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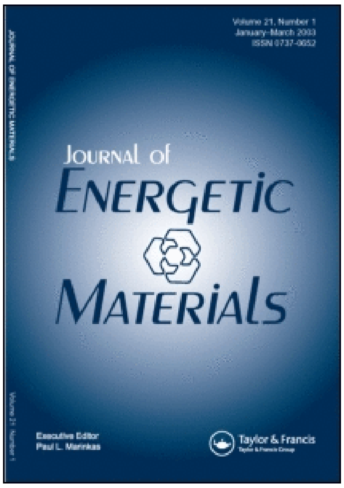

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Crystal structures and EPR spectra of nitroguanidine chloride and nitroguanidine nitrate

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CRYSTAL STRUCTURES AND EPR SPECTRA OF NITROGUANIDINE CHLORIDE AND NITROGUANIDINE NITRATE

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ABSTRACT

Crystal structures of nitroguanidine chloride and nitroguanidine nitrate were solved by x-ray diffraction. The nitroguanidine chloride crystal is triclinic, space group $P\bar{1}$, with unit cell parameters: a = 6.656(8)A, b = 6.719(9) A, c = 6.816(8)A, α = 66.8(2)°, β = 75.4(2)°, γ = 84.5(2)°, D_c = 1.7g cm^{-3}, Z = 2. The nitroguanidine nitrate crystal is monoclinic, space group $P2_1/c$ with unit cell parameters: a = 4.587(4)A, b = 6.377(6)A, c = 21.167(15)A, β = 94.7(1)°, D_c= 1.8g cm^{-3}, Z = 4. EPR spectra were detected from crystals of both compounds which had been exposed to gamma or x-radiation. The EPR spectra are assigned to NO_2 and $(NH_2)_2CN$.

INTRODUCTION

Nitroguanidine [NGu; NQ; $(H_2N)_2CNNO_2$] is a flashless propellant which is used in munitions. The structure of nitroguanidine (alpha form) is an orthorhombic lattice with 16 molecules per unit cell.[1] A recent refinement of the structure

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using neutron diffraction reports accurate H atom positions.[2] Nitroguanidine chloride and nitroguanidine nitrate are ionic compounds formed by dissolving nitroguanidine into strong hydrochloric acid and nitric acid, respectively. These "salts" crystallize as rhombohedral prisms which slowly decompose when exposed to air. (The crystals lose either HCl or HNO_2 in air, but will remain intact for several weeks when stored in a dessicator.) The crystal structure parameters of both nitroguanidine chloride and nitroguanidine nitrate were solved by x-ray diffraction. These structures are reported. Radiation initiated paramagnetic defects in both compounds were examined by using EPR (electron paramagnetic resonance).

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EXPERIMENTAL

Nitroguanidine was prepared according to the procedure described by Davis.[3] Nitroguanidine chloride crystals were prepared by dissolving 1 gram of nitroguanidine into 20 ml of concentrated hydrochloric acid at 60°C and slowly cooling the solution to room temperature. Nitroguanidine nitrate crystals were prepared by a similar procedure using concentrated nitric acid as the solvent for the nitroguanidine.

X-ray Experimental

For nitroguanidine chloride: $CH_5N_4O_2Cl$, molecular weight = 140.5, triclinic, space group $P\bar{1}$, a = 6.656(9)A, b = 6.719(9)A, c = 6.819(9)A, $\alpha = 66.8^{\circ}(2)$, $\beta = 75.4(2)^{\circ}$, $\gamma = 84.5(2)^{\circ}$, Z = 2, $d_{calc} = 1.72\ g\ cm^{-3}$. Fractional coordinates are listed in Table 1.

TABLE 1

Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Nitroguanidine Chloride (with esd's in Parentheses)

	X	Y	Z	Beq.
CL	0.2341(2)	0.7918(3)	0.2345(3)	3.2(2)
O1	-0.0121(6)	0.2872(9)	0.1840(7)	4.6(2)
O2	0.3197(7)	.3407(8)	0.0749(6)	3.8(2)
N1	0.1590(7)	0.2926(9)	0.2152(8)	3.0(2)
N2	0.1612(7)	0.2380(9)	0.4276(8)	2.9(2)
N3	0.2919(9)	0.2012(11)	0.7131(9)	3.9(2)
N4	0.5211(7)	0.2759(9)	0.3834(9)	3.4(2)
C	0.3316(8)	0.2392(9)	0.5078(9)	2.5(2)
H1	0.016(13)	0.298(13)	0.252(13)	
H2	0.025(13)	0.263(12)	0.521(12)	
H3	0.373(14)	0.188(13)	0.813(14)	
H4	0.640(14)	0.255(12)	0.464(13)	
H5	0.183(14)	0.189(14)	0.797(14)	

