Nucleophilic Addition of Hydroxylamine, Methoxylamine, and Hydrazine to Malononitrileoxime

Navamoney Arulsamy and D. Scott Bohle*

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

Received October 15, 1999

The chemistry of malononitrileoxime, $HONC(CN)_2$, with respect to nucleophilic addition to ammonia, methylamine, hydroxylamine, methoxylamine, and hydrazine is reported. Whereas the poorly nucleophilic ammonia and methylamine do not react, hydroxylamine, methoxylamine, and hydrazine add to the nitrile groups of the oxime, yielding the corresponding amidoximes and amidrazones. Depending on the stoichiometry of the reactions, hydroxylamine and hydrazine add to one or both of the nitrile groups; methoxylamine adds to only one of the nitrile groups. Three of the products, namely, cyanoacetamidoxime (**1**), 3-amino-2,3-hydroxyiminopropionitrile monohydrate (**2**·H_2O), and 3,5-diaminopyrazolone-4-oxime monohydrochloride monohydrate (**6**·HCl·H_2O), are characterized by single-crystal X-ray diffraction data. All of the products exhibit exothermic decomposition properties with heats of decomposition in the range of 500−1500 kJ mol^{-1}.

Introduction

Salts of malononitrileoxime, $M^+[ONC(CN)_2]^-$, where $M^+ = Ag^+, Li^+, Na^+, K^+, NH_4^+$, and $[C(NH_2)_3]^+$, exhibit exothermic decomposition properties.[1] Malononitrileoxime is obtained by the nitrosation of malononitrile with nitrous acid in acetate buffer (pH 2.5−3). The anion of malononitrileoxime is also known as nitrosodicyanomethanide. Structural data available for the ammonium,[1] barium,[1] silver,[2] and potassium[3] salts reveal that the anion has a significant resonance contribution for the corresponding oximate, $[O{=}N{-}C(CN)_2]^- \leftrightarrow [O{-}N{=}C(CN)_2]^-$. Electronic absorption spectra of the potassium salt measured in aqueous media at acidic pH conditions are consistent with the oximate structure.[4] Although structural features[5−8] and coordination properties[2,3,9−13] of $[ONC(CN)_2]^-$ are well studied, the chemical reactivity of the species has not been studied in detail. As part of our efforts toward the synthesis of new propellants, we were interested in the chemical reactivity of $[ONC(CN)_2]^-$ and its potential use as a precursor material in the synthesis of new nitrogen-rich compounds.

It is well-known that nitriles undergo addition reactions with ammonia,[14−17] hydroxylamine,[15,16,18−22] and hydrazine[15,16,20,23−26] with the formation of amidines, amidoximes, and amidrazones, respectively. Electron-deficient nitriles also undergo hydration and base-catalyzed alcohol addition reactions following a similar nucleophilic addition mechanism.[27] In general, electron-deficient nitriles undergo addition reaction with a wide variety of reagents including ammonia, whereas electron-rich nitriles react only with the highly nucleophilic hydroxylamine and hydrazine reagents. For example, the barium salt of dicyanamide, $Ba(N(CN)_2)_2$, an electron-rich nitrile, undergoes an ion exchange reaction with ammonium sulfate in aqueous media to form the corresponding ammonium salt, whereas its reaction with hydrazinium sulfate yields two products, namely, the corresponding hydrazinium salt at 20 °C and guanazole at 50 °C.[28]

---

[1] Arulsamy, N.; Bohle, D. S.; Doletski, B. G. *Inorg. Chem.* **1999**, *38*, 2709.

[2] Chow, Y. M.; Britton, D. *Acta Crystallogr.* **1974**, *B30*, 1117.

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

[4] Iglesias, E.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 343.

[5] Jensen, H.; Klewe, B.; Tjelta, E. *Acta Chem. Scand.* **1970**, *31A*, 151.

[6] Schädler, H.-D.; Köhler, H. *Z. Chem.* **1990**, *30*, 67.

[7] Jäger, L.; Schädler, H.-D.; Grobe, U.; Köhler, H.; Nefedov, V. I. *Z. Anorg. Allg. Chem.* **1992**, *617*, 123.

