Structures of nitroso- and nitroguanidine X-ray crystallography and computational analysis

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The X-ray structures of solid nitroguanidine (ngoH):orthorhombic, $Fdd2$, $a = 17.6181(14)$, $b = 24.848(2)$, $c = 3.5901(4)$ Å, $V = 1571.7(3)$ Å^3, $Z = 16$ and nitrosoguanidine (ngH); monoclinic, $P2_1/n$, $a = 3.64510(10)$, $b = 11.746(2)$, $c = 8.6483(14)$ Å, $\beta = 99.167(2)°$, $V = 365.55(9)$ Å^3, $Z = 4$ have been determined utilizing single crystal X-ray diffraction methods. The results are compared with the most stable gaseous configurations derived from *ab inito* calculations. The lowest energy calculated configuration for the ligands and experimentally observed crystal structures are in excellent agreement. In the solid state, both the ngoH and ngH contain discrete molecules in their unit cells which are planar (within experimental error), in the diamine configurations and are structurally identical except for an oxygen atom. In solid ngH, two ligand molecules have four nitrogen atoms arranged in a plane such that they are suitable for coordination to a nickel ion (1.945, 2.064 Å), when it is at the 1/2, 1/2, 1/2 unit-cell position giving the observed complex. As far as we are aware, this is the first instance in which a *ligand* crystal structure is essentially the same, with minor distance, angle and torsion angle changes, as the complex it forms and suggests some potentially unique properties and applications for this material.

KEY WORDS: Nitrosoguanidine; nitroguanidine; ligand; *ab initio* calculations.

Introduction

Nitrosoguanidine (ngH), prepared by the reduction of nitroguanidine (ngoH)[1] has been known for many years.[2] It is often used in a popular teaching demonstration because it explodes on heating with little danger to the demonstrator since essentially no heat is generated. Thus, a small quantity may be ignited in the palm of the hand giving an immediate puff of smoke without any significant sensation of heat.

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Nitrosoguanidine is an especially interesting ligand because in aqueous solution it forms an extremely stable Ni(II) complex[3] which is similar in color and insolubility to [Ni(dmg)$_2$]° and may contain weak metal–metal bonds. The ligand has not been studied in any detail in its reactions with transition metal ions and its mode of coordination is not known. The extreme insolubility of its reaction products may be the reason for this lack of interest. The ligand has many potential modes of coordination including the formation of an intramolecular hydrogen bond as is so prominent with α-dioximes[4] and α-amineoximes.[5]

With the organic compounds themselves we were primarily interested in seeing if the planar

character of the conjugated molecule remains the most stable in the gas state (as determined by MO-calculations) and if the X-ray structure determination gives the same configuration. This would indicate the relative importance of hydrogen bonding and lattice energies in the crystal structure. Nitrosoguanidine is an ampholyte and may exist in several neutral and ionic forms in solution. As a conjugated system, a hydrogen atom may locate so as to give structures other than the gem-diamine found with ngoH. The accurate location of the hydrogen atoms in the ngH crystal structure was especially important to see if it is predicted by *ab initio* calculations. Hydrogen atoms can be easily located by modern diffraction methods on molecules of medium to moderate molecular weight. In addition, we wanted to calculate the electron densities on the coordinating nitrogen and oxygen atoms and explain the extreme lack of coordinating ability of ngoH. Finally, a comparison of the bond distances and bond angles between the MO and X-ray structural determinations was needed to be able to estimate the predictability of the MO calculations. These were to be applied to studies on the nickel(II) complex of ngH whose X-ray structure proved to be almost impossible due to the extreme difficulty of producing single crystals.

Thus, this paper presents and discusses structure determinations of ngH and ngoH by *ab initio* MO-calculations and X-ray diffraction studies. A subsequent manuscript will apply these results in similar studies on the nature of the Ni(II)-complex of ngH.

Experimental

Nitroguanidine was obtained commercially and recrystallized from hot water (MP 246-8°). Nitrosoguanidine was prepared from it by reduction with Zn(dust) in an aqueous NH_4Cl solution as previously described.[6,7] It was difficult to determine the best molar amount of reductant because its composition was highly variable. The product was recrystallized from warm water solution, MP 160°(dec). Single crystals of both compounds were prepared by slow evaporation of aqueous solutions held at about 5°C. Nitrosoguanidine slowly decomposes in warm water solution, the rate depending on trace amounts of transition metal ions.

