4a−N5a	1.333(6)	1.37(2)	1.356(3)	1.318(5)
N5−N5a	1.303(11)	1.36(2)	1.299(3)	1.332(5)
	Angles (deg)			
N1−C2−C3	180.0	179.2(15)		179.2(7)
C2−C3−N4	123.6(3)	124.2(12)		122.4(4)
C2−C3−N4a	123.6(3)	120.2(13)		123.9(4)
N4−C3−N4a	112.7(6)	115.6(14)	113.3(3)	113.6(4)
C3−N4−N5	103.8(4)	102.8(12)	103.4(2)	105.2(3)
C3−N4a−N5a	103.8(4)	99.7(12)	103.8(2)	101.5(3)
N4−N5−N5a	109.8(3)	111.1(13)	109.8(2)	105.9(3)
N4a−N5a−N5	109.8(3)	110.8(12)	109.8(2)	113.6(3)

is given in Figure 5b with corresponding Wiberg bond orders obtained by an NBO (natural bond orbital) analysis at the RB3PW91/6-311+G* level of theory. The bond orders imply that the ring contains 7 bonds, 5 σ and 2 π, in agreement with the molecular orbital model (reflected in the optimized geometry and Wiberg bond orders). A simple valence bond description (see Figure 6) with two sets of equivalent valence bond structures *a* and *b* gives bond orders that are in good agreement with the Pauling bond orders (see Figure 5a). The Wiberg bond orders (see Figure 5b) could only be approximated (shown in *d*) by also including 10% contribution from valence bond structure *c*. Polarization of the carbon atoms by the adjacent more electronegative nitrogen atoms leads to a higher total charge on the nitrogen atoms adjacent to the carbon atoms than implied by the valence bond structures, consistent with the natural charges (NBO) but not the valency units (see Table 4). Each Cs^+ has contacts to 11 $\mathrm{N}^{\delta-}$ atoms in eight different $[\mathrm{NC\overline{CNNNN}}]^-$ anions (see Figure 7), a common coordination number for cesium salts.[47] All Coulombic interactions (listed

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(46) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1967; 239. Bond distances corresponding to bond order 1 were obtained by applying the Pauling equation $[D(n') = D_1 - 0.71 \log(n')$ where $D(n')$ = observed bond distance, D_1 = bond distance corresponding to bond order 1, n' = bond order] to molecules which contain the same bonds with the same hybridization. N≡C (sp−sp): from other nitriles, bond order 3, average bond distance 1.16 Å. C−C (sp−sp^2): 1.43 Å from Bent (Bent, H. A. *Chem. Rev.* **1961**, *61*, 283). C−N (sp^2−sp^2): from $(\mathrm{CNCl})_3$, bond order 1.5, bond distance 1.34 Å. N−N (sp^2−sp^2): from $\mathrm{CH_3{-}N{=}N{-}CH_3}$ and F−N=N−F, bond order 2, bond distance 1.23 Å.

Table 4. Observed $Cs^{+}\cdots N^{\delta-}$ Contacts and Calculated Valency Units in Cs[NC$\overline{\text{CNNNN}}$] Compared with Natural (NBO) Charges (RB3PW91/6-311+G*)

contact[a]	distance (Å)	valency units[b]	RB3PW91/6-311+G* calcd charge (NBO)
N1−Cs(#6)	3.602(2)	0.058	
N1−Cs(#7)	3.602(2)	0.058	
N1−Cs(#8)	3.334(8)	0.097	
sum of valency units to N1		0.213	−0.405 (C2 +0.307)
N4−Cs(#3) N4a-Cs(#2)	3.297(4)	0.104 (×2)	
N4−Cs(#4) N4a-Cs(#5)	3.298(4)	0.104 (×2)	
sum of valency units to N4/N4a		0.208 (×2)	−0.334 (×2) (C3 +0.084)
N5−Cs(#1) N5a-Cs(#1)	3.217(4)	0.122 (×2)	
N5−Cs(#3) N5a-Cs(#2)	3.338(5)	0.096 (×2)	
sum of valency units to N5/N5a		0.218 (×2)	−0.159 (×2)
sum of valency units to Cs/anion		1.065	−1.000 (anion)

[a] Locations of contacts are shown in Figure 6a,b. [b] Valency units were calculated using Brown's[63] 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. Brown's tables do not give R_0 or N for Cs−N contacts. For other nuclei, the values of R_0 for contacts to N and O differ by an average of 0.10 Å. R_0 for Cs−O is reported to be 2.24 Å, and therefore R_0 for Cs−N was set to $R_0 = 2.24 + 0.10 = 2.34$ Å. The value of N for Cs−O contacts is 6.6, and this value was used for the Cs−N contacts.