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1594 independent data were measured, out to a maximum sin θ/λ of 0.70, with a computer-controlled diffractometer (NICOLET P3F) using MoKα radiation. The data were collected using the θ-2θ scan technique. A constant scan rate of 29.3°/min. was used making it possible to collect a full set of data in less than eight hours. With the high rate of speed it was possible to collect a full set of data before the crystal started to decay. The structure was solved by direct methods using the symbolic addition procedure for centrosymmetric crystals.[4] Full-matrix least-squares refinement[5] was carried out using 622 reflections for which $|F_o|>4\ _F$,>4.0 or <50.0 giving a final R-factor of 5.6% (Rw = 6.8%). The final R-factor for the full set of 1594 reflections was 9.2% (Rw = 8.5).

For nitroguanidine nitrate: $CH_5N_5O_5$, molecular weight = 167.1, monoclinic, $P2_1/c$, a = 4.585(4) A, b = 6.377(6) A, c = 21.168(15) A and β = 94.7(1)$^{\circ}$, Z = 4, d_{calc} = 1.80 g cm^{-3}. Fractional coordinates are listed in Table 2.

801 independent reflections were collected to maximum sin θ/λ of 0.54, under the same conditions used for the chloride crystal. The structure was also solved by direct methods[4] and refined by full-matrix least-squares[5] on the full set of 801 reflections. The final R-factor was 5.1% (Rw = 7%).

EPR Experimental

Paramagnetic defects were produced in the crystals by using ^{60}Co gamma radiation at 77K or by using ca. 0.5 Mrad of

TABLE 2

Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Nitroguanidine Nitrate (with esd's in Parentheses)

	X	Y	Z	Beq
C	0.8972(6)	1.0982(4)	0.3757(1)	2.8(1)
N1	0.8222(5)	0.8242(4)	0.2956(1)	3.3(2)
N2	0.9674(5)	0.9102(4)	0.3483(1)	3.0(2)
N4	0.6922(6)	1.2199(4)	0.3508(1)	3.9(2)
N3	1.0534(6)	1.1422(2)	0.4279(1)	3.7(2)
N5	0.5477(5)	0.6709(4)	0.4362(1)	3.3(2)
O1	0.6065(5)	0.9077(3)	0.2707(1)	4.2(2)
O2	0.9286(5)	0.6622(4)	0.2781(1)	5.1(3)
O3	0.7579(5)	0.5640(4)	0.4560(1)	4.8(3)
O4	0.4764(5)	0.8247(3)	0.4662(1)	5.3(3)
O5	0.4106(5)	0.6288(4)	0.3847(1)	4.4(3)
H1	1.122(7)	0.823(6)	0.366(1)	
H2	0.660(8)	1.322(6)	0.372(2)	
H3	0.599(8)	1.191(6)	0.312(2)	
H4	1.227(7)	1.061(6)	0.447(2)	
H5	1.021(8)	1.241(6)	0.445(2)	

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x-radiation at room temperature. An IBM ER-200 x-band spectrometer was used to record the EPR spectra. Angular dependent hyperfine couplings of the EPR signals were examined. The instrument settings were: modulation frequency, 100 KHz; modulation amplitude, 2.0 Gpp; microwave power, 2 mw; magnetic field scan, 200 G.

RESULTS

The results of the x-ray analysis are shown in Figures 1 and 2. Bond lengths and angles for the two molecules are compared in Table 3. In both compounds there is some delocalization of the N2-C double bond throughout the entire molecule. A statistical study done on several other nitramine structures has shown that for the N-NO_2.moiety the average N-N-O angle is 117° while the O-N-O angle is significantly larger at an average value of 125°. For the two structures reported here the average N-N-O angle is 117.2(4)° and the average O-N-O angle is 125.5(4)°. The nitroguanidine molecule is planar in both crystals. In the nitrate structure the nitrate moiety itself is also planar. The closest atomic approaches between the two planes are N5...N2 at 3.17 A and O5...N1 at 3.04 A.