The products of the thermal decomposition of ngH were found to be dinitrogen and urea. No N_2O or other oxide of nitrogen could be found. Decomposition was carried out under vacuum (0.1 mm initial) and in an atmosphere of argon. Initiation was by external heating of a portion of the all glass reaction vessel. The reaction was self-sustaining only in an atmosphere of air or argon. The gases produced were cooled to dry-ice temperature and the gas remaining analyzed with a Nuclide RMS-16 mass spectrometer. The solid product was isolated and its IR spectra compared to that of an authentic sample of urea to which it was nearly identical. Traces of water were also identified by M.S. suggesting that a portion of the urea may be converted to cyanamide. In water solution ngH slowly decomposes to N_2, NH_3 and CO_2 and more complex substances. At some stage it probably releases the unstable molecule nitrosourea (nu) which has been captured by Co(III) as $[Co(ng)_2(nu)]°$.[8]

The calculated X-ray powder diffraction patterns were obtained using the structural parameters obtained from the single crystal X-ray solutions of the metal free ligand, ngH. X-ray powder patterns were calculated using DISPO from the NRCVAX[9] series of programs. These calculations on the ligands gave reasonable agreement with the measured powder spectra.

In conjunction with the experimental study, conformational and configurational equilibrium structure preferences were calculated on the ligand at the MP2(full)/6-31G* level.[10] Isomer energies, rotational barriers, excitation energies, tautomer energies were determined at levels up to QCISD(T)/6-311G**//MP2(full)6-31G* + ΔVZPE(MP2(full)/6-31G*). Calculations were carried out with Gaussian98[11] with a cluster of Alphaserver computers using direct methods.

Infrared spectra were collected on a Nicolet 500 FT-IR spectrometer. Nitrosoguanidine in methanol solution was evaporated on a AgCl disk and dried over $CaCl_2$ before the absorption measurement.

Table 1. Crystallographic Data and Refinement

	ngH	ngOH
Crystal color/needles	Yellow/needles	Colorless/needles
Empirical formula	C1 H4 N4 O1	C1 H4 N4 O2
Formula weight	88.07	104.07
Temperature	273(2) K	293(2) K
Wavelength, type	0.71073 Å, Mo K$_\alpha$	1.54056 Å, Cu K$_\alpha$
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, Fdd2
Unit cell		
a	3.64510(10) Å	17.6181(14) Å
b	11.746(2) Å	24.848(2) Å
c	8.6483(14) Å	3.5901(4) Å
β	99.167(2)°	
Volume	365.55(9) Å^3	1571.7(3) Å^3
Z, calculated density	4, 1.600(2) mg/m^3	16, 1.759(2) mg/m^3
Absorption coefficient	0.13 mm^{-1}	1.36 mm^{-1}
$F(000)$	184.10	867.64
Crystal size	0.2 mm × 0.2 mm × 0.2 mm	0.15 mm × 0.15 mm × 0.45 mm
Theta range for data collection	2.94, 23.0°	1.15–74.8.0°
Limiting indices	$-4 \le h \le 3, 0 \le k \le 12, 0 \le l \le 9$	$-22 \le h \le 22, -30 \le k \le 30, -3 \le l \le 4$
Reflections collected/unique	1426/518	2172/634
R(int)	0.032	0.029
To theta/completeness	23.0°/99%	74.8°/99.0%
Maximum and minimum transmission	0.842, 0.755	0.816, 0.569
Refinement method	Full-matrix on F^2	Full-matrix on F^2
Data/restraints/parameters	479/0/72	470/0/81
Goodness-of-fit on F^2	1.107	1.176
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.030, wR = 0.087$	$R1 = 0.029, wR = 0.045$
R indices (all data)	$R1 = 0.032, wR = 0.090$	$R1 = 0.029, wR = 0.045$
Largest difference peak and hole	$-.173/0.128$ e/Å^3	$-.180/0.160$ e/Å^3

The 300 MHz ^{1}H NMR spectra of ngH and ngoH were obtained in d^6-DMSO solution using TMS as the standard. The UV-Vis spectra were obtained using saturated aqueous solutions.

The X-ray structures were determined on Enraf-Nonius CAD4 or SMART CCD[12] instruments, solved by SHELXS, SHELXL[13] and the results have been deposited in the CCDC database. A summary of the data collection conditions, the crystal parameters and the agreement factors are given in Table 1.

