Synthesis and Thermal Decomposition Studies of New Nitroso- and Nitrodicyanomethanide Salts

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Received December 8, 1998

The lithium, barium, ammonium, and guanidinium salts of nitrosodicyanomethanide ($[ONC(CN)_2]^-$), and the lithium, sodium, barium, ammonium, guanidinium, and hydrazinium salts of nitrodicyanomethanide ($[O_2NC(CN)_2]^-$) are synthesized and characterized by infrared, UV−vis and ^{13}C NMR spectroscopy, and elemental analysis. Four of them, namely, $[NH_4][ONC(CN)_2]$, $Ba[ONC(CN)_2]_2(H_2O)$, $[NH_4][O_2NC(CN)_2]$, and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$, have also been characterized by single-crystal X-ray diffraction data. The structural data reveal that the two anions possess comparable structural features irrespective of the nature of the cation. The N−O bond distances in $[NH_4][ONC(CN)_2]$ and $Ba[ONC(CN)_2]_2(H_2O)$ are similar at 1.286(2) and 1.292(4) Å, respectively, and the anion possesses a nearly planar geometry. Nitrodicyanomethanide anions in the crystals of $[NH_4][O_2NC(CN)_2]$ and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ are also nearly planar with average N−O bond distances of 1.258(2) and 1.252(5) Å, respectively. In $Ba[ONC(CN)_2]_2(H_2O)$, the nitrosodicyanomethanide anion binds a single metal center through the nitrogen and oxygen atoms of the nitroso group while also binding two other metal centers through the cyano nitrogen atoms. In $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$, the nitrodicyanomethanide anion coordinates to the metal center only through the cyano nitrogen atoms. The thermal properties of the new compounds together with those of the known sodium, potassium, and silver salts of nitrosodicyanomethanide and the potassium and silver salts of nitrodicyanomethanide are examined by differential scanning calorimetry (DSC). The DSC data reveal that the two series of compounds undergo exothermic decomposition releasing 240−690 cal/g. The alkali metal, silver, and barium salts decompose at higher temperatures (>200 °C), whereas the nitrogenous cationic salts decompose at lower temperatures, indicating that the thermal behavior of the two anions can be significantly altered by choosing appropriate cations.

Introduction

A number of aliphatic and aromatic nitro compounds and nitrogen-rich compounds such as hydrazine and nitramines are used as explosives and propellants by virtue of their high energy content.[1−3] We and others[4−10] are interested in developing new materials with potential propellant applications, specifically aimed toward circumventing problems such as high-cost, explosion risk, and carcinogenic properties associated with some of the currently used propellants.

Salts of nitrosodicyanomethanide ($[ONC(CN)_2]^-$) and nitrodicyanomethanide ($[O_2NC(CN)_2]^-$) are attractive target molecules as propellants on the basis of their theoretically predicted similarity to nitrite and nitrate salts, respectively. Results of theoretical studies of the two anions suggest that these anions may be useful high-energy-dense materials.[11−14] A previous paper from this laboratory demonstrated significant similarity between nitrosodicyanomethanide and nitrite anions with respect to their electronic structure, electrochemical, and ligation properties.[15] Here we wish to report (1) a new high-yield synthetic procedure for silver nitrodicyanomethanide, (2) the synthesis and characterization of a number of new salts of the two anions, and (3) the thermal decomposition properties of the two series of compounds.

Experimental Section

Materials and Methods. All chemicals were obtained commercially and used without further purification. Infrared spectra were obtained as KBr disks with a Perkin-Elmer 1600 FTIR Spectrophotometer. UV−vis spectra were measured in acetonitrile solvent on a Hewlett-Packard 8453 UV−vis spectrophotometer. NMR spectra were recorded in D_2O containing sodium 2,2,2-trimethylsilylpropanecarboxylate (DSS, 0.5%, w/v) as reference at room temperature on a Bruker DRX 400K spectrometer. Thermograms were obtained using a TA Instruments DSC 2010 differential scanning calorimeter equipped with a cooling can for cooling measurements. Approximately 2 mg of the sample was placed in aluminum sample cups and crimped with a cover. The DSC runs were performed under a steady flow of argon gas and at the heating rate of 10 °C/min in the temperature range 25−600 °C. **Caution:** Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with due care.

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10.1021/ic9814064 CCC: $18.00

Syntheses. Silver, Sodium, and Potassium Salts of Nitrosodicyanomethanide. Silver nitrosodicyanomethanide was synthesized from malononitrile, sodium nitrite, and silver nitrate in acetic acid/sodium acetate buffer medium (ca. pH 3) by a literature procedure.[16] Two of the previously reported[17] alkali metal salts of nitrosodicyanomethanide, namely, the sodium and potassium salts, were synthesized by a modified known procedure as follows. An aqueous solution of the appropriate alkali nitrite (0.1 mol) was slowly added to malononitrile (6.5 g, 0.1 mol) dissolved in pH 2.75−3 acetic acid/alkali acetate buffer solution (100 mL) cooled in an ice bath at 0−5 °C. The resultant yellow solution was stirred for 30 min and filtered. The filtrate was reduced to ca. 20 mL under reduced pressure and allowed to stand at room-temperature overnight. The orange-yellow crystalline product formed was separated by filtration and dried in a vacuum oven at room temperature. Yield: sodium salt, 8.9 g (76%); potassium salt, 10.6 g (80%).

The lithium, ammonium, and guanidinium salts of nitrosodicyanomethanide were synthesized by the metathesis reaction of silver nitrosodicyanomethanide (0.404 g, 0.002 mol) with each of the chloride salts (0.002 mol) in aqueous media. For the synthesis of the barium salt, 0.5 equiv of barium chloride dihydrate (0.244 g, 0.001 mol) was used. The precipitated silver chloride was filtered off and the filtrate was stripped of solvent at reduced pressure. The residue was recrystallized from an acetonitrile:water (75:25) solvent mixture. The products were separated by filtration and dried in a vacuum oven at room temperature.