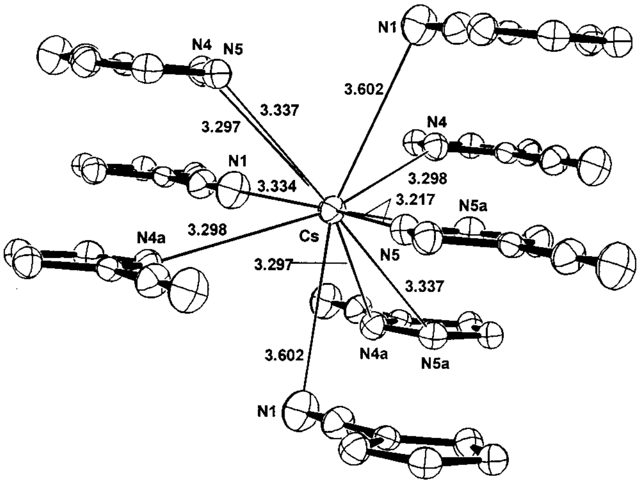

Figure 7. Coordination of the anions around Cs^{+} in the structure of Cs**1**. ORTEP[64] thermal ellipsoids represent 25% probability surfaces.

in Table 4) are greater than the sum of the ionic radii of Cs^{+} (1.88 Å[47]) and N^{3-} (1.32 Å[47]), indicating that the structure is essentially ionic. The sum of the valency units to Cs^{+} and **1** is 1.061, consistent with a single positive charge on the cation and a negative charge on the anion. Five of the 11 cation−anion contacts link the cations and anions into sheets parallel to the *ab*-plane (see Figure 3) with the C≡N group of the anions oriented parallel to the *b*-axis. The remaining six cation−anion contacts link adjacent sheets such that the anions form stacks parallel to the *c*-axis with the anions in adjacent sheets oriented 180° to one another (i.e., the C≡N group of the anions in adjacent sheets are pointed in opposite directions parallel to the *b*-axis, see Figure 4). There is net repulsion between the overall negatively charged anions; however, it may not be as much as expected by a model with the anion represented by a point negative charge at C3 as there is favorable electrostatic attraction between the partially positively charged carbon atoms and negatively charged N5 and N5a atoms (see Figure 4). The sum of the valency units between Cs^{+} and **1** in the sheets parallel to the *ab*-plane (0.549) are approximately the same as those between sheets (0.516), indicating that the structure of Cs**1** is best described as a three-dimensional array. Figure 8 shows the diamond-type lattice of the Cs^{+} ions. The hexagonal channels formed by the cations contain the anion stacks described above. The anions form an identical diamond-type lattice with the Cs^{+} ions occupying the hexagonal channels.