Results

X-ray Crystallography

In both materials the unit cell contains discrete molecules connected extensively by hydrogen bonds. In ngoH there is one intramolecular H-bond between HN3 and O2 with an O—H distance of about 1.9 Å. ORTEP[14] drawings are given in Fig. 1 with the anisotropic temperature factors drawn at the 50% level. The numbering system provided there is used throughout this paper.

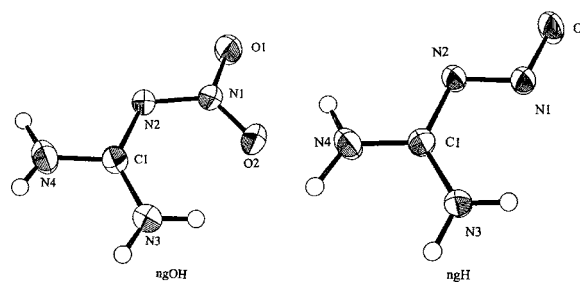Bond distances and angles are given in Table 2(a) and (b). The latter agree well with an

Fig. 1. X-ray ORTEP drawings with naming system, 50% ellipsoids.

Table 2. Bond Distance and Bond Angles for ngoH and ngH

	ngoH	ngH
(a) Bond distances (Å)		
N1—N2	1.331(2)	1.302(2)
C1—N2	1.374(3)	1.391(2)
C1—N3	1.325(2)	1.315(2)
C1—N4	1.316(3)	1.309(2)
O1—N1	1.243(2)	1.260(2)
O2—N1	1.237(3)	–
N3—H1N3	0.91(2)	0.93(3)
N3—H2N3	0.75(3)	0.91(3)
N4—H1N4	0.90(2)	0.91(2)
N4—H2N4	0.85(3)	0.83(3)
(b) Bond angles (°)		
C1—N2—N1	118.7(2)	110.8(1)
N2—C1—N4	112.3(2)	124.8(2)
N2—C1—N3	128.3(1)	115.0(2)
N3—C1—N4	119.4(2)	120.2(2)
N2—N1—O1	124.9(2)	113.5(1)
N2—N1—O2	115.1(2)	–
O1—N1—O2	120.0(1)	–
C1—N3—H1N3	118.(2)	122.(2)
C1—N3—H2N3	120.(2)	118.(2)
C1—N4—H1N4	121.(1)	123.(2)
C1—N4—H2N4	123.(2)	121.(1)
H1N4—N4—H2N4	116.(2)	115.(3)
H1N3—N3—H2N3	122.(2)	115.(4)

Table 3. Least-Squares Planes

	Distances (Å) to the plane	
	ngoH[a]	ngH[b]
N2	−0.009(4)	−0.017(2)
C1	0.005(6)	0.000(2)
O1	−0.008(2)	−0.006(2)
O2	0.025(3)	
N1	0.007(4)	0.025(2)
N4	−0.049(5)	−0.012(3)
N3	0.074(4)	0.016(3)
χ^2	486.8	366.2

[a]Equation of the plane: $8.863(16)X − 0.057(21)Y + 3.1027(19)Z = 6.104(14)$.
[b]Equation of the plane: $3.2456(13)X + 0.460(10)Y + 2.645(7)Z = 2.988(3)$.

earlier determination.[8] Of special interest is the degree of planarity in the two compounds and is provided in Table 3. For ngoH the structure is very similar to that previously reported;[15−17] but our interest was primarily in the position of the hydrogen atoms and in comparison with ngH. Thus, the hydrogen atoms were treated isotropically with variable temperature factors in the least-squares analysis. The agreement factor in both structures was quite good, allowing confidence in the hydrogen atom positions. The bond distances to hydrogen atoms may be somewhat shorter than those found in the neutron scattering study[15] or those calculated because of the unsymmetrical distribution of electrons in the bond. There is a good agreement with the previous X-ray structure[16] and with the *ab initio* calculations previously carried out on ngoH. With ngH the four hydrogen atoms are also on the amine-nitrogen atoms, the molecule is highly planar for all heavy atoms and the nitroso-oxygen is *trans* to C1. The bond distances and an-

gles are similar to those in ngoH, slightly shorter in general but with C1—N1 slightly elongated. The bonds to hydrogen atoms vary slightly as do their temperature factors but all values are reasonable based on the parameter insensitivity to X-ray data.