[8] Schädler, H.-D.; Jäger, L.; Senf, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1115.

[9] Bohle, D. S.; Conklin, B. J.; Hung, C.-H. *Inorg. Chem.* **1995**, *34*, 2569.

[10] Jäger, L.; Tretner, C.; Hartung, H.; Biedermann, M. *Chem. Ber.* **1997**, *130*, 1007.

[11] Hvastijová, M.; Kozíšek, J.; Kohout, J.; Mrozinski, J.; Jäger, L.; Svobodo, I. *Polyhederon* **1997**, *16*, 580.

[12] Mikloš, D.; Potocnak, I.; Dunaj-Jurco, M.; Jäger, L. *Acta Crystallogr. Sect. C (Cr. Str. Comm.)* **1998**, *54*, 33.

[13] Dunaj-Jurco, M.; Mikloš, D.; Potocnak, I.; Jäger, L. *Acta Crystallogr. Sect. C* **1998**, *54*, 1763.

[14] Zilberman, E. N. *Russ. Chem. Rev.* **1962**, *31*, 615.

[15] Smith, P. A. S., *Open Chain Nitrogen Compounds*; Benjamin: New York, 1965; Vol. 1, pp 137−231; 1966; Vol. 2, pp 29−63, 149−171.

[16] Schäefer, F. C. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Interscience: New York, 1970; pp 239−340.

[17] Gautier, J. A.; Miocque, M.; Farnoux, C. C. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Interscience: New York, 1975; pp 238−348.

[18] Eloy, F.; Lenaers, R. *Chem. Rev.* **1962**, *62*, 155.

[19] Metzger, H. In *Methoden der Organischen Chemie (Houben-Weyl)*; Muller, E., Ed.; Thieme Verlag: Stuttgart, 1968; Vol. 10, pp 209−213.

[20] Vaquero, J. J.; Fuentes, L.; DelCastillo, J. C.; Perez, M. I.; Garcia, J. L.; Soto, J. L. *Synthesis* **1987**, 33.

[21] Showell, G. A.; Gibbons, T. L.; Kneen, C. O.; MacLeod, A. M.; Merchant, K.; Saunders: J.; Freedman, S. B.; Patel, S.; Baker, R. *J. Med. Chem.* **1991**, *34*, 1086.

[22] Piskunova, I. P.; Eremeev, A. V.; Mishrev, A. F.; Vosekalna, I. A. *Tetrahedron* **1993**, *49*, 4671.

[23] Neilson, D. G.; Roger, R.; Heatlie, J. M. W.; Newlands, L. R. *Chem. Rev.* **1970**, *70*, 151.

[24] Watson, K. M.; Neilson, D. G. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Interscience: New York, 1975; pp 491−545.

[25] Rusanov, A. L. *Russ. Chem. Rev.* **1974**, *43*, 795.

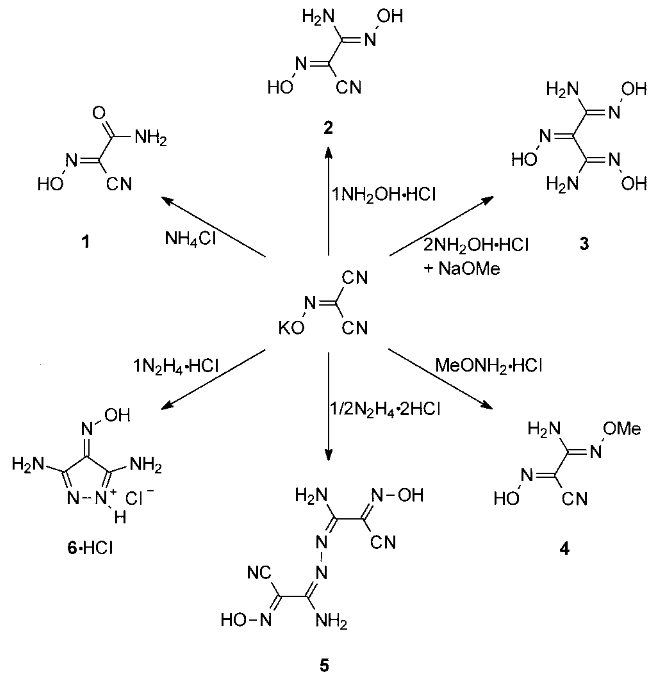
[26] Smith, R. F.; Kinder, L. L.; Walker, D. G.; Buckley, L. A.; Hammond, J. M. *J. Org. Chem.* **1977**, *42*, 1862.

