

A New Class of Flexible Energetic Salts: The Crystal Structures of the Ammonium, Lithium, Potassium, and Cesium Salts of Dinitramide

Richard Gilardi,^{*,†} J. Flippen-Anderson,[†] Clifford George,[†] and Ray J. Butcher[‡]

Contribution from the Laboratory for the Structure of Matter, Naval Research Laboratory, Washington D.C. 20375, and Department of Chemistry, Howard University, 525 College Street, N.W., Washington D.C. 20059

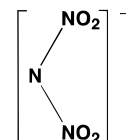
Received March 24, 1997[⊗]

Abstract: The crystal structures of the ammonium, **1**, lithium, **2**, potassium, **3**, and cesium, **4**, salts of a new nitrogen oxy anion, N_3O_4^- , have been determined. In **1** there are two interpenetrating three-dimensional lattices linked by strong hydrogen-bonding interactions between all four ammonium protons and three of the four dinitramide oxygen atoms. Even though **2–4** have similar formula units each has a completely different structure characterized by differing coordination numbers and geometries. The structure of **2** is unique in that it is the only one containing a dinitramide ion in the C_2 conformation predicted by *ab initio* studies to be the minimum energy conformation. There is good agreement between the predicted and experimental metrical parameters for the C_2 conformer of the dinitramide anion.

Introduction

In spite of the fact that the field of nitrogen oxide chemistry is considered a mature well-developed area¹ there has been much excitement over the recent discovery^{2–5} of a completely new^{6–8} stable oxy acid of nitrogen and its salts which are expected to

have both fundamental scientific interest as well as potential practical applications.¹⁹ These salts contain a new oxy anion of nitrogen, called the dinitramide anion, of the composition, N_3O_4^- and structure:



The name dinitramide for this anion is based on an extension of the nomenclature for nitramide.²⁰ Thus the free acid, $\text{NH}(\text{NO}_2)_2$, should be called dinitraminic acid. The dinitramide ion is a uniquely stable oxy anion of nitrogen and its salts are high oxygen density groupings that have been prepared with many different counterions,^{2–18} including the ammonium, lithium, potassium, and cesium salts which are the subject of this report.

In particular, the ammonium salt of dinitramide (ADN) is of great interest because it is a possible replacement for ammonium perchlorate (AP) to given an environmentally cleaner system by eliminating the emission of chloride from the rocket motors. Although it is less thermally stable and slightly more shock sensitive than AP, it is considerably more stable than the related N-nitro compounds such as alkyldinitramines $[\text{R}-\text{N}(\text{NO}_2)_2]$ ^{21,22} or nitramide.^{23,24,25}

[†] Naval Research Laboratory.

[‡] Howard University.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

(1) See for example, Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; J. W. Wiley & Sons, Inc.: New York NY, 1988; pp 326–329. Greenwood, N. N. *The Chemistry of the Elements. Developments in Inorganic Nitrogen Chemistry*; Colburn, C. B., Ed.; Elsevier Scientific Publishing Co.: Amsterdam, 1973; Vol 2.

(2) Bottaro, J. C.; Schmitt, R. J.; Penwell, P. E.; Ross, D. S. U.S. Patent no. 5,254,324; issued October 19, 1993. International patent application no. WO 91/19669, World Intellectual Property Organization, published Dec 26, 1991.

(3) Bottaro, J. C.; Schmitt, R. J.; Penwell, P. E. U.S. Patent no. 5,198,204; issued March 30, 1993. International patent application no. WO 91/19670, World Intellectual Property Organization, published Dec 26, 1991.

(4) Bottaro, J. C.; Schmitt, R. J.; Penwell, P. E. U.S. Patent no. 5,316,749; issued March 31, 1994.

(5) Bottaro, J. C.; Penwell, P. E.; Bomberger, D. Filed for US Patent 1992. International patent application no. WO 93/16002, World Intellectual Property Organization, published Aug 19, 1993.

(6) Russian authors claimed initial discovery of the ammonium salt in the early 1970's in highly classified work and have used ammonium dinitramide in rocket propulsion, see: Zak, Z. P. *Am. Inst. Aeronaut., Inc.* **1993**, 1755.

(7) Luk'yanov, O. A.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1994**, 43, 89.

(8) Luk'yanov, O. A.; Konnova, Yu. V.; Klimova, T. A.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1994**, 43, 1200.

(9) Luk'yanov, O. A.; Anikin, O. V.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1994**, 43, 1457.

(10) Shlyapochnikov, V. A.; Cherskaya, N. O.; Luk'yanov, O. A.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1994**, 43, 1522.

(11) Luk'yanov, O. A.; Shlykova, N. I.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1994**, 43, 1680.

(12) Luk'yanov, O. A.; Agevnin, A. R.; Leichenko, A. A.; Seregina, N. M.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1995**, 44, 108.

(13) Shlyapochnikov, V. A.; Oleneva, G. I.; Cherskaya, N. O.; Luk'yanov, O. A.; Gorelik, V. P.; Anikin, O. V.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1995**, 44, 1449.

(14) Shlyapochnikov, V. A.; Cherskaya, N. O.; Luk'yanov, O. A.; Anikin, O. V.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1996**, 45, 430.

(15) Luk'yanov, O. A.; Anikin, O. V.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1996**, 45, 433.

(16) Luk'yanov, O. A.; Kozlova, I. K.; Shitov, O. P.; Konnova, Yu. V.; Kalinina, I. V.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1996**, 45, 863.