In the EPR experiment single crystals of nitroguanidine chloride and nitroguanidine nitrate were irradiated at 77 K with 30 kilorads of gamma radiation from a cobalt-60 radiation source. Each of the crystal samples was consecutively

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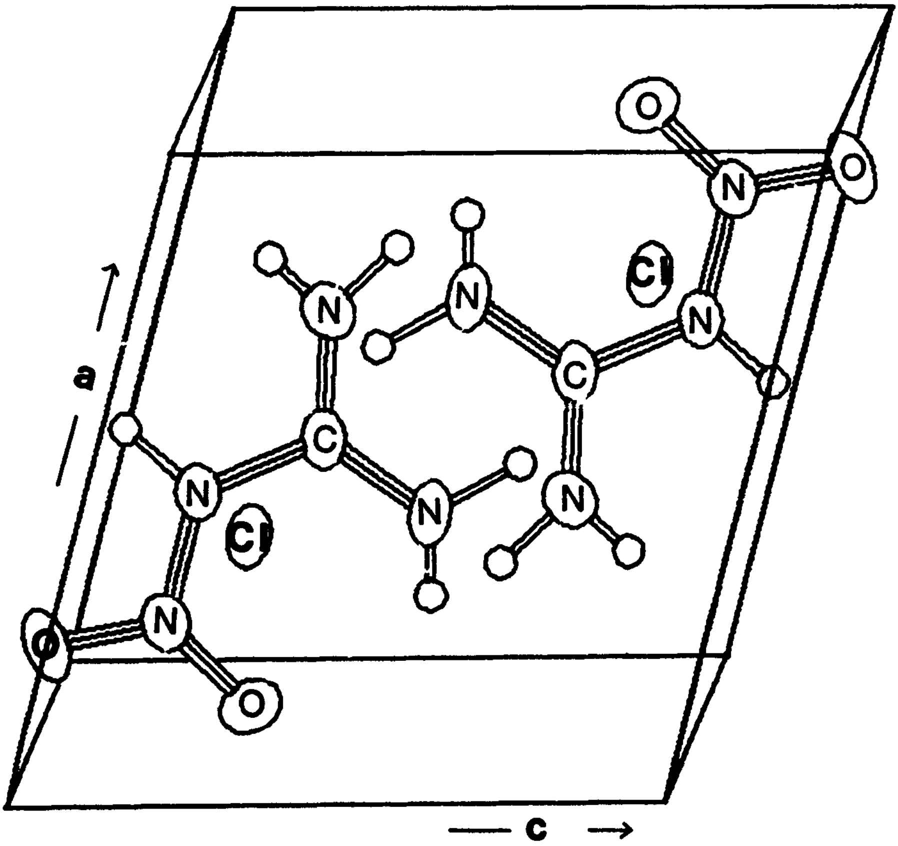

FIGURE 1

Contents of one unit cell for nitroguanidine chloride.

The view shown is drawn looking down the b axis.

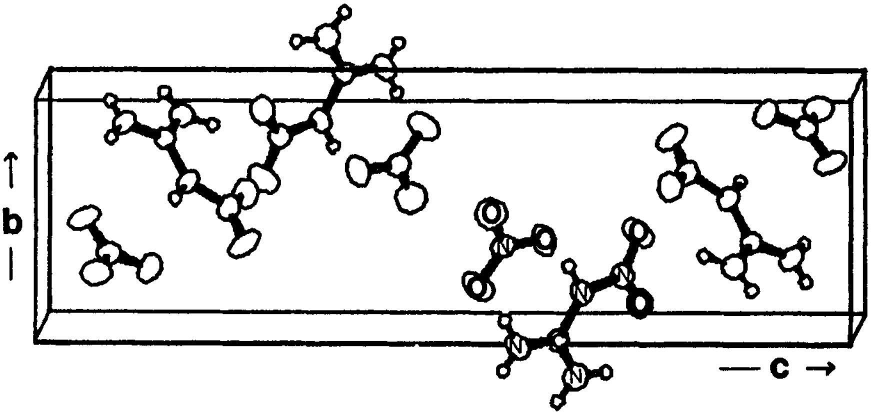

FIGURE 2

Contents of one unit cell for nitroguanidine nitrate. The view shown is drawn with the a axis coming out of the page.