[27] Schäefer, F. C.; Peters, G. A. *J. Org. Chem.* **1961**, *26*, 412.

[28] Frankel, M. B.; Burns, E. A.; Butler, J. C.; Wilson, E. R. *J. Org. Chem.* **1963**, *28*, 2428.

10.1021/jo991614t CCC: $19.00

Scheme 1



Although the acid-catalyzed hydration reaction of $[ONC(CN)_2]^-$ is known,[29] similar reactions with ammonia, hydroxylamine, and hydrazine still remain unknown. Dunaj-Jurco et al. have observed addition of methanol to one of the two nitrile groups of malononitrileoxime during their attempted synthesis of copper(II) malononitrileoxime complexes.[13,30] We undertook a comprehensive study of the reactions of malononitrileoxime with ammonia, methylamine, hydroxylamine, *O*-methylhydroxylamine, and hydrazine. In this paper, we wish to report the details of the reactions and the characterization and thermal decomposition properties of the products.

Results and Discussion

The ion metathesis reaction of $AgONC(CN)_2$ with NH_4Cl in aqueous media at room temperature yields the corresponding ammonium salt as reported previously.[1] To examine if ammonia addition can be achieved at higher temperatures, the filtrate from the metathesis reaction of $AgONC(CN)_2$ with NH_4Cl was allowed to reflux overnight. The reaction did not yield the expected amidine; instead the hydrolysis product, $HON{=}C(CN)(CONH_2)$ (**1**) is isolated in 65% yield. Similarly, a reaction between equimolar amounts of $KONC(CN)_2$ and methylamine hydrochloride in ethanol was carried out by refluxing the mixture overnight, and the reaction also yielded the hydrolysis product and not the expected *N*-methylamidine. The formation of **1** in these reactions indicates poor nucleophilicity of ammonia and methylamine under these experimental conditions and is also consistent with the known acid-catalyzed hydration of malononitrileoxime.[29]

The reactions of $KONC(CN)_2$ with hydroxylamine, *O*-methylhydroxylamine, and hydrazine yield nucleophilic addition products as shown in Scheme 1. Depending on the stoichiometry, either one or both of the nitrile groups undergo addition reaction with hydroxylamine and hydrazine. The reaction with *O*-methylhydroxylamine did not proceed beyond the addition of 1 equiv of the reagent despite prolonged reflux of the reaction mixture containing 1 equiv of $KONC(CN)_2$ and 2 equiv of *O*-methylhydroxylamine in ethyl alcohol. The observation reveals that the nitrile group of the 1 + 1 addition product, namely, 3-amino-2-hydroxyimino-3-methoxyiminopropionitrile (**4**), is significantly deactivated in comparison to the nitrile groups of malononitrileoxime.

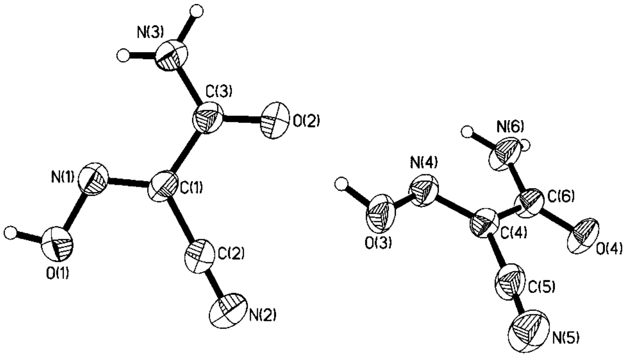


Figure 1. Views of the two cyanoacetamidoxime molecules in the crystallographic asymmetric unit. In this and the following structures, 50% thermal ellipsoids of the atoms are shown.