(17) Luk'yanov, O. A.; Shvedova, S. N.; Shepelev, E. V.; Varfolomeeva, O. N.; Malkina, N. N.; Tartakovsky, V. A. *Russ. Chem. Bull.* **1996**, 45, 1497.

(18) Shlyapochnikov, V. A.; Oleneva, G. I.; Cherskaya, N. O.; Luk'yanov, O. A.; Gorelik, V. P.; Anikin, O. V.; Tartakovsky, V. A. *J. Mol. Struct.* **1995**, 348, 103.

(19) Borman, S. *Chem. Eng. News* **1994**, Jan 17, 18.

(20) See preceding paper: Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. *J. Am. Chem. Soc.* **1997**, 119, xxx.

(21) Hammel, E. E.; Heights, C.; Olsen, R. E. British Patent no. 1,126591, 1968.

(22) Cherednichenko, L. V.; Lebedev, B. A.; Gidaspov, B. V. *Zh. Org. Khim.* **1978**, 14, 735.

(23) Marlies, C. A.; La Mer, V. K.; Greenspan, J. *Inorg. Synth.* **1939**, 1, 68.

The minimum energy structure of the dinitramide ion has been of great interest.^{26–32} *Ab initio* calculations for the isolated $\text{N}(\text{NO}_2)_2^-$ ion indicate^{26–33} that the minimum energy structure has C_2 symmetry. Experimental measurements indicate that in the solid state and even in solution the dinitramide ion often has C_1 symmetry, i.e., no symmetry.³³ However, this is not in conflict with theory for the calculations also show that the potential energy surface is quite shallow in the neighborhood of its minimum energy conformation. Thus it is to be expected that the conformation adopted by the dinitramide ion will depend markedly on its steric and electronic environment.

The first reported crystal structure to contain the dinitramide ion was that of a coordination complex with rhenium in which the dinitramide moiety was covalently linked to the metal through its central nitrogen atom.³⁴ In this structure the dinitramide ion was highly asymmetric with differences in the two N–N bonds exceeding 0.1 Å. However the conformations adopted by the dinitramide ion in the structures³⁵ of its simple ionic salts, such as reported herein, display slight, but often significant, distortions from C_2 symmetry.

The structure of the lithium salt is particularly interesting as it is the only known example³⁶ containing a dinitramide anion exhibiting the C_2 geometry predicted to be the minimum energy conformation by *ab initio* calculations. The structure of the ammonium derivative is of particular interest as it reflects the ability of its tetrahedrally arrayed ammonium protons to direct the self-assembly of these complementary components into polymeric motifs. Strong, selective, and directional hydrogen bonding has been noted³⁷ as a most powerful organizing force in molecular assembly resulting in the formation of one-, two-, and three-dimensional hydrogen-bonded architectures. An earlier study³⁸ involving cubane-1,3,5,7-tetracarboxylic acid with hydrogen-bonding donors arranged in a tetrahedral fashion, however, has shown that this does not necessarily result in a three-dimensional supramolecular assembly.

(24) (a) For review, see: Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973; p 160. (b) Kresge, A. J.; Tang, Y. C. *J. Chem. Soc., Chem. Commun.* **1980**, 309.

(25) (a) Arrowsmith, C. H.; Awwal, A.; Euser, B. A.; Kresge, A. J.; Lau, P. P. T.; Onwood, D. P.; Tang, Y. C.; Young, E. C. *J. Am. Chem. Soc.* **1991**, *113*, 172. (b) Arrowsmith, C. H.; Kresge, A. J.; Tang *J. Am. Chem. Soc.*, **1991**, *113*, 179.

(26) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D.; Dogimont, C. *J. Mol. Struct. (THEOCHEM)* **1987**, *153*, 249.

(27) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D.; Bourasseau, S. *J. Mol. Struct. (THEOCHEM)* **1989**, *187*, 251.

(28) Brinck, T.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **1991**, *56*, 5012.

(29) Politzer, P.; Seminario, J. M.; Concha, M. C.; Redfern, P. C. *J. Mol. Struct. (THEOCHEM)* **1993**, *287*, 235.

(30) Politzer, P.; Seminario, J. M. *Chem. Phys. Lett.* **1993**, *216*, 348.

(31) Michels, H. H.; Montgomery, J. A., Jr. *J. Phys. Chem.* **1993**, *97*, 6602.

(32) Mebel, A. M.; Lin, M. C.; Morokuma, K.; Melius, C. F. *J. Phys. Chem.* **1995**, *99*, 6842.

(33) Christie, K. O.; Wilson, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. *Inorg. Chem.* **1996**, *35*, 5068.

(34) Trammell, S.; Goodson, P. A.; Sullivan, B. P. *Inorg. Chem.* **1996**, *35*, 1421.

(35) An article reporting the structures of the biguanidinium salts of dinitramide has been submitted: Martin, A.; Pinkerton, A. A.; Gilardi, R. D.; Bottaro, J. C. *Acta Crystallogr.* **1997**, *B53*, 504.

(36) Of the 23 salts of dinitramide whose structures have been completed in our laboratories, 21 have C_1 symmetry, the lithium salt has C_2 symmetry while that of the dinitroazetidinium salt has mirror (m) symmetry: Butcher, R. J.; Gilardi, R. G. *J. Chem. Crystallogr.*, submitted for publication.