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TABLE 3

Selected Bond Lengths and Bond Angles

Bonds	Nitroguanidine Chloride	Nitroguanidine Nitrate
C-N3	1.281(7)	1.297(4)
C-N4	1.314(7)	1.297(4)
C-N2	1.379(7)	1.380(3)
N2-N1	1.350(6)	1.367(3)
N1-O1	1.216(6)	1.206(3)
N1-O2	1.214(6)	1.213(3)
N5-O3		1.226(3)
N5-O4		1.228(3)
N5-O5		1.242(3)
N2-H5	1.01(8)	0.96(4)
Angles		
N4-C-N3	122.3(5)	123.2(3)
N4-C-N2	122.7(5)	122.3(3)
N3-C-N2	115.0(5)	114.4(2)
C-N2-N1	126.4(4)	125.2(2)
N2-N1-O1	114.3(4)	120.4(2)
N2-N1-O2	120.0(4)	114.2(3)
O1-N1-O2	125.7(5)	125.4(3)
O3-N5-O4		120.2(4)
O3-N5-O5		120.5(4)
O4-N5-O5		119.3(4)

transferred to the EPR cavity and EPR spectra were recorded at 77 K. A three line EPR spectrum was observed from both nitroguanidine chloride and nitroguanidine nitrate. (Spectra of reference positions of the crystals are shown in Fig. 3. a-b). The three lines have an intensity ratio of 1:1:1 and are each attributed to a ^{14}N hyperfine coupling (I=1). The radical assigned to these spectra is NO_2. Each crystal was rotated in the magnetic field to record the orientation dependence of the EPR spectra. The ^{14}N principal values and direction cosines calculated from the nitroguanidine chloride spectra and nitroguanidine nitrate spectra, respectively, are given in Table 4. The maximum principal ^{14}N coupling in the NO_2 of nitroguanidine nitrate was found to be ca. 10 G greater than the same coupling in the nitroguanidine chloride. When the crystals were warmed to room temperature the EPR signals from the NO_2 radicals decayed.

A separate EPR experiment was performed by exposing crystals of nitroguanidine chloride and nitroguanidine nitrate to x-radiation at room temperature. In the case of nitroguanidine nitrate no free-radical signals were detected, but the nitroguanidine chloride crystals at room temperature gave EPR signals which persisted for several hours. Fig. 4a is attributed to EPR signals from three different free-radicals: (1) Radical I is assigned to NO_2 which has weak broad signals at room temperature, (2) Radical II has a pattern of 9 EPR lines and (3) Radical III has two visible lines in this

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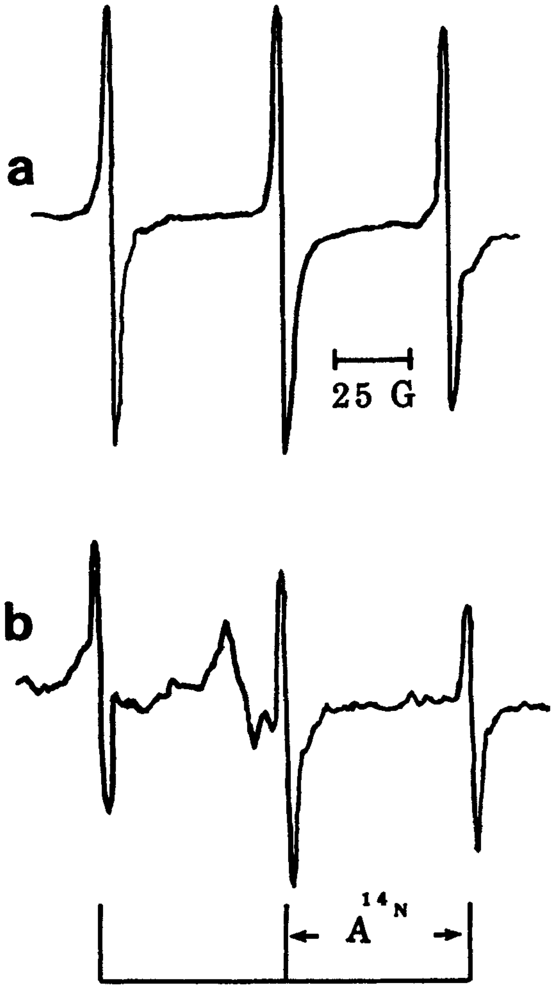

FIGURE 3

(a) The first-derivative EPR spectrum at 77 K of NO_2 in a Nitroguanidine Chloride Crystal is shown. The orientation is H_0 parallel to the Y reference axis. (b) The first-derivative EPR spectrum of NO_2 in a Nitroguanidine Nitrate crystal is shown. The orientation is H_0 parallel to the Z reference axis. The radicals were formed by exposing these crystals to 30 Krads of γ-radiation at 77 K.