The reaction of $KONC(CN)_2$ with 0.5 equiv of $N_2H_4 \cdot 2HCl$ in aqueous medium yields *N,N′*-di-3,3′-(3-amino-2-hydroxyiminopropionitrilo)hydrazone (**5**) as follows. The reaction mixture is light yellow colored immediately after the mixing of the reactants. However, the color turns slowly to deep red on standing the solution for ca. 12 h, and reddish brown crystals of the hydrazone **5** begin to separate from the solution. The reaction reaches near completion in 3 d, with the crystallization of the product in 86% yield. The presence of a strong absorption band at 2238 cm^{-1} in the IR spectrum together with the analytical data obtained for the product unambiguously demonstrate the assigned structure **5**. The product is soluble in dimethyl sulfoxide, slightly soluble in water, and insoluble in solvents such as acetone, methanol, THF, and acetonitrile. In dimethyl sulfoxide solution, the hydrazone undergoes rapid reorganization, forming protonated pyrazoloneoxime and malononitrileoximate anion. The ^{13}C NMR spectrum measured in DMSO-d_6, exhibits two sets of peaks, as described in the Experimental Section, corresponding to the two species in solution.

Structural Data. Compounds **1**, **2**·H_2O, and the new heterocyclic compound, **6**·HCl·H_2O, have also been characterized by single-crystal X-ray crystallography. Views of the structures are given in Figures 1−3. Selected bond distances and angles are listed in Table 1.

1. Crystals of the compound contain two structurally similar $HONC(CN)(CONH_2)$ molecules in the crystallographic asymmetric unit. The molecules are planar, consistent with the presence of sp^2 and sp hybridized carbon atoms and delocalization of π bonds in the structure. The dihedral angle between the planes passing through the two molecules is 54°. The oxime hydrogen atoms of the two molecule are intermolecularly hydrogen bonded to the amide oxygen atom of the neighboring molecule with corresponding O···O distances of 2.580(3)

---

[29] Köhler, H.; Seifert, B. *Z. Anorg. Chem.* **1970**, *379*, 1.

[30] Dunaj-Jurco, M.; Mikloš, D.; Potocnák, I.; Jäger, L. *Acta Crystallogr., Sect. C.* **1996**, *C52*, 2409.

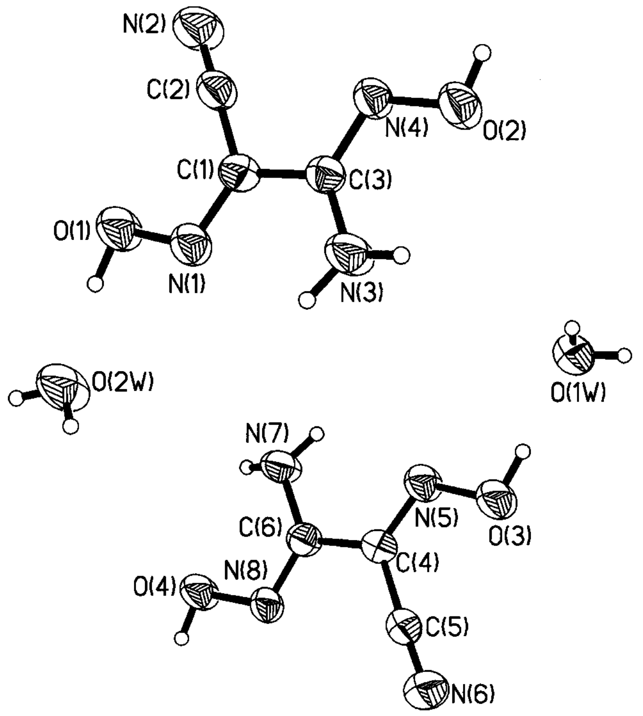


Figure 2. Views of the two pairs of 3-amino-2,3-di(hydroxyimino)propionitrile and solvated water molecules in the crystallographic asymmetric unit.