$Li[ONC(CN)_2]$. Yield: 0.180 g (90%). IR (KBr, cm^{-1}): 2226 (m), 2211 (s), 2177 (m), 1432 (m), 1402 (m), 1354 (s), 1318 (s), 1152 (m), 743 (s), 528 (s). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 301 (10 690), 416 (66), 472 (73). ^{13}C NMR: δ 118.29, 113.16, 112.29. Anal. Calcd for C_3N_3OLi: C, 35.68; N, 41.61. Observed: C, 35.27; N, 41.28.

$Ba[ONC(CN)_2]_2(H_2O)$. Yield: 0.305 g (89%). IR (KBr, cm^{-1}): 3601 (w), 3529 (m), 2239 (m), 2228 (s), 1624 (m), 1389 (m), 1375 (m), 1345 (s), 1263 (s), 1219 (s), 596 (m), 566 (m). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 298 (25 874), 401 (220), 472 (110). ^{13}C NMR: δ 118.33, 113.22, 112.17. Anal. Calcd for $C_6H_4N_6O_4Ba$: C, 20.98, H, 0.59; N, 24.46. Observed: C, 20.95, H, 0.53; N, 24.35.

$[NH_4][ONC(CN)_2]$. Yield: 0.152 g (68%). IR (KBr, cm^{-1}): 3220−3140 (m), 2230 (s), 2222 (m), 1686 (w), 1402 (s), 1325 (s), 1274 (s), 1232 (s), 1185 (m), 1079 (w), 1038 (w), 594 (m), 568 (w). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 301 (9630), 472 (66). ^{13}C NMR: δ 118.33, 113.21, 112.37. Anal. Calcd for $C_3H_4N_4O$: C, 32.15; H, 3.60; N, 49.98. Observed: C, 31.96; H, 3.69; N, 49.52.

$[C(NH_2)_3][ONC(CN)_2]$. Yield: 0.235 g (76%). IR (KBr disk, cm^{-1}): 3479 (s), 3403 (s), 3377 (s), 3178 (m), 3096 (m), 2224 (s), 1671 (m), 1654 (s), 1578 (w), 1560 (w), 1371 (m), 1347 (s), 1266 (s), 1226 (s), 574 (w), 551 (w), 520 (w). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 301 (11 366), 472 (86). ^{13}C NMR: δ 160.79, 118.34, 113.21, 112.36. Anal. Calcd for $C_4H_6N_6O$: C, 31.17; H, 3.92; N, 54.53. Observed: C, 31.09; H, 4.00; N, 54.54.

Salts of Nitrodicyanomethanide. Silver nitrodicyanomethanide was synthesized by the ammonium cerium(IV) nitrate oxidation of potassium nitrosodicyanomethanide as follows. To a solution of $K[ONC(CN)_2]$ (4.62 g, 0.035 mol) in acetic acid/potassium acetate buffer (pH 3, 20 mL) was added slowly a solution of $[NH_4]_2[Ce(NO_3)_6]$ (38.06 g, 0.07 mol) in water (50 mL) with stirring. The solution turned dark red immediately, but on continued stirring for 30 min, it turned yellow. An aqueous solution (20 mL) of silver nitrate (6.23 g, 0.035 mol) was added to the clear yellow solution and the precipitated yellow solid was filtered and washed successively with cold water (50 mL) and absolute ethanol (20 mL) to give 4.96 g of the product. On slow evaporation of the filtrate another crop of the product was obtained (1.9 g). The combined products were recrystallized from acetonitrile: water (50:50) mixture as light yellow crystals. Total yield after recrystallization: 6.5 g (85%). The IR and UV−vis spectral features of the product were identical to those reported in the literature.[18]

The known potassium salt was synthesized as described in the literature.[21] The lithium, sodium, barium, ammonium, hydrazinium, and guanidinium salts were also synthesized by a similar procedure to those described for the synthesis of nitrosodicyanomethanide salts above. In the synthesis of the barium salt, ca. 0.03 g of a byproduct crystallized out from the aqueous filtrate and was characterized as $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ by single-crystal X-ray crystallography.

$Li[O_2NC(CN)_2]$. Yield: 0.170 g (73%). IR (cm^{-1}): 2244 (s), 2238 (s), 1420 (s), 1383 (s), 1298 (s), 1173 (m), 745 (m), 538 (m). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 316 (11 556), 419 (100). ^{13}C NMR: δ 117.20, 82.60. Anal. Calcd for $C_3N_3O_2Li$: C, 30.80; N, 35.92. Observed: C, 30.35; N, 35.66.

$Na[O_2NC(CN)_2]$. Yield: 0.216 g (81%). IR (cm^{-1}): 2228 (s), 2220 (s), 1441−1298 (s), 1165 (s), 744 (s). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 316 (10 523), 418 (211). ^{13}C NMR: δ 117.21, 82.66. Anal. Calcd for $C_3N_3O_2Na$: C, 27.08; N, 31.58. Observed: C, 26.98; N, 31.39.

$Ba[O_2NC(CN)_2]_2$. Yield: 0.320 g (91%). IR (cm^{-1}): 2220 (s), 2211 (s), 1402 (s), 1363 (s), 1356 (s), 1343 (s), 1320 (s), 1294 (s), 1154 (m), 753 (m), 668 (w), 574 (w), 560 (w), 534 (m), 526 (w). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 314 (27 022), 418 (95). ^{13}C NMR: δ 117.23, 82.67. Anal. Calcd for $C_6N_6O_4Ba$: C, 20.16; N, 23.51. Observed: C, 20.34; N, 23.54.

$[NH_4][O_2NC(CN)_2]$. Yield: 0.212 g (83%). IR (cm^{-1}): 3256−3220 (m), 2226 (s), 2214 (s), 1482 (s), 1404−1320 (s), 1302 (s), 1150 (s), 749 (s), 573 (m), 532 (s), 524 (m). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 316 (11 413), 418 (95). ^{13}C NMR: δ 117.23, 82.64. Anal. Calcd for $C_3H_4N_4O_2$: C, 28.13; N, 43.74. Observed: C, 28.30; N, 43.87.