Computational analysis

Sixteen geometries for ngH were optimized at MP2(full)/G-31G* and resulted in stable minima. The final results are summarized in Fig. 2 in pictorial form. Eight of these had one hydrogen atom located on the nitroso-oxygen and eight had the hydrogen atom attached to the central nitrogen atom. A final form investigated was the diamine structure. It turned out to be the most stable. A drawing of it is given in Fig. 4. It is noteworthy that all of the structures remained highly planar except #1. This illustrates the importance of conjugation in this molecule.

Figure 3 shows drawings of the ngoH molecule obtained using *ab initio* optimized parameters. In this case, six structures that were examined all reached a steady state without imaginary temperature factors. In three cases, a hydrogen atom was located on an oxygen atom and in two it was on the central N atom. In one case, the molecule was the diamine tautomer. Again, the molecules remained very planar on optimization.
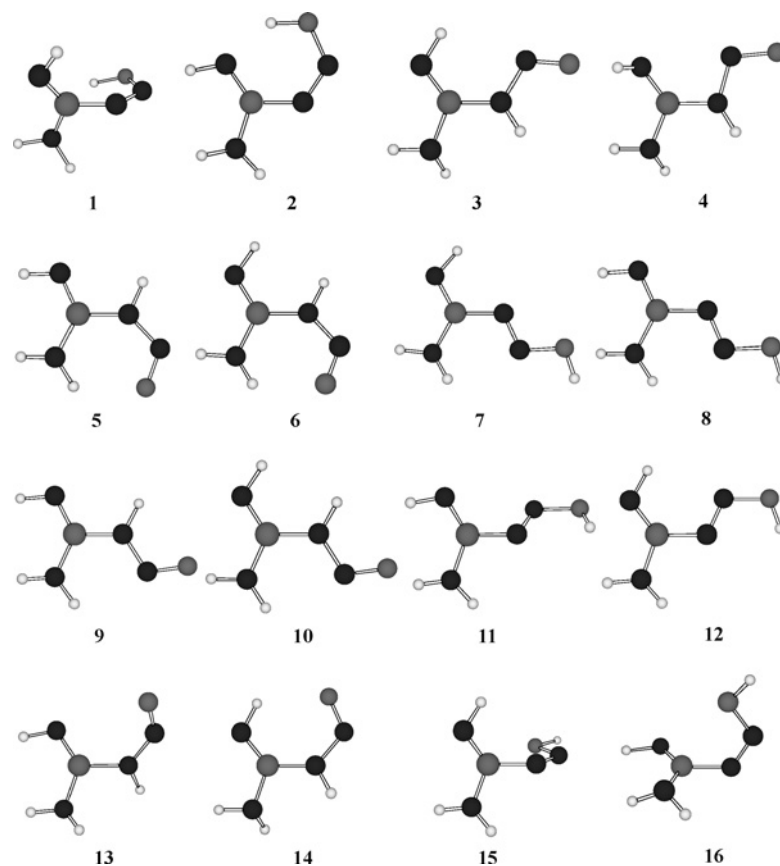
Fig. 2. Optimized geometries for nitrosoguanidine (gas state).

Table 4 contains the calculated relative energies of formation and other thermodynamic properties of the ngH and ngoH conformations investigated. The standard in both cases is the diamine structure that is the most stable for each molecule. The "cttc" sequence defines the *cis–trans* geometry starting from a unique hydrogen atom on the left. There is no clear preference for having the hydrogen atom on oxygen or the central nitrogen atom in either molecule. There is however a clear preference for the diamine structure in both cases. This amounts to at least 2.7 and 10.2 kcal/mol for ngH and ngoH, respectively. For isodemic reactions (same number and type of bond) to which these comparisons nearly subscribe the computation of thermodynamic quantities is likely to be fairly precise.[18] The entropy changes and the

corrections for zero point energies are small and nearly constant for the different structures and have not been used in the calculations. Intramolecular hydrogen bonding may play a major part in stabilizing structure #2, which is very similar to the "most stable" isomer.

The most stable structures of ngH and ngoH as obtained from the MO-calculations are given in Fig. 4. They are essentially identical except for the additional oxygen atom in the latter. The bond distances and angles resulting from these calculations are given in Table 5.

