Structure of the nitrosoguanidine complexes of nickel(II) and copper(II) by X-ray crystallography and computational analysis

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Using the X-ray structure of solid nitrosoguanidine (ngH), potential structures of its complex with aqueous nickel(II) were surmised. A single-crystal X-ray diffraction determination of the Ni(II) complex confirmed one of these configurations. The X-ray structural parameters were compared with the most stable gaseous configurations derived from ab initio-MO calculations. The lowest energy calculated configuration of the nickel(II) complex and the X-ray crystal structure are in excellent agreement. The neutral diamagnetic, planar, red-colored [bis(nitrosoguanidate)nickel(II)] complex, $[Ni(ng)_2]°$, is nitrogen coordinated in the *trans* configuration. It is highly insoluble in all solvents investigated, and has essentially the same crystal symmetry and unit-cell dimensions as the free ligand. In ligand crystals, two molecules have four nitrogen atoms aligned 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. Furthermore, the complexes stack, as in $[Ni(dmg)_2]°$, placing the nickel ions in nearly perfect positions for weak metal–metal bonding between adjacent layers at the near optimum distance of 3.65(1) Å. This results in a tight, linear macromolecule having low volatility and the extremely low solubility observed. As far as we are aware this is the first instance in which a ligand crystal structure is essentially the same as the complex it forms, with minor differences in bond distances, angles and torsion angles, and suggests some potentially unique properties and applications for this material.

Keywords: Nitrosoguanidine; Nickel(II); Copper(II); Complex; Gaussian98

1. Introduction

Nitrosoguanidine (ngH), prepared by the reduction of nitroguanidine (ngOH), has been known for many years [1,2]. It is used in a popular teaching demonstration that makes use of its explosive nature as there is little danger to the demonstrator because essentially no heat is generated in the decomposition.

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$$H_2N$$

$$C = N$$

$$H_2N \qquad N = O$$
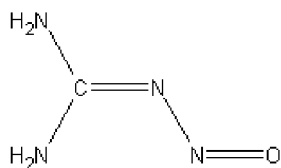
Nitrosoguanidine(ngH)

This ligand is potentially capable of existing in many forms due to H-atom migration and ionization [1,3]. It is a weak acid and in aqueous solution exists predominately in the non-ionic form. The hydrogen atoms are expected to be amine-N bound but it is likely that, under certain conditions, one of them is bound to the imine-N or the oxygen. In the latter case the ligand is an α-amineoxime, a class of compounds that readily coordinates to transition metal ions, especially Cu(II) and Ni(II), using an intramolecular hydrogen bond [4]. The products of the thermal decomposition of ngH have not yet been described.

NgH is a metal ion complexing reagent behaving specifically as a precipitant for planar +2 ions such as Ni(II), Cu(II), Co(II), Pd(II) and, to a lesser extent, Pt(II). With aqueous nickel ion a red precipitate forms on mixing with very dilute solutions (pH > 6) of the reagent, reminiscent of the formation of [Ni(dmg)$_2$]$^\circ$. Pd(II) forms an analogous yellow solid. Many years ago the properties of the nickel(II) complex of ngH were studied [5] because of its apparent similarity to the Ni-dmg complex and its potential use as an analytical reagent. Our interest was in the short nickel–nickel bond supposedly responsible for the red color of the precipitate [6] and for its extreme water insolubility. Those unpublished studies were not successful, however, in determining the structure of the complex or the nature of the Ni–Ni bond.

The metal ion complexes of ngH are extremely insoluble in most solvents, very stable toward dissociation, decomposition or ligand replacement. The Ni(II) complex dissociates slowly and dissolves under dilute acid conditions, pH < 4. Some structures for these complexes were suggested [7] but no definitive structural information is available. Many configurations are possible for the metal complex, including forms with five-membered 2N-rings and six-membered rings with N and O atom coordination. Potentially, the hydrogen atoms can be attached at several positions, including a form in which two ligands are *cis* with an intramolecular H-bond. The high precision of modern-day X-ray crystallography should allow the location of the H-atoms in a small molecule such as [Ni(ng)$_2$]$^\circ$.

X-ray crystallography appeared to be the method most suited to understanding this complexation but we were hampered by the difficulty of making suitable crystals. Attempts to crystallize these complexes (over a period of several years) have produced only one solvent, anhydrous dimethylsulfoxide (DMSO), which at its boiling temperature dissolves a measurable amount of solute. It is not clear, however, whether changes (oxidation) take place in this dissolution; suitable crystals were never obtained on cooling DMSO saturated solutions. We therefore decided to work on this problem from several approaches, expecting to be able to eventually suggest the most plausible complex structure. Our approach was: (1) to compare the structures and energies of formation of the ligand and complex by ab initio-MO calculations and arrive at a

thermodynamically stable structure in the gas phase; (2) to study the powder diffraction pattern of the complex and try to obtain at least the dimensions and symmetry of the unit cell and then attempt a structure solution based on powder diffraction X-ray data using both the Ni and Pd complexes (assumed to be isomorphous) and neutron powder diffraction data; (3) to apply extensively all crystallization methods to obtain an X-ray structure of the complex; and (4) to use the MO output to help in the solution of powder and single crystal X-ray structures.