$[C(NH_2)_3][O_2NC(CN)_2]$. Yield: 0.298 g (88%). IR (cm^{-1}): 3470−3210 (m), 2218 (s), 1680−1652 (s), 1560 (m), 1408 (s), 1360 (s), 1296 (s), 1151 (s), 741 (m), 670 (w). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 316 (11 451), 418 (32). ^{13}C NMR: δ 117.19, 82.76. Anal. Calcd for $C_4H_6N_6O_2$: C, 25.18; H, 3.52; N, 48.94. Observed: C, 25.30; H, 3.56; N, 48.87.

$[N_2H_5][O_2NC(CN)_2]$. Yield: 0.210 g (73%). IR (cm^{-1}): 3245 (m), 3026 (m), 2219 (s), 1497 (m), 1406 (s), 1344 (s), 1294 (s), 1153 (m), 1104 (m), 1083 (m), 964 (m), 753 (m), 575 (w), 534 (m), 526 (w), 497 (w). UV−vis, in acetonitrile, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 316 (11 345), 418 (252). ^{13}C NMR: δ 117.35, 82.69. Anal. Calcd for $C_3H_5N_5O_2$: C, 25.18; H, 3.52; N, 48.94. Observed: C, 25.29; H, 3.56; N, 49.04.

Computational Details. The calculations described here were performed using *Gaussian94* implemented on a Silicon Graphics Iris Indigo workstation.[19] Full optimizations were performed initially at the restricted Hartree−Fock(HF) level using the polarized split valence 6-31G* basis sets before the final optimizations, which were performed by density functional theory using Becke's three-parameter functional[20] and triple split valence basis sets, 6-311+G*. It has recently been shown that related nitrogen oxide anions exhibit Hartree−Fock instability and that an effective method to model this is with Becke's three-parameter hybrid functionals.[21] The choice of basis set stems from the well-known difficulty in calculations of anions with limited basis sets. In general,

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Table 1. Crystallographic Data for $[NH_4][ONC(CN)_2]$, $Ba[ONC(CN)_2]_2(H_2O)$, $[NH_4][O_2NC(CN)_2]$, and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$

	$[NH_4][ONC(CN)_2]$	$Ba[ONC(CN)_2][H_2O)]$	$[NH_4][O_2NC(CN)_2]$	$Ba(O_2NC(CN)_2)(Cl)(H_2O)_2$
empirical formula	$C_3H_4N_4O$	$C_6H_2N_6O_3Ba$	$C_3H_4N_4O_2$	$C_3H_4N_3O_4BaCl$
fw	112.20	343.48	128.10	318.88
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	13.221(2)	7.3131(9)	4.9015(14)	5.9064(9)
b, Å	9.8372(12)	18.467(2)	7.7721(11)	6.3799(12)
c, Å	8.6207(10)	8.1396(8)	8.2622(14)	11.452(2)
α, deg	90	90	114.809(11)	96.791(12)
β, deg	97.298(10)	110.778(9)	90.56(2)	95.735(12)
γ, deg	90	90	99.950(14)	98.456(12)
V, Å^2	1112.1(2)	1027.8(2)	280.21(11)	420.83(13)
Z	8	4	2	2
reflctns collected	1311	2423	1274	1948
max/min transm	0.6372/0.5103	0.6650/0.5027	0.5933/0.5438	0.0772/0.0264
ρ_{calcd}, g cm^{-3}	1.339	2.220	1.518	2.517
μ, mm^{-1}	0.106	3.867	0.129	5.016
$R_1{}^a$ $[F > 4\sigma\|F\|]$	0.0301	0.0263	0.0335	0.0282
$wR_2{}^b$	0.0830	0.0632	0.0894	0.0706
S_{gof}	1.054	1.028	1.054	1.147
weighting scheme^c	$w^{-1} = \sigma^2F_o{}^2 + (0.0421P)^2 + 0.34P$	$w^{-1} = \sigma^2F_o{}^2 + (0.0287P)^2 + 0.78P$	$w^{-1} = \sigma^2F_o{}^2 + (0.0521P)^2 + 0.05P$	$w^{-1} = \sigma^2F_o{}^2 + (0.0475P)^2 + 0.38P$

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\}/\Sigma\{w(F_o{}^2)^2\}]^{1/2}$. ^{c} $P = (F_o{}^2 + 2F_c{}^2)/3$.

the best models for these systems include polarization functions on all heavy atoms and preferably on the hydrogen atoms as well.[22−24]

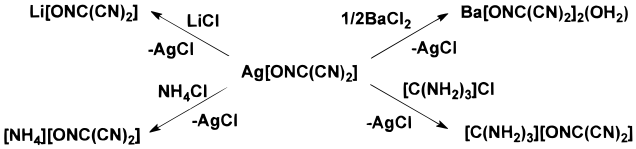
Crystallographic Structure Determination. X-ray diffraction data were collected for single crystals of compounds $[NH_4][ONC(CN)_2]$, $Ba[ONC(CN)_2]_2(H_2O)$, $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$, and $[NH_4][O_2NC(CN)_2]$ on a Siemens P4 Diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\,26$ Å; $\lambda(K\alpha_2) = 0.713\,54$ Å] and a graphite monochromator at 25 °C. In each case the diffraction data was measured using ω scans. The intensities of three standard reflections monitored every 100 reflections during the respective data collections indicated negligible crystal decomposition. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using structure solution programs from the SHELXTL system.[25] Important crystallographic parameters are collected in Table 1.