(37) (a) Wright, J. D. *Molecular Crystals*, 2nd ed.; Cambridge University Press: Cambridge, 1994. (b) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (c) Frankenbach, G. M.; Etter, M. C. *Chem. Mater.* **1992**, *4*, 272.

(38) Butcher, R. J.; Bashir-Hashemi, A.; Gilardi, R. D. *J. Chem. Crystallogr.* **1997**, *27*, 99.

Experimental Section

Data Collection. Clear, colorless crystals of **1**, **3**, and **4** synthesized by previously determined methods^{2–5} were obtained from SRI, while **2** was obtained from W. Koppes, Naval Surface Warfare Center, Indian Head, MD. These were glued to the end of a thin glass fiber and transferred to a Siemens R3/V (for **1**, **3**, and **4**) or a Siemens P4/S (for **2**) diffractometer using Mo $K\alpha$ (**1** and **4**) or Cu $K\alpha$ (**2** and **3**) radiation and a graphite monochromator. Cell dimensions and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of accurately centered reflections. These are listed with other relevant crystal data in Table 1.

Structure Solution and Refinement. The structures were solved by direct methods using the SHELXTL package of computer programs.³⁹ Neutral atom scattering factors were used⁴⁰ with corrections for real and imaginary anomalous dispersion.⁴¹ All structures were refined by full-matrix least-squares methods based on F^2 using SHELXL-93⁴² and used all unique data. Non-hydrogen atoms were refined anisotropically while hydrogen atoms (for **1**) were located in difference Fourier syntheses and refined isotropically. The final cycle of full-matrix least-squares refinement converged at $R(F) = 0.0307$, $R(F^2) = 0.0714$, based on 1119 observed reflections [$I > 2.0\sigma(I)$] and 90 variable parameters, and $R(F) = 0.0426$, $R(F^2) = 0.0888$ for all data for **1**; $R(F) = 0.0409$, $R(F^2) = 0.1068$, based on 210 observed reflections [$I > 2.0\sigma(I)$] and 39 variable parameters, and $R(F) = 0.0464$, $R(F^2) = 0.1112$ for all data for **2**; $R(F) = 0.0281$, $R(F^2) = 0.0798$, based on 581 observed reflections [$I > 2.0\sigma(I)$] and 74 variable parameters, and $R(F) = 0.0297$, $R(F^2) = 0.0966$ for all data for **3**; $R(F) = 0.0169$, $R(F^2) = 0.0416$, based on 1075 observed reflections [$I > 2.0\sigma(I)$] and 146 variable parameters, and $R(F) = 0.0197$, $R(F^2) = 0.0492$ for all data for **4**. Fractional coordinates and equivalent thermal factors for **1–4** are listed in S10–S13 in Supporting Information, respectively. A comparison of selected anion metrical parameters for **1–4** is listed in Table 2.

Results and Discussion

In all cases the structures consist of cations and anions either linked by hydrogen bonds, as in the case of **1**, or by electrostatic interactions between the metal cations and the dinitramide anions as in **2–4**. Figures 1–4 show the arrangement of dinitramide ions about the central metal ions in **2–4** (Figure 3 and 4 for Cs1 and Cs2), respectively. Figures 5–8 highlight different aspects of the extensive hydrogen bonding in **1** involving all four ammonium hydrogen atoms and the dinitramide anions (*vide infra*).

Even though the lithium, potassium, and cesium ions are all group 1A cations, no two compounds are isostructural. This reflects the sensitivity of the dinitramide ion to its local environment, as seen in other structures containing the dinitramide moiety, but also stems from the fact that the ionic radius of the three cations are markedly different (Li^+ , 0.68 Å; K^+ , 1.33 Å; Cs^+ , 1.67 Å⁴³). Thus the coordination numbers and coordination environments for the three metal salts differ markedly (see Supporting Information).

(39) Sheldrick, G. M. SHELXTL, Crystallographic System (Siemens Analytical Instrument Division, Madison, Wis), 1986.

(40) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*, The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(41) Cromer, D. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(42) Sheldrick, G. M.; Schneider, T. R. *Methods Enzymol.*, in press. This is a full-matrix least-squares refinement package that uses all data and refines on F^2 rather than the traditional F . The various parameters used in this refinement process are defined as follows: $R(F) = \sum |F_o - F_c| / \sum F_o$ and $R(F^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$ and a and b are variable parameters whose optimal values are usually suggested by the program during the refinement process. The goodness-of-fit parameter (s) is based on F^2 and defined as $s = \{\sum [w(F_o^2 - F_c^2)^2] / [n - p]\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

(43) Values from: *The Handbook of Physics and Chemistry*, 62nd ed., CRC Press: Boca Raton, FL, 1981.