A list of the calculated relative charges on the atoms of both molecules is given in Table 6. The addition of a second oxygen atom to the nitroso-nitrogen causes very little change in the rest of the molecule. As expected, the nitrogen to which it is
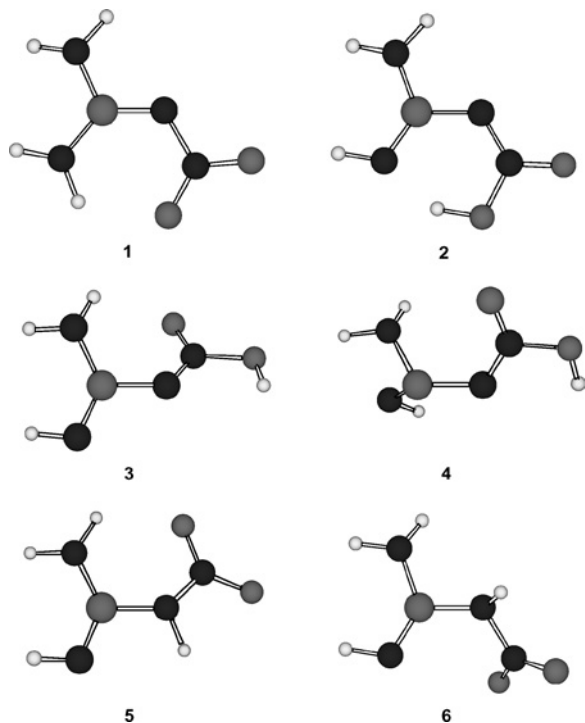
Fig. 3. Optimized geometries for nitroguanidine.

attached does become more positive which would oppose its coordination to a positive metal ion.

The X-ray powder diffraction patterns, for identification and purity determination, were sharp and intense. For ngH it consisted of the following d-spacings: 3.15, 3.45, 4.82, 3.04, 6.79, 5.80, 3.09 Å; ngoH: 4.90, 4.15, 2.91, 3.62, 2.33, 2.00 Å, in order of decreasing intensity. These values were in good agreement with the spectra calculated from the single crystal X-ray structure parameters.

The proton NMR spectra in d^6-DMSO were quite diffuse especially with ngoH, indicating extensive intramolecular exchange or exchange with water impurities in the solvent. The observed absorptions (relative intensity) at $300°$K were as follows: ngH: 7.734(1), 7.458(1), 7.089(1); ngoH: 7.470(1) ppm downfield versus TMS. Rapid proton exchange is expected due to the extensive delocalization suggested by the extreme planarity of the molecule and the relative shortness of the bonds between heavy atoms.

The UV-Vis spectra of ngH and ngoH in water are very similar. In order of decreasing intensity the peak absorptions are at 298, 285, 221, and 404 for the former and they are 298, 285, 221 nm at $295°$ for the latter. Only the weak shoulder at lower energies distinguishes the nitroso compound and gives it its faint yellow color. While it is known that the color of ngH—water solutions is sensitive to pH and temperature,[1] structural and or ionization modifications in solution have not been identified.

Discussion

The computational studies showed considerable differences in the energy of formation of the isomers. Internal hydrogen bonding did not play a significant role. With both compounds there was a clear preference for the diamine structure and furthermore the essentially planar state was strongly retained. The calculated bond distances and angles were nearly the same for ngH and ngoH and showed an average deviation (neglecting hydrogen atoms) of 0.010 Å and 4.4°. The degree of planarity was hardly distinguishable. The entropy of formation was small for all structures and so the free energy changes paralleled those of the enthalpy.

The agreement between the bond distances from both calculated and X-ray studies previously given[15] and those reported here for ngoH is excellent. As previously suggested, there are some significant differences between the calculated and observed values; notably, the lengthening of the N1—N2 bond and the shortening of the N2—C1 bond in the calculated distances. The same effect, slightly magnified, appears with ngH . These differences have been attributed to a combination of both intra and intermolecular hydrogen bonding. This explanation becomes less likely when one finds the same effect with the nitroso compound in which the hydrogen bonding is somewhat different, having no intramolecular hydrogen bond between O1 and a hydrogen of N4. Thus, while one cannot rule out hydrogen bonding and or crystal