$[NH_4][ONC(CN)_2]$. Data were collected for a light yellow plate with dimensions 0.16 × 0.40 × 0.72 mm. The compound crystallizes in the monoclinic space group $C2/c$ with eight pairs of the cations and anions in the unit cell. A total of 985 ($R_{int} = 0.0176$) observed independent reflections [$F > 4\sigma|F|$] were collected in the 2θ range 5.18°−76.36°, with the data gathered having $-15 \leq h \leq 1$, $-1 \leq k \leq 11$, $-10 \leq l \leq 10$. The data were corrected for absorption and Lorentz polarization effects. All hydrogen atoms were located in successive Fourier maps and refined isotropically, whereas the non-hydrogen atoms were refined anisotropically.

$Ba[ONC(CN)_2]_2(H_2O)$. Data were collected for a yellow block of dimensions 0.12 × 0.40 × 0.40 mm. The compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. A total of 1820 ($R_{int} = 0.0293$) observed independent reflections [$F > 4\sigma|F|$] were collected in the 2θ range 4.42°−50°, with the data gathered having $-1 \leq h \leq 8$, $-1 \leq k \leq 21$, $-9 \leq l \leq 9$. The data were corrected for absorption and Lorentz polarization effects. The hydrogen atoms of the coordinated water molecule could not be located in the Fourier maps, and were not included in the structure solution. All non-hydrogen atoms were refined anisotropically.

$[NH_4][O_2NC(CN)_2]$. Data were collected for a yellow block with dimensions 0.18 × 0.30 × 0.42 mm. The compound crystallizes in the triclinic space group $P\bar{1}$ with two pairs of the cations and anions in the unit cell. A total of 963 ($R_{int} = 0.0149$) observed independent reflections [$F > 4\sigma|F|$] were collected in the 2θ range 5.46°−50°, with the data gathered having $-1 \leq h \leq 5$, $-8 \leq k \leq 8$, $-9 \leq l \leq 9$. The data were not corrected for absorption. All hydrogen atoms were located in successive Fourier maps and refined isotropically, whereas the non-hydrogen atoms were refined anisotropically.

Scheme 1



$Ba[O_2NC(CN)_2](Cl)(H_2O)_2$. Data were collected for a yellow block of dimensions 0.18 × 0.30 × 0.42 mm. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. A total of 1476 ($R_{int} = 0.0245$) observed independent reflections [$F > 4\sigma|F|$] were collected in the 2θ range 5.46°−50°, with the data gathered having $-6 \leq h \leq 1$, $-7 \leq k \leq 7$, $-13 \leq l \leq 13$. The data were corrected for absorption and Lorentz polarization effects. All hydrogen atoms were located in successive Fourier maps and refined isotropically, whereas the non-hydrogen atoms were refined anisotropically.

Results and Discussion

Syntheses. The previously reported syntheses for the sodium, potassium, cesium, and rubidium salts of nitrosodicyanomethanide involve the metathesis reactions of the silver salt with alkali metal chlorides.[17] As described in the Experimental Section we have observed that the sodium and potassium salts can be directly obtained from the reaction of the alkali nitrites and malononitrile in acetic acid/alkali acetate buffer at pH ca. 3. The new lithium, ammonium, guanidinium, and barium salts were synthesized by the metathesis of the silver salt with appropriate halides in aqueous media (Scheme 1).

Although a method is available for the synthesis of silver nitrodicyanomethanide, the method involving potassium permanganate oxidation yields less than 50% product.[18] Therefore, a new high yield method is developed for the synthesis. Potassium nitrosodicyanomethanide is oxidized by 2 equiv of ammonium cerium(IV)nitrate in acetic acid/sodium acetate buffer at pH ca. 3. The nitrodicyanomethanide anion formed is then precipitated as the silver salt in ca. 85% yield. The new lithium, sodium, barium, ammonium, hydrazinium, and guanidinium together with the previously described potassium salts were synthesized by metathesis reactions as shown in Scheme 2.

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Scheme 2

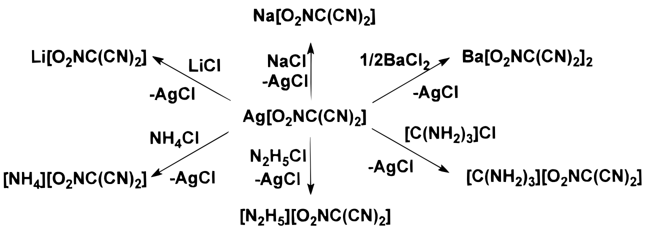

Table 2. Bond Distances (Å) and Angles (deg) for $[NH_4][ONC(CN)_2]$

N(1)−O(1)	1.286(2)	N(1)−C(1)	1.314(2)
C(1)−C(2)	1.418(2)	C(1)−C(3)	1.424(2)
C(2)−N(2)	1.142(2)	C(3)−N(3)	1.139(2)
O(1)−N(1)−C(1)	116.39(13)	N(1)−C(1)−C(2)	121.71(13)
N(1)−C(1)−C(3)	117.85(13)	C(2)−C(1)−C(3)	120.44(13)
N(2)−C(2)−C(1)	176.9(2)	N(3)−C(3)−C(1)	179.5(2)

During an attempted synthesis of the hydrazinium salt of nitrosodicyanomethanide, a novel condensation product, namely, 3,5-diaminopyrazolone oxime, was obtained. The cyano groups in nitrosodicyanomethanide also underwent condensation reactions with hydroxylamine, the details of which will be described elsewhere.