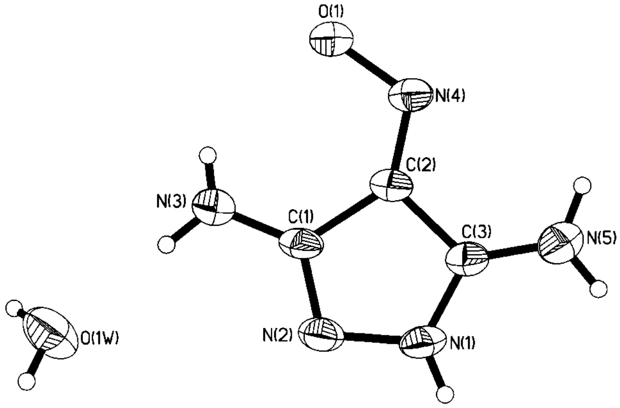


Figure 3. View of protonated 3,5-diaminopyrazolone-4-oxime and solvated water molecule in the crystals of **6**·HCl·H$_2$O.

and 2.684(3) Å, leading to a layer-like arrangement of the molecules.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1, 2·H$_2$O, and 6·HCl·H$_2$O

	1		
O(1)–N(1)	1.359(3)	N(1)–C(1)	1.283(3)
C(3)–O(2)	1.223(4)	C(3)–N(3)	1.329(4)
O(1)–N(1)–C(1)	113.5(2)	O(2)–C(3)–N(3)	123.4(3)
	2·H$_2$O		
O(1)–N(1)	1.367(3)	C(1)–N(1)	1.284(3)
C(3)–N(4)	1.289(3)	N(4)–O(2)	1.416(2)
O(1)–N(1)–C(1)	111.7(2)	N(4)–C(3)–N(3)	127.2(2)
	6·HCl·H$_2$O		
N(1)–N(2)	1.415(4)	N(1)–C(3)	1.310(5)
N(2)–C(1)	1.298(4)	C(1)–N(3)	1.322(5)
C(1)–C(2)	1.491(5)	C(2)–N(4)	1.280(5)
C(2)–C(3)	1.471(5)	C(3)–N(5)	1.311(5)
N(4)–O(1)	1.353(4)		
N(5)–C(3)–N(1)	127.7(3)	N(5)–C(3)–C(2)	126.1(3)
N(1)–C(3)–C(2)	106.1(3)	C(2)–N(4)–O(1)	113.2(3)

Table 2. Differential Scanning Calorimetry Data for the Compounds

compound	T_{onset}, °C	$T_{\max}$, °C	ΔH, kJ mol^{-1}
1	188 ± 2	194 ± 2	1110 ± 20
2·H$_2$O	115 ± 2	124 ± 2	1500 ± 20
3	131 ± 1	150 ± 5	1320 ± 240[a]
4	175 ± 2	215 ± 5	730 ± 20
5	180 ± 1	185 ± 1	1430 ± 40
	204 ± 1	212 ± 1	
	265 ± 1	307 ± 1	
6·HCl·H$_2$O	224 ± 2	242 ± 2	500 ± 40
6	270 ± 1	284 ± 1	830 ± 10

[a] Sample cup shattered due to explosion during the experiment.

2·H$_2$O. In this crystal also the crystallographic asymmetric unit contains two structurally similar molecules of 3-amino-2,3-di(hydroxyimino)propionitrile molecules, together with two water molecules. In each of the propionitrile molecules, the oxime groups are disposed in trans geometry with respect to the dioxime C–C bond. All atoms of each of the molecules with the exception of the hydrogen atoms are nearly plana,r with the maximum deviations from their least-squares planes being 0.0427 Å (O$_{\mathrm{amidoxime}}$) and 0.0577 Å (N$_{\mathrm{amidoxime}}$), respectively. The observed relatively shorter C–N$_{\mathrm{amine}}$ and longer C–N$_{\mathrm{oxime}}$ bond distances together with the remaining C–N$_{\mathrm{oxime}}$ and N–O distances are indicative of extended delocalization of π bonds in the structure. Specifically, the C–N$_{\mathrm{amine}}$ bond exhibits significant π character. The two water molecules in the structure are involved in intermolecular hydrogen bonding with one another and with each of the two 2-hydroxyimino oxygen atoms as reflected in the O(1W)···O(2W), O(1W)···O(3), and O(2W)···O(1) interatomic distances of 2.748(3), 2.671(3), and 2.632(3) Å, respectively. In both molecules the amine nitrogen atoms are involved in intramolecular hydrogen bonding interaction with the amidoxime oxygen atoms, with the corresponding interatomic distances O(2)···N(3) and O(4)···N(7) being 2.604(3) and 2.614(3) Å, and the with the two 2-hydroxyimino nitrogen atoms, with the associated N(1)···N(3) and N(5)···N(7) interatomic distances being 2.753(3) and 2.745(3) Å, respectively.