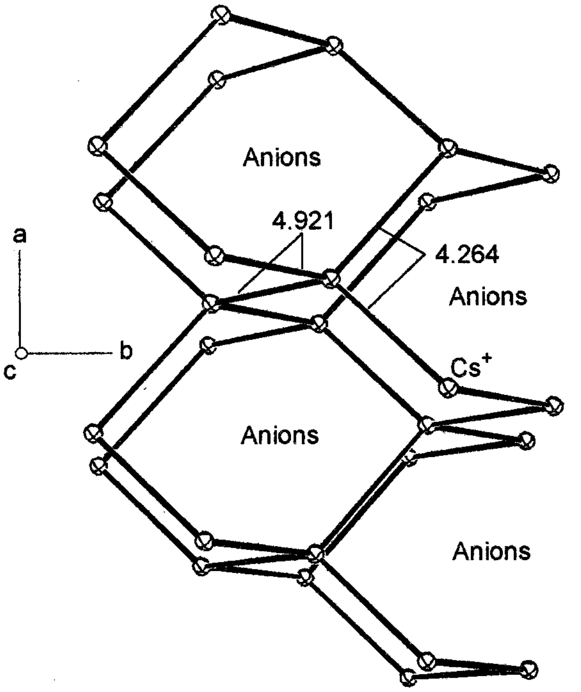

Figure 8. Diamond-type (tetrahedral) lattice formed by the cations in Cs**1**. The anions occupy the hexagonal channels formed by the cations. The lattice formed by the anions is identical with Cs^{+} ions filling the hexagonal channels. ORTEP[64] thermal ellipsoids represent 25% probability surfaces.

Chemistry of Cs[NC$\overline{\text{CNNNN}}$]. Removing one electron from or adding one to the 6π aromatic CNNNN ring in **1** could result in formation of new radical species. Therefore we investigated by theoretical methods (UB3PW91/6-311+G*) the oxidation of **1** to the 5π neutral and the reduction of **1** to the 7π dianion.

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(47) Huheey, J. H. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; pp 509−11.

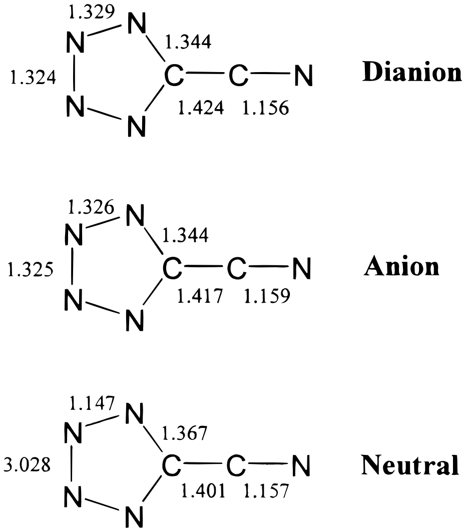

Figure 9. B3PW91/6-311+G* optimized geometries of $[\mathrm{NC\overline{CNNNN}}]^{\bullet}$, $[\mathrm{NC\overline{CNNNN}}]^{-}$, and $[\mathrm{NC\overline{CNNNN}}]^{\bullet 2-}$.

The ionization potential of **1** was calculated to be +450.7 kJ/mol. Optimization of the geometry of $[\mathrm{NC\overline{CNNNN}}]^{\bullet}$ (see Figure 9) and subsequent calculation of its vibrational spectrum resulted in a N5−N5a bond length of 3.028 Å and one imaginary frequency (i60.13 cm^{-1}), indicating that $[\mathrm{NC\overline{CNNNN}}]^{\bullet}$ is unstable, probably with respect to dissociation to $(\mathrm{CN})_2$ and N_2 (gas phase $\Delta H_{\mathrm{diss}} = -1118.6$ kJ/mol[48]). To the best of our knowledge, no evidence for an unsubstituted $\mathrm{R\overline{CNNNN}}$ radical has been presented; however, 2,3-disubstituted tetrazolinyl radicals have been prepared[49] and investigated. An attempt to

$$2[\mathrm{NC\overline{CNNNN}}] \rightarrow 2(\mathrm{CN})_2 + 3\mathrm{N}_2 \tag{4}$$