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	NH ₄ ⁺ (1)	Li ⁺ (2)	K ⁺ (3)	Cs ⁺ (4)
Crystal Data				
formula	[NH ₄] ⁺ [N ₃ O ₄] ⁻	Li ⁺ [N ₃ O ₄] ⁻	K ⁺ [N ₃ O ₄] ⁻	Cs ⁺ [N ₃ O ₄] ⁻
<i>M_r</i>	124.07	112.97	145.13	238.94
system	monoclinic	tetragonal	monoclinic	orthorhombic
space group	<i>P2₁/c</i>	<i>I4₁/a</i>	<i>P2₁/n</i>	<i>Pc2₁/b</i>
<i>a</i> , Å	6.914(1)	5.9164(4)	6.614(1)	7.740(2)
<i>b</i> , Å	11.787(3)	5.9164(4)	9.280(2)	9.059(2)
<i>c</i> , Å	5.614(1)	19.712(3)	7.198(1)	14.818(4)
β , deg	100.40(2)		97.58(1)	
<i>V</i> , Å ³	450.0(2)	689.99(12)	437.94(13)	1038.9(4)
<i>Z</i>	4	8	4	8
<i>F</i> (000)	256	448	288	864
<i>D_c</i> mg/m ³	1.831	2.175	2.201	3.055
wavelength, Å	0.71073	1.54178	1.54178	0.71073
μ , mm ⁻¹	0.187	2.018	10.17	7.060
<i>T</i> , °C	223(2)	223(2)	296(1)	233(2)
crystal shape	prism	plate	plate	parallelepiped
crystal size	0.38 × 0.23 × 0.12	0.25 × 0.25 × 0.12	0.42 × 0.18 × 0.08	0.38 × 0.14 × 0.12
crystal color	colorless	colorless	colorless	colorless
Data Collection				
diffractometer	Siemens R3/v	Siemens P4S	Siemens R3/v	Siemens R3/v
collection method	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$
number measured	1409	322	673	1185
number unique	1316 (<i>R</i> _{int} = 1.18%)	237 (<i>R</i> _{int} = 2.42%)	593 (<i>R</i> _{int} = 2.20%)	1102 (<i>R</i> _{int} = 1.49%)
number observed	1119 (<i>F</i> > 4σ(<i>F</i>))	210 (<i>F</i> > 4σ(<i>F</i>))	581 (<i>F</i> > 4σ(<i>F</i>))	1075 (<i>F</i> > 4σ(<i>F</i>))
θ range, deg	3.00 to 30.06	7.82 to 57.41	7.83 to 57.18	2.63 to 26.05
number standards	3	3	3	3
frequency	97	97	97	97
absorption correction			SHELXA	semiempirical
<i>T</i> _{max} , <i>T</i> _{min}			0.5088, 0.2362	0.9783, 0.5772
Refinement				
refinement type	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
data/restraints/parameters	1303/0/90	237/0/39	587/0/74	1088/1/146
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ 3.07, <i>wR</i> ₂ 7.14	<i>R</i> ₁ 4.09, <i>wR</i> ₂ 10.68	<i>R</i> ₁ 2.81, <i>wR</i> ₂ 7.98	<i>R</i> ₁ 1.69, <i>wR</i> ₂ 4.16
<i>R</i> indices (all data)	<i>R</i> ₁ 4.26, <i>wR</i> ₂ 8.88	<i>R</i> ₁ 4.64, <i>wR</i> ₂ 11.12	<i>R</i> ₁ 2.97, <i>wR</i> ₂ 9.66	<i>R</i> ₁ 1.97, <i>wR</i> ₂ 4.92
goodness of fit on <i>F</i> ²	1.028	1.155	1.090	1.086
H refinement	isotropic			
extinction corr.	$\chi = 0.011(4)$	0.013(2)	$\chi = 0.0073(14)$	0.0014(2)
max, min peak, eÅ ⁻³	0.207, -0.186	0.229, -0.235	0.256, -0.217	0.592, -0.977
scattering factors	atomic scattering factors from <i>International Tables for X-ray Crystallography</i> , 1974; Vol. IV			

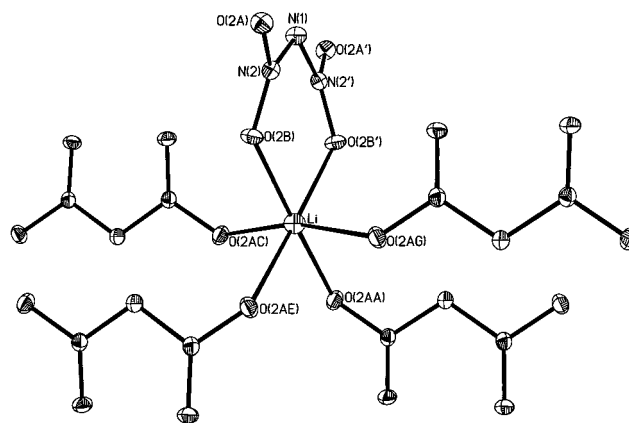
Table 2. Selected Metrical Parameters in Dinitramide Salts

parameter	NH ₄ ⁺	Li ⁺	K ⁺	Cs ⁺ ^a	
N1–N2, Å	1.376(1)	1.366(3)	1.384(3)	1.377(8)	1.383(7)
N1–N3, Å	1.359(1)	1.366(3) ^b	1.351(3)	1.360(8)	1.366(7)
N2–O2A, Å	1.236(1)	1.254(3)	1.227(3)	1.230(7)	1.219(7)
N2–O2B, Å	1.227(1)	1.227(3)	1.227(3)	1.244(7)	1.246(7)
N3–O3A, Å	1.252(1)	1.254(3) ^b	1.239(3)	1.232(7)	1.241(7)
N3–O3B, Å	1.223(1)	1.227(3) ^b	1.232(3)	1.235(7)	1.229(7)
N2–N1–N3, deg	113.20(8)	114.5(2)	114.0(2)	115.1(4)	115.3(4)
O2A–N2–O2B, deg	123.35(9)	121.5(2)	123.7(2)	123.1(6)	123.1(6)
O2A–N2–N1, deg	113.03(8)	111.7(2)	112.1(2)	113.0(5)	112.8(5)
O2B–N2–N1, deg	123.38(8)	126.6(2)	124.0(2)	123.4(5)	124.0(5)
O3A–N3–O3B, deg	122.18(9)	121.5(2) ^b	121.1(2)	122.4(5)	121.4(5)
O3A–N3–N1, deg	114.40(8)	111.7(2) ^b	113.0(2)	112.6(5)	112.7(5)
O3B–N3–N1, deg	125.14(9)	126.6(2) ^b	125.8(2)	124.9(5)	125.9(5)

^a There are two formula units in the unit cell for this structure. ^b In this structure the central nitrogen lies on a crystallographic 2-fold axis, thus both halves of the dinitramide ion are related by symmetry.