6·HCl·H$_2$O. The structure consists of well-separated protonated 3,5-diaminopyrazolone-4-oxime species, chloride anions, and solvated water molecules. All nonhydrogen atoms of the pyrazoloneoxime are nearly planar, with the maximum deviation being that of the oxime nitrogen atom at 0.0153 Å. The two double bonds of the two nitrogen atoms in the five-membered ring are significantly longer while the rest of the three bonds are shorter than typical C–N double bonds and C–C and N–N single bonds, respectively. The C–N and N–O bond distances involving the oxime group also exhibit a similar trend (Table 1), indicating the presence of π-bond delocalization over the protonated species.

Thermal Properties. Differential scanning calorimetry data obtained for the products reveal exothermic decomposition behavior (Table 2). None of these compounds exhibited sensitivity toward shock or static electricity during the studies. Compounds **4** and **6**·HCl·H$_2$O exhibit a sharp endotherm corresponding to the melting of the solids, together with exothermic peaks at 158 and 136 °C, respectively. Whereas the DSC plots of the remainder of the compounds contain single exothermic peaks, the plot of **5** exhibits three closely spaced exothermic peaks, indicating that the compound undergoes stepwise decomposition. It was also observed that

3 explodes at ca. 130 °C during the DSC experiments, shattering the sample cup.

The exothermic decomposition pattern observed for the compounds is consistent with the general behavior of nitroxy groups (such as nitro, nitroso, or oximino) substituted organic compounds.[31] The relatively lower heat of decomposition (ΔH) observed for **4** and **6**·HCl·H_2O and **6** could be attributed to the presence of the electron-donating methoxy or amino groups in the structures.

Conclusions

The reactivity of malononitrileoxime toward a number of nucleophilic reagents has been studied. The observed moderate reactivity of the nitrile groups of malononitrileoxime results from the electron-withdrawing property of the oxime substituent. A series of nitrogen-rich molecules with exothermic decomposition properties analogous to the parent species and oximes are synthesized. The reaction between equimolar amounts of $KONC(CN)_2$ and N_2H_4·2HCl yields a new heterocyclic compound, namely, 3,5-diaminopyrazolone-4-oxime as its monohydrochloride monohydrate. It may be possible to further modify some of the products described in this paper. For example, under suitable experimental conditions, it may be possible to effect ring closure in the explosive propionitriledioxime **3**, leading to the formation of 4-nitroso-3,5-diaminoisoxazole-2-oxime, and it may also be possible to oxidize the nonexplosive pyrazoloneoxime **6** to 3,5-dinitropyrazolone-4-oxime or 2,3,4-trinitropyrazole.

Experimental Section

Materials and Methods. All chemicals were obtained commercially and used without further purification. Infrared spectra were obtained as KBr disks with an FTIR Spectrophotometer. UV−vis spectra were measured in water solvent. Proton and ^{13}C NMR spectra were recorded in dimethyl sulfoxide-d_6 on a 400 MHz NMR Instrument. Thermograms were obtained using a 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 per min in the temperature range 25−500 °C.

Reactions of Malononitrileoxime. A number of new products were synthesized from the reactions of the silver or potassium salts of malononitrileoxime with ammonium chloride, methylamine hydrochloride, hydroxylamine hydrochloride, methoxylamine hydrochloride, and hydrazine dihydrochloride as described below.

Cyanoacetamideoxime (1). To a suspension of $AgONC(CN)_2$ (1.04 g, 5 mmol) in water (10 mL) was added a solution of NH_4Cl (0.272 g, 5 mmol) in water (10 mL) with stirring. The precipitated AgCl was removed by filtration, and the filtrate was allowed to reflux overnight. The solution was filtered, rotary evaporated to a small volume (5 mL), and allowed to stand at room temperature. The crystalline product formed was characterized as **1**. Yield: 0.370 g (65%). IR (KBr, cm^{-1}): ν(CN) 2239. UV−vis (water) λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$): 228 (5482), 286 (5396). ^1H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, $J = 41.5$ Hz). ^{13}C NMR (400 MHz, DMSO-d_6): δ 109.3, 128.1, 160.2. Anal. Calcd for $C_3H_3N_3O_2$: C, 31.87; H, 2.67; N, 37.16. Found: C, 31.92; H, 2.67; N, 37.05.