IR and UV−Vis Spectra. The IR spectra of the new compounds, namely, the lithium, barium, ammonium, and guanidinium salts of nitrosodicyanomethanide, and the lithium, sodium, barium, ammonium, hydrazinium, and guanidinium salts of nitrodicyanomethanide exhibit similar features as those of the known silver and potassium salts of both anions. The spectra of the nitrosodicyanomethanide salts exhibit cyanide stretching absorption bands in the 2239−2211 cm^{-1} region and three broad absorption bands associated with the coupling of the ν(NO) and ν(CC) modes in the 1375−1219 cm^{-1}, consistent with those of other compounds reported in the literature.[15] The IR spectra of the nitrodicyanomethanide salts exhibit cyanide stretching absorption bands in the 2244−2211 cm^{-1} region and several closely spaced peaks in the 1400−1200 cm^{-1} region.[26]

The electronic spectra of the new nitrosodicyanomethanide salts also exhibit characteristic $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ electronic transitions at ca. 301 and 476 nm, respectively, similar to the spectrum of the previously described tetramethylammonium nitrosodicyanomethanide in acetonitrile.[15] The UV−vis spectra of the lithium and barium salts exhibit an additional absorption at 401 nm, which can be attributed to the solvatochromic effect of water.[15,17,18] The spectra of the nitrodicyanomethanide salts exhibit the $\pi \rightarrow \pi^*$ transition red shifted to 316 nm and the n $\rightarrow \pi^*$ transition blue shifted to ca. 418 nm. As will be discussed below, the C−N$_{\text{nitroso}}$ bond distance in the nitrodicyanomethanide anion is significantly longer than the C−N$_{\text{nitro}}$ bond distance in the nitrosodicyanomethanide anion.

Structural Data. Four of the compounds, namely, $[NH_4][ONC(CN)_2]$, $Ba[ONC(CN)_2]_2(H_2O)$, $[NH_4][O_2NC(CN)_2]$, and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ have been characterized by three-dimensional X-ray diffraction data. Selected bond distances and angles are listed in Tables 2−5.

Structure of $[NH_4][ONC(CN)_2]$. The crystal contains tightly packed ammonium and nitrosodicyanomethanide ions. A view of the anion is shown in Figure 1. Two of the ammonium ion hydrogen atoms are hydrogen bonded to the oxygen atoms of two neighboring anions with the associated N···O distances of 2.830 and 2.916 Å leading to an infinite chain structure. All atoms of the anion are nearly planar with the nitroso nitrogen atom (N(1)) deviating from the plane by 0.015 Å. A similar pattern has also been observed in the structures of $K[ONC(CN)_2]$ and $Ag[ONC(CN)_2]$.[27,28] The corresponding N−O and C−N bond distances are 1.246(4) and 1.334(5) Å, respectively, in the potassium salt, and 1.18(2) and 1.44(2) Å, respectively, in the silver salt. The anion in the latter salts also exhibit planarity.[27,28]

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ba[ONC(CN)_2]_2(H_2O)$

N(1)−O(1)	1.286(4)	N(4)−O(2)	1.298(4)
C(1)−N(1)	1.313(5)	C(4)−N(4)	1.313(5)
C(1)−C(2)	1.433(6)	C(4)−C(5)	1.433(5)
C(1)−C(3)	1.420(6)	C(4)−C(6)	1.439(6)
C(2)−N(2)	1.144(5)	C(5)−N(5)	1.135(5)
C(3)−N(3)	1.140(6)	C(6)−N(6)	1.130(6)
O(1)−N(1)−C(1)	117.4(3)	O(2)−N(4)−C(4)	117.3(3)
N(1)−C(1)−C(3)	118.8(4)	N(4)−C(4)−C(5)	123.8(4)
N(1)−C(1)−C(2)	122.0(4)	N(4)−C(4)−C(6)	117.4(4)
C(3)−C(1)−C(2)	119.2(4)	C(5)−C(4)−C(6)	118.7(4)
N(2)−C(2)−C(1)	177.4(5)	N(5)−C(5)−C(4)	176.1(5)
N(3)−C(3)−C(1)	177.7(5)	N(6)−C(6)−C(4)	178.2(5)

Table 4. Bond Distances (Å) and Angles (deg) for $[NH_4][O_2NC(CN)_2]$

N(1)−O(1)	1.261(2)	N(1)−O(2)	1.252(2)
N(1)−C(1)	1.363(2)	C(1)−C(2)	1.406(2)
C(1)−C(3)	1.406(2)	C(2)−N(2)	1.142(2)
C(3)−N(3)	1.143(2)		
O(2)−N(1)−O(1)	120.77(11)	O(2)−N(1)−C(1)	120.15(12)
O(1)−N(1)−C(1)	119.09(12)	N(1)−C(1)−C(2)	118.67(12)
N(1)−C(1)−C(3)	117.84(12)	C(2)−C(1)−C(3)	123.26(13)
N(2)−C(2)−C(1)	179.3(2)	N(3)−C(3)−C(1)	179.1(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$

O(1)−N(1)	1.261(5)	O(2)−N(1)	1.234(5)
N(1)−C(1)	1.376(5)	C(1)−C(3)	1.401(6)
C(1)−C(2)	1.410(6)	C(2)−N(2)	1.133(6)
C(3)−N(3)	1.151(6)		
O(2)−N(1)−O(1)	121.3(3)	O(2)−N(1)−C(1)	120.2(4)
O(1)−N(1)−C(1)	118.5(3)	N(1)−C(1)−C(3)	119.3(4)
N(1)−C(1)−C(2)	117.6(3)	C(3)−C(1)−C(2)	122.8(4)
N(2)−C(2)−C(1)	178.4(4)	N(3)−C(3)−C(1)	178.4(4)

Structure of $Ba[ONC(CN)_2]_2(H_2O)$. The structure consists of an infinite three-dimensional network of repeating $Ba[ONC(CN)_2]_2(H_2O)$ units. The crystallographic asymmetric unit contains a barium atom coordinated to a water molecule and two nitrosodicyanomethanide anions. Although, the asymmetric unit contains two anions, the coordination mode and all other structural features of the two are comparable. Each of the anions is bonded to four different barium centers, leading to a three-dimensional network arrangement. Specifically, the oxygen and nitrogen atoms of the nitroso group of the anion are bonded to a single barium center, while the two cyano nitrogen atoms are bonded to two different barium centers; the nitroso oxygen atom is also bonded to yet another barium center. The bonding interaction of the anion with two neighboring barium centers leads to the three-dimensional network arrangement of the ions. As shown in Figure 2, each barium center is surrounded by four nitroso oxygens, one water oxygen, four cyano nitrogens, and two nitroso nitrogens. The Ba−O bond distances are in the

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(26) Kolbe, A.; Köhler, H. *Z. Anorg. Allg. Chem.* **1970**, *373*, 230.