For **2**, the lithium ion is in a distorted octahedral environment of six oxygens, four of which are linked via an O2A type oxygen atom and two linked through an O2B oxygen atom forming a chelate ring.⁴⁴ The Li–O distances range from 2.028(5) to 2.200(2) Å, the *cis* angles range from 74.5(1)° to 102.1(2)°, and the *trans* angles range involving the O2A oxygen atoms are 174.0(2)°, while that for the O2B oxygen atoms is 167.7(3)°.

For **3** the coordination number for the potassium ion is nine with eight oxygen atoms and one nitrogen atom and

**Figure 1.** Coordination sphere for the lithium ion in **2**.

distances ranging from 2.810(2) to 3.065(2) Å. In **4** there are two molecules in the asymmetric unit and the two cesium ions are in very different environments. The coordination number⁴⁵ for Cs1 is 12 with an O₁₁N coordination environment and distances ranging from 3.078(4) to 3.534(6) Å. For Cs2 the coordination number is 11 with an O₉N₂ environment and distances ranging from 3.072(5) to 3.548(5) Å.

(44) In all four structures, the two oxygen atoms at either end of an anion which are *anti* to one of the N–N bonds are labeled with a suffix A, while the other two are labeled with the suffix B.

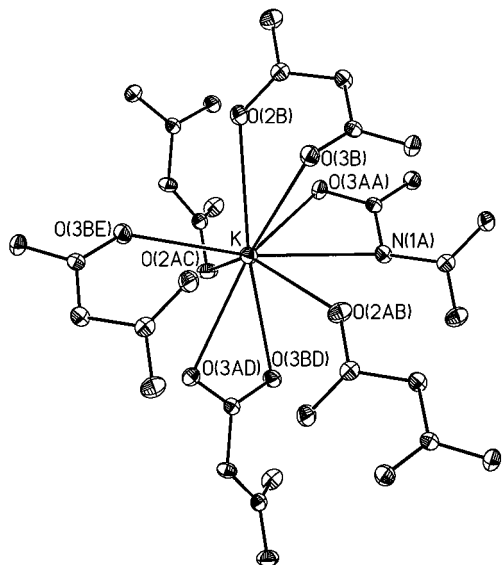


Figure 2. Coordination sphere for the potassium ion in **3**.

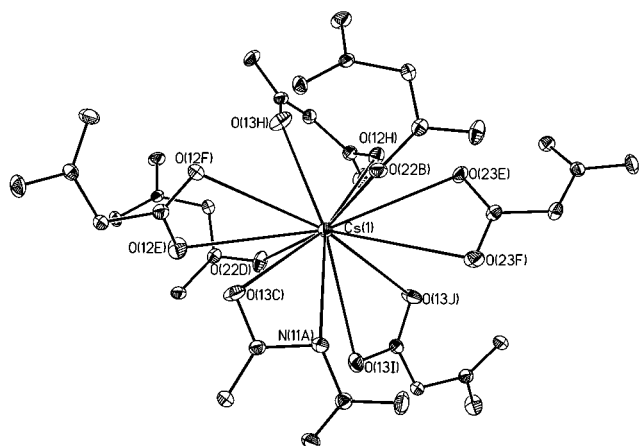


Figure 3. Coordination sphere for the Cs1 ion in **4**.

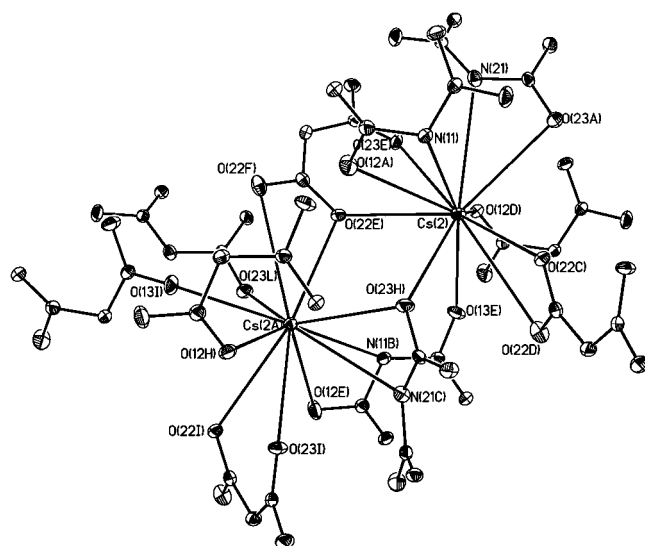


Figure 4. Coordination sphere for the Cs2 ion in **4**.