Table 4. Calculated Energetics of Formation and Interchange

Geometry	E (hartree)	H (relative)	S (relative)	G (relative)	E
ngH					
Diamine (std)	−332.8325432	0.00	0.00	0.00	53.451
1(OH) ctcc	−332.8097088	−14.329	0.161	−14.377	53.478
2(OH) tccc	−332.8243968	−5.112	−1.017	−4.809	53.562
3(NH) cct	−332.8191923	−8.378	−0.764	−8.150	53.857
4(NH) tct	−332.8226851	−6.186	−0.728	−5.969	53.623
5(NH) ttc	−332.8184654	−8.834	−1.132	−8.496	53.599
6(NH) ctc	−332.8171869	−9.636	−0.702	−9.427	53.855
7(OH) cttt	−332.8101713	−14.039	−1.020	−13.735	53.652
8(OH) tttt	−332.8276456	−3.076	−1.027	−2.670	53.857
9(NH) ttt	−332.8247932	−4.863	−1.299	−4.476	53.324
10(NH) ctt	−332.8126464	−12.485	−1.225	−12.120	53.554
11(OH) tctc	−332.8178033	−9.249	−1.839	−8.701	53.761
12(OH) cctc	−332.8093639	−14.545	−2.352	−13.790	53.434
13(NH) tcc	−332.8243970	−5.112	−2.352	−4.411	53.434
14(NH) ccc	−332.8041963	−17.788	−1.118	−17.455	53.432
15(OH) ccct	−332.8085317	−14.866	−1.342	−14.465	53.584
16(OH) tcct	−332.8019006	−19.229	−1.849	−18.678	53.664
ngoH					
1(std)	−407.6681783	0.0	0.0	0.0	57.701
2(OH) tccc	−407.6519102	−10.209	−0.081	−10.186	58.026
3(OH) tttc	−407.6264417	−26.19	+0.412	−26.312	57.953
4(OH) cttc	−407.6342541	−21.29	+2.012	−21.889	56.880
5(NH) tc	−407.6217427	−29.14	−0.148	−29.095	57.782
6(NH) tt	−407.6421145	−16.36	−1.108	−16.030	57.936

std: for isomer.

lattice energy for this effect, there is also the strong possibility that the MO-calculations are not modeling the conjugated bonding in this molecule perfectly.

The crystalline molecular structures of ngH and ngoH are nearly exactly the same. Both are planar molecules utilizing the same internal *cis* arrangement. The oxygen atom of ngH is directed away from the chelate ring where a metal ion could

ngH   ngoH
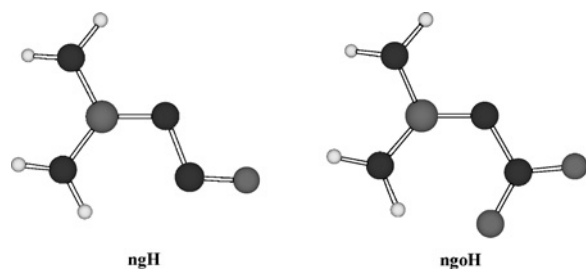
Fig. 4. Most stable configurations (gas).

coordinate. This is important, as we will show in a subsequent paper that metal ions can slip into the crystal lattice and form a four-coordinate planar complex without modifying the original ligand crystal structure. Incidentally, the second oxygen of ngoH is in a position preventing chelation to a metal ion without rotation around the N—N bond. This would reduce the planarity of the molecule and affect the conjugation. While intermolecular hydrogen bonding is important in both solid structures it apparently does not strongly influence the geometries of the individual molecules. The X-ray bond distances deviate from those calculated by an average 0.025, 0.026 Å, while the bond angles have an average deviation of 2.1, 2.4° (ngH, ngoH). This we consider to be good agreement and substantiate the ability of the Gaussian98-MO method to give accurate solutions. This will be relied upon again when results on the metal ion complexes are presented.

Table 5. Distances (Å) and Angles (°) in Most Stable State (Calculated)

	ngoH	ngH
Distances (Å)		
N1—N2	1.358	1.351
C1—N2	1.313	1.303
C1—N3	1.339	1.360
C1—N4	1.363	1.361
O1—N1	1.214	1.176
O2—N1	1.184	–
N3—H1N3	0.99	1.00
N3—H2N3	1.00	1.00
N4—H1N4	1.00	1.00
N4—H2N4	1.00	1.00
Angles (°)		
C1—N2—N1	119.9	111.0
N2—C1—N3	130.8	126.7
N3—C1—N4	116.2	115.7
N2—C1—N4	114.0	117.6
N2—N1—O1	115.5	114.1
N2—N1—O2	121.9	–
O1—N1—O2	122.6	–
C1—N4—H1N4	118.	116.
C1—N4—H2N4	119.	117.
C1—N3—H1N3	114.	114.
C1—N3—H2N3	117.	117.
H1N3—N3—H2N3	115.	115.
H1N4—N4—H2N4	119.	116.