(27) Chow, Y. M.; Britton, D. *Acta Crystallogr.* **1974**, *B30*, 1117.

(28) Skopenko, V. V.; Zub, Yu. L.; Porai-Koshits, M. A.; Sadikov, G. G. *Ukr. Khim. Zh. (Russ. Ed.)* **1979**, *45*, 811; *Chem. Abstr.* **1979**, *91*, 202606s.

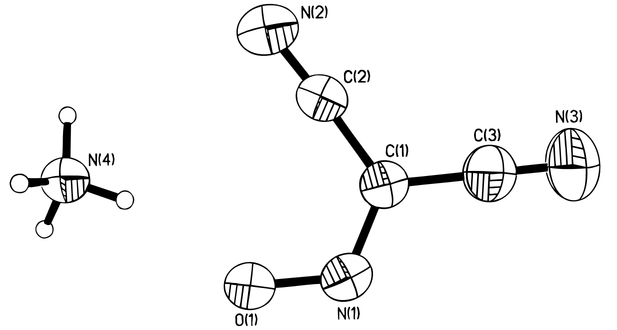

Figure 1. View of $[ONC(CN)_2]^-$ anion and ammonium cation in the crystals of $[NH_4[ONC(CN)_2]$. In this and the following structures, 50% thermal ellipsoids of the atoms are shown.

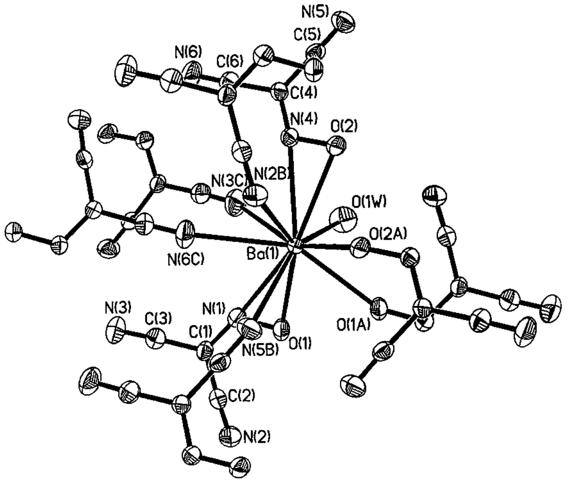

Figure 2. View of barium coordination environment in $Ba[ONC(CN)_2]_2(H_2O)$. Symmetrically generated atoms except those coordinated to Ba(1) are not labeled.

range 2.810(3)−2.874(3) Å and the Ba−N bond distances are in the range 2.900(3)−3.146(5) Å. Both anions are planar with the nitroso nitrogen atoms (N(1), N(4)) deviating from the least-squares planes passing through all atoms of each of the anions by 0.015 and 0.033 Å, respectively. Once again, in the two anions, the N−O bond distances (1.286(3) and 1.298(4) Å) are significantly smaller than the C−N bond distances (both at 1.313(5) Å) associated with the nitroso nitrogen atom and methanide carbon atom. The observation is consistent with the trend observed in the corresponding silver,[27] potassium,[28] and ammonium salts.

Structure of $[NH_4][O_2NC(CN)_2]$. The crystal contains well-separated ammonium and nitrodicyanomethanide ions. A view of the ions is shown in Figure 3. The anion in this structure is also planar with one of the oxygen atoms (O(1)) deviating from the least-squares plane formed by all atoms of the anion by 0.062 Å. A similar pattern in the N−O and C−N bond distances and planarity of the anion are also reported for silver nitrodicyanomethanide.[29] In the latter structure, however, the nitrodicyanomethanide anion coordinates to the silver ion through the two cyano nitrogen atoms and the two oxygen atoms, and the nitrogen−silver coordination is stronger in comparison to the oxygen−silver coordination. There is no hydrogen-bonding interaction between the ammonium and nitrosodicyanomethanide species.

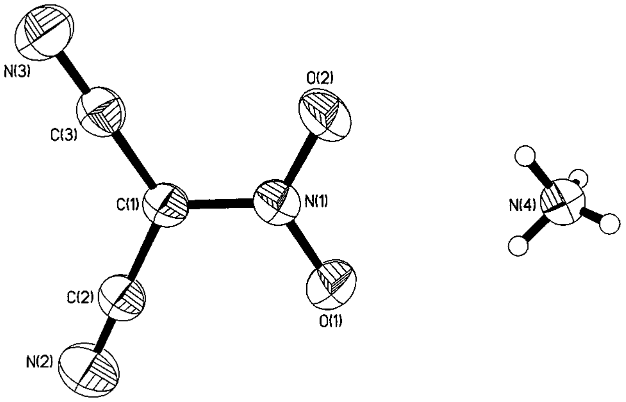

Figure 3. View of the $[O_2NC(CN)_2]^-$ anion and ammonium cation in the crystals of $[NH_4][ONC(CN)_2]$.

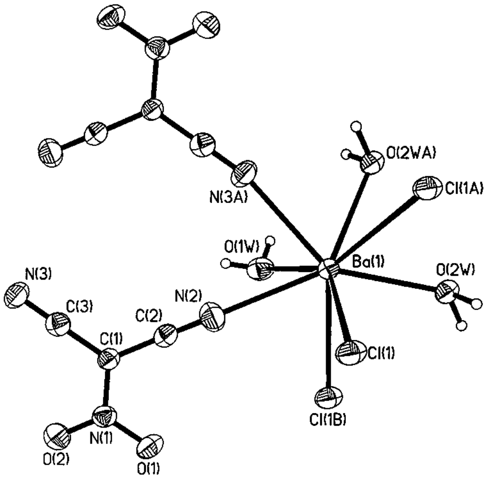

Figure 4. View of the barium coordination environment in $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$. Symmetrically generated atoms except those coordinated to Ba(1) are not labeled.