Another reaction with equimolar amounts of $KONC(CN)_2$ and $MeNH_2$·HCl in absolute ethanol solvent after overnight reflux also yielded **1**.

3-Amino-2,3-di(hydroxyimino)propionitrile Monohydrate (2·H_2O). To a solution of NH_2OH·HCl (0.695 g, 10 mmol) in absolute ethanol (100 mL) was added $KONC(CN)_2$ (1.33 g, 10 mmol). The suspension was heated to reflux for 6 h. Colorless crystals of KCl formed on cooling to room temperature were filtered off. The solvent from the colorless filtrate was stripped off under reduced pressure, and the white solid formed was recrystallized from hot water as colorless crystals. Yield: 1.25 g (86%). IR (KBr, cm^{-1}): ν(CN) 2246. UV−vis (water) λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$): 298 (6160). ^1H NMR (400 MHz, DMSO-d_6): 3.52 (b, 2H), 5.78 (s, 2H), 10.72 (s, 1H), δ 13.77 (b, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 108.7, 126.7, 146.4. Anal. Calcd for $C_3H_6N_4O_3$: C, 24.66; H, 4.14; N, 38.35. Found: C, 24.86; H, 4.10; N, 38.41.

1,3-Diamino-1,2,3-tri(hydroxyimino)propane (3). To a solution of NH_2OH·HCl (1.39 g, 20 mmol) in absolute ethanol (100 mL) were added $KONC(CN)_2$ (1.33 g, 10 mmol) and NaOMe (0.54 g, 10 mmol). The suspension was stirred at room temperature for 2 h and then heated to reflux for 6 h. Colorless crystals of KCl and NaCl formed on cooling to room temperature were filtered off. The solvent from the colorless filtrate was stripped off under reduced pressure, and the white solid formed was recrystallized from hot water as colorless fibrous crystals. Yield: 1.45 g (90%). UV−vis (water) λ_{max}, nm (ϵ, M^{-1}-cm^{-1}): 264 (4850). ^1H NMR (400 MHz, DMSO-d_6): δ 5.49 (s, 2H), 6.17 (s, 2H), 9.33 (b, 1H), 10.12 (s, 1H), 11.98 (b, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 143.8, 145.3, 148.2. Anal. Calcd for $C_3H_7N_4O_3$: C, 22.36; H, 4.38; N, 43.47. Found: C, 22.17; H, 4.33; N, 42.95.

3-Amino-2-hydroxyimino-3-methoxyiminopropionitrile (4). To a solution of NH_2OMe·HCl (0.835 g, 10 mmol) in absolute ethanol (25 mL) was added $KONC(CN)_2$ (1.33 g, 10 mmol). The suspension was heated to reflux for 6 h. The precipitated KCl on cooling to room temperature was filtered off. The solvent from the colorless filtrate was removed by rotary evaporation, and the yellow solid formed was recrystallized from hot water as fine needles. Yield: 1.21 g (85%). IR (KBr, cm^{-1}): ν(CN) 2244. UV−vis (water) λ_{max}, nm (ϵ, M^{-1}-cm^{-1}): 234 (4310), 296 (6805). ^1H NMR (400 MHz, DMSO-d_6): δ 2.81 (s, 3H), 6.10 (b, 2H), 13.97 (s, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 61.6 (q, $J = 143.3$ Hz), 108.4, 125.8, 146.0. Anal. Calcd for $C_4H_6N_4O_2$: C, 33.81; H, 4.25; N, 39.42. Found: C, 33.88; H, 4.27; N, 39.51.

A similar reaction of $KONC(CN)_2$ with 2 equiv of NH_2OMe·HCl also yielded **4** and did not yield the expected 1 + 2 addition product.