TABLE 4

Principal ^{14}N Hyperfine Couplings of NO_2 in γ-irradiated Samples

Nitroguanidine Chloride

$A^{14}N$(Gauss)	Direction Cosines[a,c]		
	X	Y	Z
44.2	-0.5867	-0.5395	-0.6039
57.6	+0.7190	-0.6901	-0.0820
61.8	+0.3725	+0.4823	-0.7929

Nitroguanidine Nitrate

$A^{14}N$(Gauss)	Direction Cosines[b,c]		
	X	Y	Z
49.7	-0.6380	+0.2734	-0.7198
53.4	+0.2704	+0.9549	+0.1233
70.0	+0.7211	+0.1158	-0.6831

a Space group $P\bar{1}$ yields a single EPR site

b Space group $P2_1/C$ yields two EPR sites

c The EPR reference axes (XYZ) are arbitrary

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spectrum. Because the EPR lines of NO_2 at room temperature are broadened they did not significantly interfere with the other EPR signals and it was possible to analyze the 9 line pattern of Radical II in Fig. 4a (Analysis of Radical III was not possible because of overlapping with lines from Radical II).

The spectrum of Radical II is attributed to two different ^{14}N hyperfine couplings. The orientation dependence of these couplings was analyzed to give the ^{14}N principal values for Radical II (listed in Table 5). This radical is believed to form from the guanidine portion of the molecule since there are two nitrogen-14 couplings. A possible structure for this radical is $(H_2N)_2CN$ where the amino groups are conformationally inequivalent resulting in the smaller ^{14}N coupling from only one of the amino nitrogens.

When the crystal was cooled below room temperature the intensity of the NO_2 EPR lines increased. This is shown in Fig. 4a-c. The temperature dependence of the intensities and linewidths is reversible. Other researchers have reported a similar temperature dependence of EPR signals from NO_2 in polycrystalline N_2O_4.[6] The linebroadening effect possibly involves a nuclear relaxation mechanism similar to that suggested for EPR signals from radiation initiated free radicals in cyanoguanidine.[7]

DISCUSSION

The crystal structure of nitroguanidine (neat) indicates that the four protons of the neutral nitroguanidine molecule

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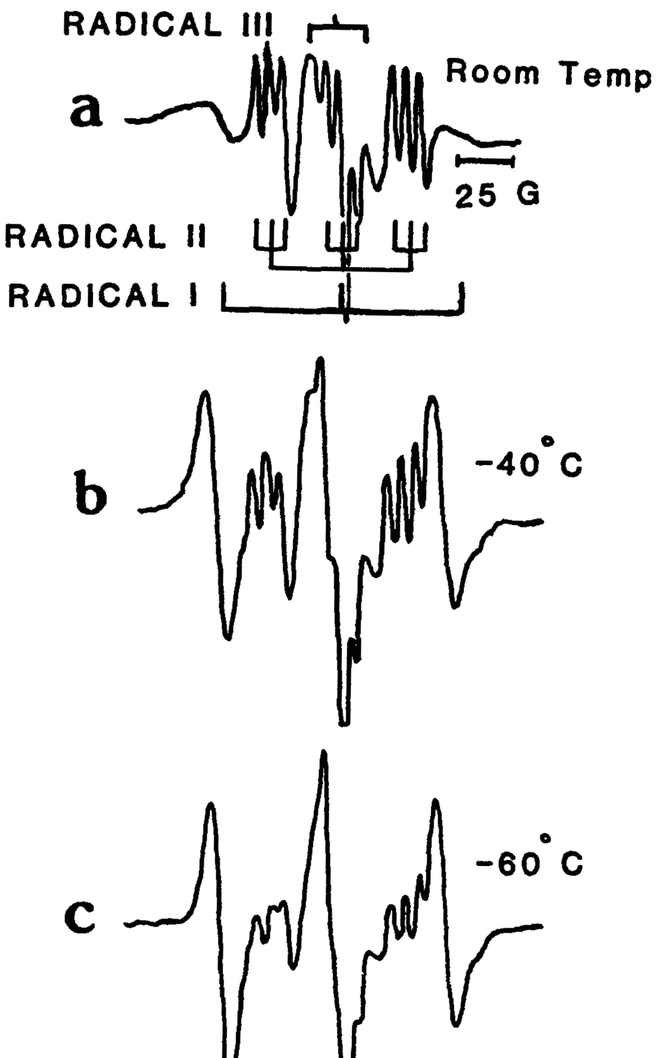