oxidize Cs**1** using AsF_5 gave an orange solid whose weight indicated uptake of all of the added AsF_5, slightly more than 2 equiv. The FT-Raman spectrum shows two separate sets of AsF_5 vibrations (735.9, 684.5, 385.2 and 724.6, 664.0, 374.1 cm^{-1}) indicative of the presence of two chemically different coordinated AsF_5 units. The FT-Raman spectrum also shows vibrations at 262.6 and 217.8 cm^{-1} which we tentatively assign to the two N−As stretching vibrations. Applying hard−soft acid−base (HSAB) theory[50] we estimate that coordination of the first AsF_5 unit to **1** is exothermic ($\Delta E = -159.0$ kJ/mol)[51] with 0.56 electron (ΔN)[51] transferred from basic **1** to acidic AsF_5. Coordination of the second AsF_5 unit will be somewhat less favorable. The highest occupied in plane nitrogen based σ type orbitals (nitrogen lone pairs) of **1** are the HOMO-2 (Figure 10a, N5/N5a), HOMO-3 (Figure 10b, N4/N4a), and HOMO-7 (Figure 10c, N1). A recent paper by Hoffmann[52] has shown that, for qualitative applications such as relative orbital energies and orbital shapes, Kohn−Sham (KS) orbitals obtained from density functional theory calculations (such as our B3PW91 calculations) compare very well with the more widely accepted Hartree−Fock (HF) orbitals. We are therefore confident that the orbitals listed above are representative of the nitrogen lone pairs, and we propose that the coordinated AsF_5 units likely reside on N5 and N4, with coordination to N5a sterically hindered by the AsF_5 attached to N5, as shown in **8**.

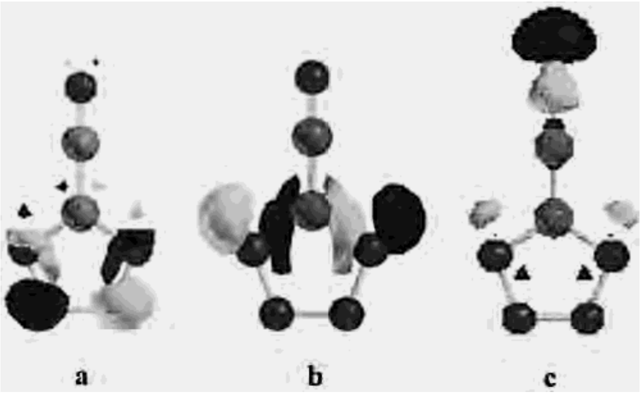

Figure 10. Chem3D Ultra[66] molecular orbital surface plots using an electron density isocontour limit of 0.100 au of (a) the HOMO-2, (b) HOMO-3, and (c) HOMO-7 molecular orbitals of $[\mathrm{NC\overline{CNNNN}}]^{-}$ obtained from the RB3PW91/6-311+G* calculation of **1**.

Optimization of the geometry of $[\mathrm{NC\overline{CNNNN}}]^{\bullet 2-}$ (see Figure 9) and subsequent calculation of the vibrational spectrum showed that there are only small changes in the bond distances and stretching frequencies upon addition of one electron to the π^* LUMO of **1**, and no imaginary frequencies were observed, consistent with the radical dianion being a stable species in the gas phase. 7π radicals are stable and of current interest.[53−57] The electron affinity of **1**(g) was calculated to be +427.4 kJ/mol, and the enthalpy of reduction of Cs**1**(s) to CsM**1**(s) (M = Cs, K) was calculated to be −297.4 kJ/mol[58a] with cesium and −290.3 kJ/mol[58b] with potassium. Our preliminary investigations of the reduction of Cs**1**(s) with potassium do not rule out formation of the dianion (experimental details are included with

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(48) $\Delta H_{\mathrm{diss}} = [2(E(\mathrm{C_2N_2})) + 3(E(\mathrm{N_2}))] - [2(E(\mathrm{C_2N_5}^{\bullet})] = [2(-185.62067) + 3(-109.51001)] - [2(-349.67261)] = -0.42615$ au $= -1118.6$ kJ/mol.

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(51) Calculated (RB3PW91/6-311+G*) adiabatic ionization potential and electron affinity of **1** are 450.7 kJ/mol (4.55 eV) and 427.4 kJ/mol (4.43 eV), respectively. χ_{B} (absolute electronegativity of the base) = 0.5(IP + EA) = 0.5(4.67 + 4.43) = 4.55 eV. η_{B} (absolute hardness of the base) = 0.5(IP − EA) = 0.5(4.67−4.43) = 0.12 eV. χ_{A} and η_{A} for AsF_5 have previously been determined[69] to be 10.44 and 5.14 eV, respectively. ΔN (number of electrons transferred from base to acid) $= (\chi_{\mathrm{A}} - \chi_{\mathrm{B}})/2(\eta_{\mathrm{A}} + \eta_{\mathrm{B}}) = (10.44-4.55)/2(5.14 + 0.12) = 0.56$ electrons. ΔE (energy gained on complexation) $= -0.25(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^2/(\eta_{\mathrm{A}} + \eta_{\mathrm{B}}) = -0.25(10.44-4.55)^2/(5.14 + 0.12) = -1.65$ eV $= -159.0$ kJ/mol.