It is generally known that amines and amide-nitrogens are good electron-pair-sharing groups with transition metal ions. Nitroso-nitrogens are not as effective and nitro groups are very poor but may use the electron pairs on the oxygen for coordination. The calculated atomic charges in Table 6 show some interesting differences between ngH and ngoH. First, N3, the amine nitrogen, has an

Table 6. Calculated Atom Charges

Atom	ngH	ngoH
C1	+0.31	+0.39
N1*	+0.08	+0.43
N2	−0.25	−0.26
N3*	−0.72	−0.73
N4	−0.70	−0.70
O1	−0.26	−0.34
O2	–	−0.40

*Coordinating sites.

appreciable negative charge in both molecules. On the other hand, N1 becomes much more positive when the second oxygen atom is present. Thus, if chelation were to occur in the nitro compound the ligand would have to use an oxygen atom for coordination. Because of space considerations this could occur only after rotation of the nitro-oxygens out of the plane of the molecule with the concurrent loss of the internal binding energy of the ligand. Thus, it would be anticipated that ngoH would only chelate with metal ions that can provide that energy. Perhaps Hg(II)?

An interesting aspect of the solid structure of ngH is the relative placement of adjacent molecules. Two molecules are related by an inversion through a point at 1/2, 1/2, 1/2 in the unit cell. All atoms of both molecules are in a single plane and pairs of N1 and N3 atoms form a nearly symmetrical coordination cavity (Fig. 5). The distances from the nitrogen atoms to the center of the cavity at 1/2, 1/2, 1/2 are 2.039 and 1.864 Å. The cavity is of nearly perfect size for a first transition metal ion such as Ni(II) for four-coordinate-planar coordination. In fact, such a complex does form (with the release of two H^+) and the cell dimensions and symmetry are almost exactly the same as that of the ligand. Preliminary experiments show that Ni^{+2} does diffuse into the lattice and form the complex when single ligand crystals are in contact
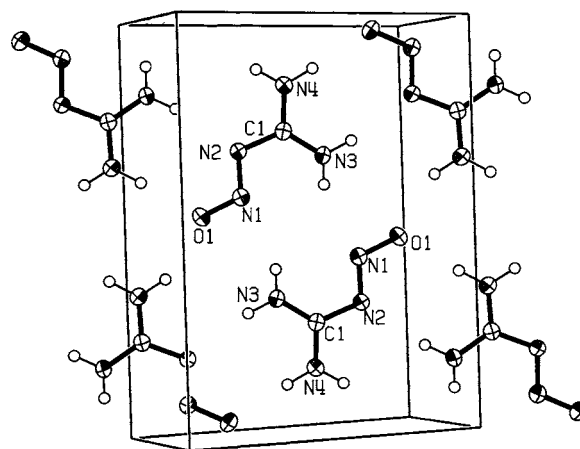
Fig. 5. Unit cell of ngH showing the cavity between two molecules.

with methanol solutions of Ni(II). Ligand solubility in that solvent is small. It is not clear at present how deep into the crystal the metal ions travel. We are of the opinion that this is the first reported incidence of such an occurrence and are presently working on the diffusion of metal ions into the lattice of single ngH crystals.

Conclusions

Nitrosoguanidine has a structure very similar to that of nitroguanidine. It has all four hydrogens in two nearly equivalent amine groups. All atoms are essentially in a single plane. *Ab initio* MO-calculations predict the same geometry in the gas state for an individual molecule as that found in the crystalline state by single crystal X-ray diffraction methods. Hydrogen bonding in the crystalline state and lattice interactions, while important, do not modify the structure, although they may affect the molecule conjugation and thus perturb the bond distances slightly. In the crystal lattice two molecules of ngH are located in a plane *trans* to each other such that a cavity exists, which can be filled by a metal ion at the 1/2, 1/2, 1/2 position giving 4N coordination to the metal ion without significant modification of the ligand lattice.

Supplementary material Atomic coordinates, structure factors, positional parameters, anisotropic thermal parameters, least-squares planes and dihedral angles for *N*-nitrosoguanidine CCDC (185116), and *N*-nitroguanidine CCDC (185118) were deposited with the Cambridge Crystallographic Data Centre. This material can be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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