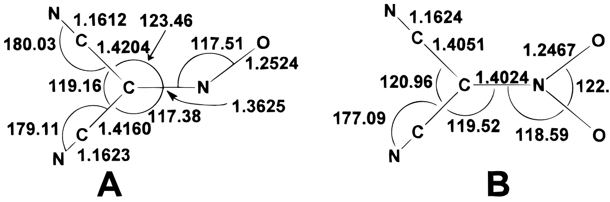

Figure 5. Ground-state structures for nitrosodicyanomethanide (A) and nitrodicyanomethanide (B) calculated with density functional theory, B3LYP/6-311+G*. Both are rigorously planar; A has C_s symmetry and B has C_{2v} symmetry. Bond lengths reported in Å, while angles listed in degrees.

Structure of $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$. The structure consists of octacoordinated barium atoms. The barium coordination sphere consists of two symmetrically related pairs of nitrodicyanomethanide ligands and water molecules, three symmetrically related chloride ligands, and another water molecule, as shown in Figure 4. Therefore, the crystallographic asymmetric center contains one barium atom, one nitrodicyanomethanide ligand, one chloride ligand, and two water molecules. Both cyano nitrogen atoms of nitrodicyanomethanide are coordinated to two barium centers with the associated Ba−N bond distances of 2.839(4) and 2.907(4) Å. One of the two water molecules in the asymmetric unit is coordinated to two barium centers with Ba−O bond distances of 2.777(3) and 2.886(3) Å. The other water molecule is coordinated to a barium center with the Ba−O bond distance of 2.915(3) Å. The chloride atom is coordinated to three neighboring barium centers with Ba−Cl bond distances of 3.174(1), 3.272(1), and 3.179(1) Å.

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(29) Chow, Y. M.; Britton, D. *Acta Crystallogr.* **1974**, *B30*, 147.

Table 6. Crystallographic, Vibrational Spectroscopic (cm^{-1}), and Theoretical Data for Nitroso- and Nitrodicyanomethanide Salts

compound	r(O−N), Å	r(N−C), Å	ν(C≡N)	ν_a, ν_s(ONC)	ν_a, ν_s(ONO)	ν(NC)	refs
$[K][ONC(CN)_2]$	1.287(1)	1.324(2)	2229, 2218	1325, 1275	−	−	14, this work
$[Ag][ONC(CN)_2]$	1.18	1.44	2246, 2232	1322, 1270	−	−	15
$[NH_4][ONC(CN)_2]$	1.286(2)	1.314(2)	2230, 2222	1325, 1274	−	−	this work
$Ba(ONC(CN)_2)_2(H_2O)$	1.292(2)[a]	1.313(5)[a]	2239, 2228	1345, 1263	−	−	this work
$[Ag][O_2NC(CN)_2]$	1.252(6)[a]	1.373(6)[a]	2222, 2212	−	1408, 1341	1300	11, 16
$[NH_4][O_2NC(CN)_2]$	1.256(2)[a]	1.363(2)	2226, 2214	−	1404, 1352	1302	this work
			Theoretical Data				
$[ONC(CN)_2]^-$	1.2524	1.3625	2286, 2263	1402, 1347	−	−	this work
$[O_2NC(CN)_2]^-$	1.2467	1.4024	2288, 2264	−	1469, 1347	1304	this work

[a] Average distance.

As in the former structure, the nitrodicyanomethanide anion is nearly planar with O(2), deviating from the mean least-squares plane passing through all atoms in the anion by 0.070 Å. The N−O and N−C bond distances and associated bond angles (Table 5) are also comparable to the corresponding bond distances in the ammonium and silver salts.[29] However, unlike in the structure of the silver salt,[29] the anion coordinates to the metal center only through the two cyano nitrogen atoms in the present structure.

Theoretical Results. Structural data obtained for nitroso- and nitrodicyanomethanide salts reveal significantly smaller C−C distances and larger $C-N_{nitroso}$ or $C-N_{nitro}$ distances, suggesting that unique bonding features are present in the anions. Therefore, to understand the nature of bonding, we have performed calculations based on density functional theory (B3LYP/6-311+G*). Structures for the optimized ground-state geometries for the two anions together with calculated bond distances and angles are shown in Figure 5. Both ground states are planar with the nitrosodicyanomethanide having C_s symmetry and the nitrodicyanomethanide C_{2v} symmetry. Postoptimization frequency calculations for both conformations confirm that these stationary points correspond to local minima. Important experimental and theoretical metric and vibrational data for both nitroso- and nitrodicyanomethanide anions and salts are collected in Table 6. Figure S2 depicts the vibrational modes for the nitrodicyanomethanide anion and lists their frequencies and shifts upon isotopic substitution with ^{15}N into the nitro group.

Differential Scanning Calorimetry. The thermal decomposition properties of the new nitrosodicyanomethanide and nitrodicyanomethanide salts and those of the known alkali metal, barium, and silver salts were studied by differential scanning calorimetry. The results are collected in Table 7, and thermograms of $Li[ONC(CN)_2]$ and $[NH_4][O_2NC(CN)_2]$ are shown in Figure S1. Both series of compounds undergo exothermic decomposition in the wide temperature range, 102−390 °C. The thermograms of sodium, potassium, barium, ammonium, and guanidinium salts of nitrosodicyanomethanide, and sodium, potassium, ammonium, guanidinium and hydrazinium salts of nitrodicyanomethanide also exhibit an endothermic process prior to the exothermic decomposition temperatures corresponding to the melting of the solids. A comparison of the decomposition behavior of the salts reveals that the alkali metal, barium, and silver salts decompose in a narrow temperature region, whereas the nitrogenous cationic salts decompose in a wide temperature region. Compounds $Li[ONC(CN)_2]$, $Ag[ONC(CN)_2]$, and $Ba[ONC(CN)_2]_2(H_2O)$ have also been found to shatter the sample cups when the experiments were run with more than 3 mg quantities at scan rates >10 °C/min. The nitrogenous cationic salts undergo stepwise decomposition, with the first decomposition occurring at a much lower temperature (Table 7), suggesting that the nitrogenous cations decrease the thermal stability of both nitroso- and nitrodicyanomethanide anions. The hydrazinium salt of nitrodicyanomethanide releases the highest molar heat of combustion, whereas the ammonium and guanidinium salts of both anions release considerably lower calories of molar heat of combustion.