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(58) The change in the volume of **1** upon addition of an electron was estimated to be negligible, and thus the volumes of $\mathrm{Cs_2[NC\overline{CNNNN}]}$ (157.6 Å^3) and $\mathrm{CsK[NC\overline{CNNNN}]}$ (148.7 Å^3) were calculated by adding the volume of Cs^+ (18.82 Å^3) or K^+ (9.86 Å^3) to the volume of Cs[**1**] (138.8 Å^3). The lattice enthalpies were calculated to be +1657.1 and +1693.2 kJ/mol by substituting the volumes into eq 2, where $\alpha = 9918$ kJ/mol and $\beta = -179.0$ kJ/mol. (a) $\Delta H_{\mathrm{red.}}$ with Cs = (IP)(Cs) + U(Cs**1**) + (EA)(**1**) − $U(\mathrm{Cs_2C_2N_5})$ = 375.7 + 556.6 + 427.4 − 1657.1 = −297.4 kJ/mol. **(**b) $\Delta H_{\mathrm{red.}}$ with K = (IP)(K) + U(Cs**1**) + (EA)(**1**) − $U(\mathrm{CsKC_2N_5})$ = 418.9 + 556.6 + 427.4 − 1693.2 = −290.3 kJ/mol.

the Supporting Information). We estimate that 2 Cs_2**1**(s) may be unstable with respect to dissociation to 4 CsCN(s) and 3 N_2(g) ($\Delta H_{\mathrm{diss}} = -132.4$ kJ/mol)[59] and that 2 CsK**1**(s) may be unstable with respect to dissociation to 2 CsCN(s), 2 KCN(s), and 3 N_2(g) ($\Delta H_{\mathrm{diss}} = -167.4$ kJ/mol).[60]

Preliminary investigations into the reaction of S_2N^+ or sulfur cations with Cs**1** indicate that the cations react via nucleophilic attack on the cations by the nitrogen atoms of **1** rather than by cycloaddition across the CN bond.[61] This is consistent with the high Lewis basicity of the N atoms of **1**, especially N5 and N5a.

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Supporting Information Available: Experimental details of the reduction of Cs**1** with potassium in liquid ammonia, a table listing anisotropic thermal parameters for Cs**1**, ^{13}C and ^{14}N NMR spectra of Cs**1**, FT-IR of K**1**, FT-Raman spectrum of CsN_3, FT-Raman spectrum of Cs**1**·$x$$AsF_5$ ($x \approx 2$), ROB3PW91/6-311+G* calculated frequencies of $[\mathrm{NC}\overline{\mathrm{CNNNN}}]^{\bullet}$, $[\mathrm{NC}\overline{\mathrm{CNNNN}}]^{-}$, and $[\mathrm{NC}\overline{\mathrm{CNNNN}}]^{\bullet 2-}$, and ORTEP diagram of the unit cell of Cs**1**, and ORTEP diagram of the Cs−N contacts from the anion to the cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(59) $\Delta H_{\mathrm{diss}} = 4(\Delta H_f°(\mathrm{CsCN})^{34}) + 3(\Delta H_f°(\mathrm{N_2})) - 2(\Delta H_f°(\mathrm{Cs_2}\mathbf{1})) = 4(-107.5) + 3(0) - 2(-148.8) = -132.4$ kJ/mol.

(60) $\Delta H_{\mathrm{diss}} = 2(\Delta H_f°(\mathrm{KCN})^{34}) + 2(\Delta H_f°(\mathrm{CsCN})^{34}) + 3(\Delta H_f°(\mathrm{N_2})) - 2(\Delta H_f°(\mathrm{CsK}\mathbf{1})) = 2(-117.9) + 2(-107.5) + 3(0) - 2(-141.7) = -167.4$ kJ/mol.

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