The supramolecular assembly of ammonium dinitramide is of crucial importance in determining its density and thus its usefulness as an energetic material and so is worthy of detailed examination. For **1** the four ammonium protons are involved in strong hydrogen bonds to the oxygen atoms of surrounding dinitramide ions (see Table 3). These hydrogen bonds are directed tetrahedrally to set up a three-dimensional arrangement.

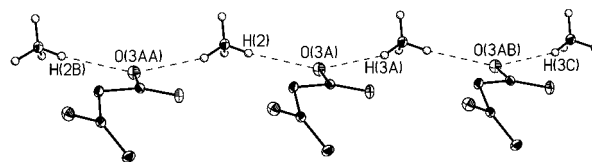


Figure 5. Propagation of hydrogen bonds along the *c* axis in **1** via H2 and H3 linkages to O3A.

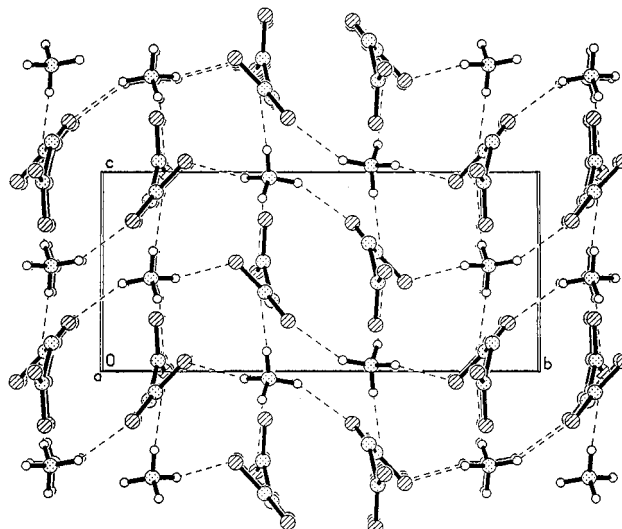


Figure 6. Hydrogen bonding occurring in the *bc* plane of **1**.

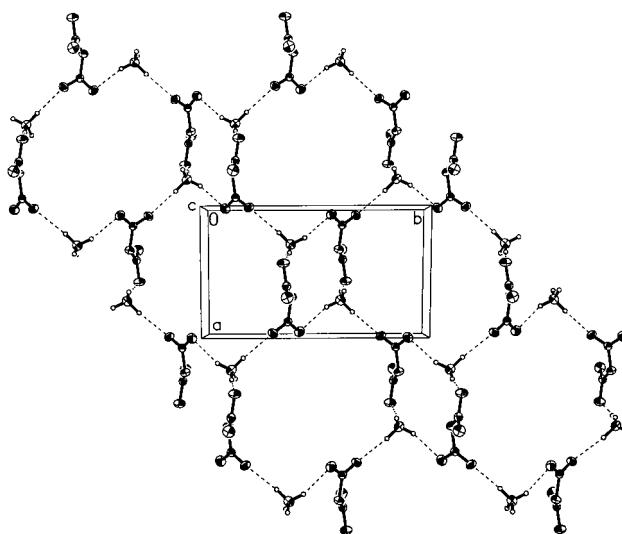


Figure 7. Hydrogen bonding network occurring in the *ab* plane of **1**.

This can best be illustrated in stages by considering the hydrogen bonding to the two nitro groups. Figure 5 first illustrates a hydrogen-bonding chain propagating along the *c* axis involving the N3–O3A–O3B nitro groups linking via O3A to two of the four hydrogen atoms (H2 and H3) of adjoining ammonium ions. N4, H2, N3, O3A, and O3B are all coplanar (maximum deviation from the plane of 0.072 Å for N3) with the hydrogen bond between O3A and H3 from the next ammonium ion making an angle of 27.3° with this plane. These planes occur at repeat distances along the *b* axis at $y = 1/8, 3/8, 5/8, 7/8$, etc.,

(45) For interactions which are of an electrostatic nature there is a somewhat arbitrary dividing line between what is or is not an interaction. This is particularly so in the case of **4**. Table S4 lists all interactions which are less than the sum of the ionic radii. Of these, the longest interaction between Cs₂–N₂₃ at 3.680(6) Å can be excluded as this distance is the result of the closer contacts between Cs₂ and O_{23A}/O_{23B}. With this exclusion the coordination numbers of Cs₁ and Cs₂ are 12 and 11, respectively.

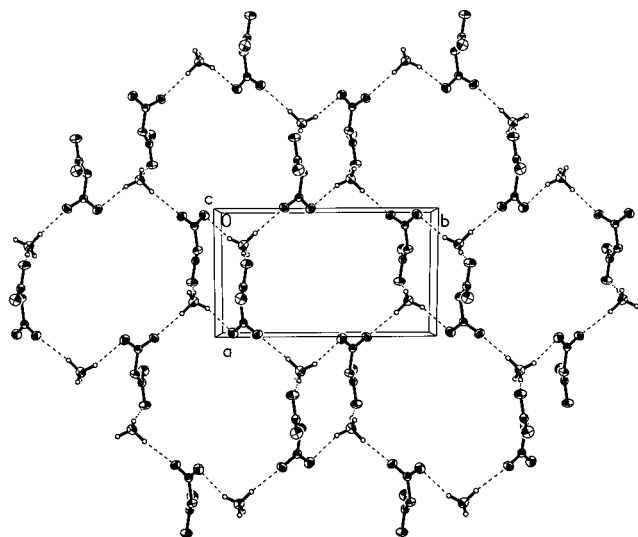


Figure 8. Hydrogen bonding network occurring in the *ab* plane of **1** translated by one unit cell length in the *a* direction.