Table 7. Differential Scanning Calorimetric Data for the Compounds

compound	T_{onset}, °C	T_{range}, °C	ΔH [c]	
			cal/g	kcal/mol
$Li[ONC(CN)_2]$	307.14	307−334	−651.3	−65.78
$Na[ONC(CN)_2]$[a]	310.00	310−358	−554.9	−64.95
$K[ONC(CN)_2]$[a]	308.57	308−362	−486.1	−64.72
$Ba[ONC(CN)_2)_2(H_2O)$[a]	263.67	263−354	−307.1	−105.50
$Ag[ONC(CN)_2]$	218.00	218−239	−242.9	−49.10
$[NH_4][ONC(CN)_2]$[a]	126.62	127−205	−187.8	−55.30
	284.18	284−398	−305.9	
$[C(NH_2)_3][ONC(CN)_2]$[a]	180.00	180−246	−278.4	−53.76
	312.28	312−365	−70.4	
$Li[O_2NC(CN)_2]$	339.98	339−390	−689.8	−80.7
$Na[O_2NC(CN)_2]$[a]	381.90	382−402	−641.6	−85.4
$K[O_2NC(CN)_2]$[a]	390.00	375−410	−532.8	−79.5
$Ba[O_2NC(CN)_2]_2$	360.65	360−387	−340.0	−121.5
$Ag[O_2NC(CN)_2]$	255.61	256−360	−282.4	−61.5
$[NH_4][O_2NC(CN)_2]$[a]	229.03	229−312	−328.4	−42.1
$[C(NH_2)_3][O_2NC(CN)_2]$[a]	187.00	187−315	−190.0	−45.9
	340.00	340−412	−80.0	
$[N_2H_5][O_2NC(CN)_2]$[a,b]	102.00	102−160	−295.0	−95.5
	272.00	272−325	−160.2	
	332.86	333−368	−212.4	

[a] A sharp endothermic peak corresponding to the melting of the solids is observed prior to the exothermic peak(s). [b] An endothermic peak is observed after the first exotherm. [c] Error on ΔH is 0.2 cal/g or 0.02 kcal/mol.

The increased thermal stability and higher heats of combustion observed for the lithium and sodium salts of the two anions can be attributed to the low atomic weight of the two cations and its consequent close packing of the ions in the solid state. The observed trend of decreased thermal stability and lower heats of combustion for the ammonium and guanidinium salts parallels the influence of amino and other basic-group substituents on the thermal behavior of nitroaromatic compounds.[30] The significantly higher heat of combustion observed for hydrazinium nitrodicyanomethanide can be attributed to the well-known exothermic decomposition properties of hydrazine.

Conclusions

Structural data obtained for $[NH_4][ONC(CN)_2]$, $Ba[ONC(CN)_2]_2(H_2O)$, $[NH_4][O_2NC(CN)_2]$, and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ in this work together those available in the literature for $Ag[ONC(CN)_2]$, $K[ONC(CN)_2]$, and $Ag[O_2NC(CN)_2]$ reveal that in both anions the bond distances between the nitroso or nitro nitrogen atom and the dicyanomethanide carbon atom are

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(30) Kamlet, M. J.; Adolf, H. G. *Propellents Explosives Pyrotech.* **1979**, *4*, 30.

larger than the typical C−N double bond distance and the C−C bond distances are considerably smaller than the typical C−C single bond. These bond distances together with the observed planarity of both anions indicate the presence of delocalization of a double bond over the whole anionic species, and these results correlate with predictions from ab initio quantum mechanical calculations. In $Ba[ONC(CN)_2]_2(H_2O)$, the observed coordination of the anion to the metal center through the oxygen and all nitrogen atoms indicates that the negative charge is not localized on the nitroso group, but rather, it is delocalized over the whole anion. The observed coordination of nitrodicyanomethanide anion exclusively through the cyano nitrogen atoms in $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ also suggests that the negative charge is not localized on the two oxygen atoms. Thermal decomposition properties of several salts of the two anions, as examined by differential scanning calorimetry, suggest that the salts are high energy-density compounds. The DSC data also reveal that the thermal stability of the two anions is significantly influenced by the nature of the cation. Nitrogeneous cations lower the decomposition temperature of both anions while increasing the temperature range in which the decomposition occurs. Salts of nitrodicyanomethanide release more thermal energy in comparison to that released by the salts of nitrosodicyanomethanide, and the trend could be attributed to the presence of more oxygen in the former anion.

Acknowledgment. We gratefully acknowledge financial support from the Air Force Office of Scientific Research, Grants F49620-96-1-0417 and 98-1-0461.

Supporting Information Available: Tables of positional parameters (S1−S4), bond distances and angles for $Ba[ONC(CN)_2]_2(H_2O)$ (S5) and $Ba[O_2NC(CN)_2](Cl)(H_2O)_2$ (S6), anisotropic displacement parameters (S7−S10), hydrogen atom coordinates (S11−S13) and calculated vibrational modes, and frequencies for the nitroso- and nitrodicyanomethanide anions (S14, S15); a figure, S1, depicting the vibrational modes of the nitrodicyanomethanide anion, and a figure S2, showing the thermograms for $Li[ONC(CN)_2]$ and $[NH_4][O_2NC(CN)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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