FIGURE 4

The first-derivative EPR spectrum of x-irradiated Nitroguanidine Chloride is shown at the orientation with H_o parallel to the direction [-.574,.819,.000]: (a) at room temperature, (b) at -40°C, and (c) at -60°C. The signal linewidths of Radical I (NO_2) show a reversible temperature dependence.

TABLE 5

Principal ^{14}N Hyperfine Couplings of Radical II in x-irradiated Nitroguanidine Chloride

$A\ ^{14}N$ Gauss	Direction Cosines		
	X	Y	Z
28.4	-0.0634	+0.1591	-0.9852
30.1	+0.9947	-0.0703	-0.0753
47.3	-0.0813	-0.9847	-0.1538
4.8	+0.5626	-0.8218	-0.0898
6.2	+0.0097	-0.1021	+0.9947
9.6	+0.8267	+0.5605	+0.0495

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are located on the amino nitrogens.[1] The formation of nitroguanidine nitrate and nitroguanidine chloride takes place by protonation of the nitroguanidine group. This forms the positive nitroguanidine ion which coordinates with the negative nitrate or chloride ion. In solution there is evidence for protonation at the amino nitrogen position when the amino protons are replaced with methyl groups.[8] In the solid state chloride and nitrate compounds the nitroguanidine protonates at the imino nitrogen position (N2). In nitroguanidine nitrate the N2—H5 bond length is .96 A and in nitroguanidine chloride the N2-H5 bond length is 1.01 A.

The packing of both crystals is influenced by hydrogen bonding. In the chloride crystal the chlorine ion acts as an acceptor in two hydrogen bonds. In one N2 is the donor with an N...Cl distance of 2.99 A and N-H...Cl angle of 161.1° In the other N4 is the donor with an N...Cl distance of 3.27 A and N-H...Cl angle of 152.9°. In the nitrate crystal there are two intermolecular guanidine-nitrate hydrogen bonds. In one N2 is the donor and O5 is the acceptor with an N...O distance of 2.77 A and an N-H...O angle of 168.3°. In the other hydrogen bond N3 is the donor and O4 is the acceptor with an N...O distance of 2.87A and an N-H...O angle of 158.6°. There is also a short O4...O4 intermolecular approach at 2.65 A.

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In a similar compound, guanidinium chloride, the analogous N...Cl average distance is 3.303 A.[9] In the compound aminoguanidine chloride the N...Cl distance is 3.74 A.[10]

The EPR results indicate that nitroguanidine chloride is more susceptible to radiation initiated radical formation than is nitroguanidine nitrate. At low temperatures (77 K) both compounds exhibited radical formation with exposure to mild gamma radiation (30 Krads). In both compounds the radical observed is attributed to NO_2 (see Fig. 3). This radical has been observed in other EPR experiments.[11] Exposure of these compounds to heavier dosages (1 Mrad) of γ-radiation at 77 K produced no additional free radicals in nitroguanidine nitrate, but a very complex EPR spectrum was observed in nitroguanidine chloride which has EPR lines attributed to chlorine-35 and chlorine-37 hyperfine couplings. (This EPR spectrum is not shown. The complexity of the spectrum requires more analysis.) At room temperature, exposure to x-radiation produced radicals in nitroguanidine chloride only (see Fig. 4). A suggested assignment of the radical structure is $(H_2N)_2$ CN since couplings from two inequivalent nitrogens are observed. The C-N3 bond in nitroguanidine chloride (1.288 A) is much shorter than the C-N4 bond (1.313 A). The unpaired electron formed at the site of homolytic bond cleavage (-N2 N1-) would favor delocalization to the shorter C-N3 bond. This suggests that the smaller ^{14}N hyperfine coupling in Table 5 is from N3 and the larger ^{14}N hyperfine coupling is from N1.

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