Table 3. Hydrogen-Bonding Metrical Parameters

parameter	H···O bond length	N—H···O Angle	symmetry
N—H1···O2A	2.153	155.7	2 -x, -y, -z
N—H2···O3A	2.210	159.8	1 + x, y, 1 + z
N—H3···O3A	2.219	155.5	1 + x, y, z
N—H4···O2B	2.230	167.4	x, 0.5 - y, 0.5 + z

and are seen in edge-on projection in Figure 6 which illustrates the packing arrangement in the *bc* plane.

The nitro group, N2, O2A, and O2B, twists out of the aforementioned layers to form hydrogen bonds between O2A and O2B of one nitro group and the H1 and H4 protons of ammonium ions in adjoining layers. This hydrogen-bonding pattern repeats down the *b* axis forming an approximate helix.

The hydrogen bonding links visible in an *ab* projection form a two dimensional sheet that involves three of the four protons for each ammonium ion, H1, H2, and H4. Two interpenetrating patterns, shown in Figures 7 and 8 are needed to completely fill this projection. As can be seen from these two figures, if the patterns are translated by one unit cell length in the *a* direction they are superimposable. The fourth proton on each ammonium ion, H3, points along the *c* axis and links these sheets in the third dimension, forming two independent three-dimensional networks.

The overall geometry of the dinitramide ion is similar to that observed in both the rhenium coordination compound³⁴ and also the biguanidinium salts.³⁵ In both cases the nitro groups are twisted out of the central NNN plane and the two N—N bond lengths are asymmetric with differences ranging from 0.023 Å to >0.1 Å for the rhenium dinitramide. For **1**, **2**, **3**, and **4** the differences in the two N—N bonds are 0.017(1), 0.000, 0.033(3), and 0.017(8), respectively. Thus, with the exception of the symmetrical lithium structure, there is a long and short N—N bond (see Table 2). However in no case are the bonds as short as a N=N double bond (1.245 Å) nor as long as a N—N single bond (1.454 Å).⁴⁶ This indicates some degree of delocalization and is reflected in the NNN angles which are intermediate between expected sp² and sp³ values at 113.20(8)°, 114.5(2)°, 114.0(2)°, 115.1(4), and 115.3(4), for **1**, **2**, **3**, and **4**, respectively.

In all cases the nitro groups are twisted out of the central NNN plane by varying amounts (see Table 4). There are two

Table 4. Selected Twist and Torsion Angles for the Dinitramide Ion

parameter	NH ₄ ⁺	Li ⁺	K ⁺	Cs ⁺ (1)	Cs ⁺ (2)
twist _i ^a	25.6	15.8	20.2	23.2	10.8
twist _{ii} ^a	20.8	15.8	18.0	14.3	13.2
bend _i ^b	5.1	4.6	4.4	6.6	4.0
bend _{ii} ^b	5.3	4.6	3.3	3.6	2.1
O···O ^c	2.591	2.593	2.557	2.579	2.511
tors ^d	37.9	29.6	31.2	32.1	20.8

^a This is a measure of the amount by which the nitro group has rotated out of the N2—N1—N3 plane and is calculated by averaging the two torsion angles N—N—N—O for a particular nitro group (values brought below 90° by adding or subtracting 180°). ^b This represents the pyramidalization of the nitro N atoms with expected values of 0° for ideal sp² and 54.8° for ideal sp³ conformations. ^c The separation of the two closest nitro oxygen atoms. ^d A pseudotorsion angle defined between the two closest N—O bonds in the molecule belonging to different nitro groups, e.g., O2B—N2···N3—O3B.

possible steric and electronic factors involved here. If the central nitrogen is sp³ hybridized then a 27° rotation of the nitro groups from the central NNN plane makes them approximately perpendicular to the lone pair orbitals thereby optimizing possible conjugation.²⁹ On the other hand if the central nitrogen is sp² hybridized then one lone pair will be in the p orbital perpendicular to the NNN plane in which case a 0° twist would optimize possible conjugation for the nitro groups. From a steric point of view a twist of 0° or 90° would maximize and minimize steric repulsions between closest nitro oxygen atoms.

Ab initio and other theoretical calculations^{28–32,35} have concluded that the potential energy surface for rotation of the nitro groups is very shallow. It was found³⁵ that the important factors in producing molecular orbitals similar to those found for experimental geometries were; inequivalent N—N bond lengths, some twisting of the nitro groups, and a smaller NNN angle than that predicted from optimized geometry. From these studies it can be seen that the metrical parameters of the dinitramide ion are easily and strongly influenced by its environment. Two such important factors which should affect the overall dinitramide geometry are the presence of hydrogen-bonding interactions with the dinitramide ion and the formation of chelate rings involving the nitro oxygen atoms.

For **1–4** the nitro twist angles range from 10.8 to 25.6° while the minimum O···O contact between the nitro groups ranges from 2.511 to 2.591 Å, respectively (see Table 4). It might be expected from the above discussion that differences in the nitro twist could be correlated with metrical parameters such as the N—N bond lengths or the NNN angle. However there appears to be no obvious correlation between the dinitramide metrical parameters and the nitro twist angles. In structures **2**, **3**, and **4** the dinitramide ions form chelate rings with Li⁺, K⁺, and Cs⁺, respectively, while in **1** there is extensive and strong hydrogen bonding interactions.