***N,N′*-Di-3,3′-(3-amino-2-hydroxyiminopropionitrilo)hydrazone (5).** To an aqueous solution (50 mL) of N_2H_4·2HCl (0.525 g, 5 mmol) was added $KONC(CN)_2$ (1.330 g, 10 mmol) at room temperature with stirring. The light yellow solution was allowed to stand at room temperature for 3 d. Large reddish brown crystals formed were filtered and dried in vacuo overnight at room temperature. Yield: 0.950 g (86%). IR (KBr, cm^{-1}): ν(CN) 2238. UV−vis (water) λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$): 310 (24166), 396 (2558). Anal. Calcd for $C_6H_6N_8O_2$: C, 32.44; H, 2.72; N, 50.44. Found: C, 32.44; H, 2.80; N, 50.28. The product underwent structural reorganization in dimethyl sulfoxide solution as evident from its ^{13}C NMR spectrum (in DMSO-d_6) forming protonated 3,5-diaminopyrazolone-4-oxime and malononitrileoximate anion. ^1H NMR (400 MHz, DMSO-d_6): δ 9.8−6.8 (b). ^{13}C NMR (400 MHz, DMSO-d_6): 142.4, 143.3, 152.2 and 107.6, 111.0, 116.3. The first set of peaks corresponds to the protonated 3,5-diaminopyrazolone-4-oxime, and the second set corresponds to $[ONC(CN)_2]^-$. The small discrepancy between the first set of peaks to those of **6**·HCl·H_2O in the ^1H and ^{13}C NMR spectra is attributable to the possibility of deutrium exchange during structural reorganization of **5**, difference in the associated anions, and absence of solvated water molecule in **5**.

3,5-Diaminopyrazolone-4-oxime Monohydrochloride Monohydrate (6·HCl·H_2O). In this synthesis equimolar amounts of $KONC(CN)_2$ and N_2H_4·2HCl (1.050 g, 10 mmol) were used. The reddish brown crystals formed over a period of 3 days were filtered and dried in vacuo overnight at room temperature. Yield: 1.65 g (91%). UV−vis (water) λ_{max}, nm (ϵ,

---

(31) *Chemistry of Energetic Materials*; Olah, G. A.; Squire, D. R., Eds.; Academic Press: San Diego, 1991.

$M^{-1}cm^{-1}$): 310 (12355), 386 (1376). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.41 (t, J = 50.7, 1H), 8.4−7.8 (b, 4H), 14.59 (b, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 143.5, 144.3, 151.4. Anal. Calcd for $C_3H_8N_5O_2Cl$: C, 19.84; H, 4.44; N, 38.57; Cl, 19.52. Found: C, 20.05; H, 4.43; N, 38.34; Cl, 19.35. A similar reaction using $N_2H_4 \cdot H_2O$ instead of $N_2H_4 \cdot 2HCl$ yielded the free pyrazoloneoxime (**6**) as orange-red crystals. Yield: 1.10 g (87%). UV−vis (in water) λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$): 310 (14010), 394 (1722). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.5−5.9 (b, 4H), 11.02 (s, 1H). ^{13}C NMR: δ 141.8 (b), 143.9, 153.5. Anal. Calcd for $C_3H_5N_5O$: C, 28.35; H, 3.96; N, 55.10. Found: C, 28.50; H, 3.90; N, 54.95.

Crystallographic Data. X-ray diffraction data were collected for **1**, **2**·H_2O, and **6**·HCl·H_2O on a P4 diffractometer. Single crystals of the compounds were mounted on a glass fiber using epoxy resin. Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity for any of the crystals. The data for **6**·HCl·H_2O were corrected for Lorentz-polarization effects and absorption, whereas those of **1** and **2**·H_2O were not corrected for absorption. The structures were solved by direct methods and refined by least-squares techniques on F^2 using SHELXTL program.[32] In the three structural refinements, all atoms were located in the difference maps during successive cycles of least-squares. The positions of the non-hydrogen atoms were refined anisotropically, whereas those of the hydrogen atoms were refined isotropically.

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 crystallographic data and positional parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1**, **2**·H_2O, and **6**·HCl·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991614T

---

[32] Sheldrick, G. M., SHELXTL Version 5.04; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.