Of the 23 dinitramide salts whose structures have been determined to date³⁸ (including those in this study) the lithium salt is the only example where the dinitramide ion adopts the C₂ conformation which has been predicted by theoretical calculations to be the minimum energy conformation. A comparison of the metrical parameters for the C₂ minimum energy conformation predicted³¹ by *ab initio* methods with those found for lithium salt shows similar values. In the former case the predicted N—N distance is 1.377 Å, the NNN angle is 112.9°, the N—O distances are similar at 1.254 and 1.249 Å, the two NNO angles are 123.1 and 113.6°, respectively, and the O···O pseudotorsion angle is 43.0°. The major differences between the predicted metrical parameters and those actually found are in the much greater asymmetry of the two N—O bond

(46) N—N and N=N values from: *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Volume C.

lengths at 1.254(3) and 1.227(3) Å for the internal and external N–O bonds, and a moderate increase in the NNN angle to 114.5(2)°. Apart from these differences, however, the predicted and experimental metrical parameters for the C_2 structure are remarkably similar.

The $N_3O_4^-$ ion is isoelectronic with N_2O_5 and therefore it is of interest to examine the similarities and differences between these two moieties. While N_2O_5 in the solid state has been shown⁴⁷ to consist of NO_2^+ and NO_3^- ions, in the gas phase N_2O_5 is a molecular species and its structure has been determined using electron diffraction methods.⁴⁸ In this study it was concluded that the $-NO_2$ groups were undergoing large amplitude torsion motion about a point of minimum energy corresponding to a structure of C_2 symmetry and with dihedral angles between $-NO_2$ and $-NON-$ planes of $\sim 30^\circ$. Observed metrical parameters were N=O 1.188(2) Å, N–O 1.498(4) Å, O=N=O 133.2(6)°, N–O–N 111.8(16)°. These parameters are very similar to those observed in dinitramide structures apart from the larger values observed for the O=N=O angle and the N–O length.

One of the salient points that emerges from the N_2O_5 study is the very low barrier for rotation of the $-NO_2$ groups with respect to the NON plane. A theoretical study⁴⁹ of the same molecule has concluded that “the potential energy surface along the NON bending and especially along the NO_2 twisting motions is very flat”. Thus with respect to the very low barrier for rotation of the $-NO_2$ groups with respect to the NON plane the N_2O_5 and $N_3O_4^-$ moieties are remarkably similar. The effect of this can be seen in the wide variation in observed torsion angles (see Table 4) found in structures of the NH_4^+ , Li^+ , K^+ , and Cs^+ salts of $N_3O_4^-$.

Conclusions

The crystal structures of the ammonium, lithium, potassium, and cesium salts of dinitramide illustrate the sensitivity of this anion to its local environment. Even though each has the same stoichiometry no two are isostructural and the coordination numbers and environments for the three metal salts differ markedly. The lithium ion is surrounded by six oxygen donors,

(47) (a) Grison, E.; Eriks, K.; De Vries J. L. *Acta Crystallogr.* **1950**, *3*, 290. (b) Eriks, K.; De Vries, J. L. *Acta Crystallogr.* **1950**, *3*, 293.

(48) McClelland, B. W.; Hedberg, L.; Hedberg, K.; Hagen, K. *J. Am. Chem. Soc.* **1983**, *105*, 3789.

(49) Stirling, A.; Papal, I.; Mink, J.; Salahub D. R. *J. Chem. Phys.* **1994**, *100*, 2910.

the potassium ion is nine coordinate with an O_8N coordination environment. For the cesium salt there are two formula units in the asymmetric unit and the two cesium ions has different coordination numbers and environments. One is 12 coordinate with an $O_{11}N$ coordination environment while the other is 11 coordinate with an O_9N_2 coordination environment.

For the ammonium ion there is extensive hydrogen bonding involving all four ammonium protons. Three of these protons are involved in hydrogen bonding in the ab plane forming two-dimensional sheets. Two interpenetrating patterns are required to completely fill this area. The fourth ammonium proton directed along the c axis links these sheets into two interpenetrating lattices.

With the exception of the lithium salt, there are similarities in the metrical parameters of the dinitramide ions. All have inequivalent N–N and N–O bond distances and nitro groups which are twisted from the central NNN plane by varying amounts. Both the N–N distances and the NNN angles are intermediate between expected values for an sp^3 - or sp^2 -hybridized central nitrogen atom. It has been postulated that the twisting of the nitro groups is necessary to maximize the potential for conjugation with the lone pairs of the central nitrogen atom.

The lithium salt is the only example where the C_2 conformation of the dinitramide ion, predicted by theoretical studies to be the minimum energy conformation, has been observed experimentally. There is good agreement between the predicted and experimental metrical parameters for the dinitramide ion.

Acknowledgment. R.J.B. acknowledges the ASEE-Navy Summer Faculty Research Program for the award of Summer Faculty Fellowships to the Naval Research laboratory for the summer of 1996. R.G. acknowledges the financial support from the Office of Naval Research, Mechanics Division.

Supporting Information Available: Packing diagrams (for **2–4**), hydrogen bonding diagram (for **1**), and tables of bond lengths and angles (for **1–4**), anisotropic displacement parameters (for **1–4**), hydrogen coordinates and isotropic displacement parameters (for **1**), and fractional coordinates and equivalent thermal factors (for **1–4**) (17 pages). See any current masthead for ordering and Internet access instructions.

JA9709280