This article describes the results of these attempts, which ultimately led to a complete structure determination. Along the way it was found that a unique set of circumstances led to a special relationship between solid ngH [8] and $[Ni(ng)_2]°$, which may have useful applications.

2. Experimental and theoretical methods

Nitroguanidine was obtained commercially and recrystallized from water. Nitrosoguanidine was prepared from ngOH by reduction in an aqueous NH_4Cl solution using powdered zinc as described by Sabetta *et al.* [1]. It was recrystallized from warm water solution, mp 160°C (dec.). Single crystals suitable for Ni(II) diffusion were prepared by slow evaporation of aqueous solutions held at about 5°C. ngH slowly decomposes in warm water, especially if traces of Cu(II) are present. $[Ni(ng)_2]°$ was obtained as a fine red powder when a slightly alkaline (NH_3) aqueous solution of ngH was treated with an excess of a solution of nickel chloride. It was collected on a fine filter, washed exhaustively with water, ethanol and acetone and then dried under vacuum. The palladium complex (yellow) was prepared by a similar method using K_2PdCl_4. No solvent has been found that will dissolve a discernable amount of either of these complexes at moderate temperatures.

Attempts to prepare single crystals of $[Ni(ng)_2]°$ were unsuccessful for many years. The two most likely solvents appeared to be DMSO and dimethylformamide (DMF). Many experimental approaches to crystallization with these and other solvents in the presence and absence of water using thermal gradients in an open or sealed tube were unsuccessful. Diffusion experiments of various types were tried in which solutions of one of the trio (NH_3, Ni^{2+}, ngH) were diffused into the others dissolved in DMSO, DMF or water. Even when high concentrations of polyethyleneglycol or glycerine were present to decrease the diffusion rate, only very tiny crystalline aggregates were obtained. One significant problem appears to be that the ligand decomposes before large crystals can be formed. Some attempts were successful in giving discernable crystals by generating Ni^{2+} very slowly through the electrical oxidation of a large nickel electrode in a slightly basic DMF solution containing the ligand, but this could not be improved upon sufficiently to provide crystals of the minimum size needed. Eventually small single crystals were obtained by forming the complex by diffusion in a solvent mixture consisting of DMF, 2% DMSO and 1% water. Very dilute solutions were used and a trace of a base (either potassium acetate or 2,4,6-trimethylpyridine) was present to react with the protons generated. Over a period of about 5 days [bis(nitrosoguanidate)nickel(II)] crystals were sometimes obtained. The dark red crystalline material was collected and a few crystals were large enough (*ca* $0.002 \times 0.002 \times 0.015$ mm) for use. The composition of the solid phase is somewhat variable when formed in this way. The first crystal for which

we were able to collect an X-ray data set contained about 18% of the theoretical amount of nickel ion, based upon the least-squares refinement of the occupancy factor using a reasonable temperature factor. A subsequent data set on a crystal formed under slightly different conditions, including a higher metal ion concentration, gave a metal ion occupancy of essentially 1.0 (see section 3). Nevertheless, all crystals were much smaller than those usually used for a complete X-ray structural study. In order to reduce scattering during data collection, the crystals were mounted on a short ($\sim$2 mm), very thin glass fiber cut from pyrex fiberglass, which was glued to a much longer fiber of glass of the usual dimensions. To increase the diffracted intensities, a Nonius rotating anode X-ray source was used at nearly its maximum rated anode current.

Crystals of the copper(II)-ng complex were also difficult to prepare. Eventually, small brown crystals were obtained by slowly electrolyzing an anhydrous DMSO solution of ngH containing a small amount of KBr using copper electrodes. In this solvent the ligand is stable indefinitely. The filtered solution, saturated in complex, was allowed to sit in open air for about a week, during which time water was absorbed from the air and crystals formed. Mounted on a fiberglass fiber, the crystals diffracted well enough to give a good set of X-ray data on a standard CCD setup with slightly elongated collection times.

All of the X-ray powder patterns were measured on a high precision diffractometer using a 2 cm compressed disk of the compound with a liquid nitrogen cooled detector. The usual parameters were: scan range 5–60°; step size 0.02°; count time 2 s; wavelength Cu, 1.54059 Å . The intensities were corrected for background, the peaks centered using 15 points and then integrated. The complexes gave sharp but low intensity peaks compared to other standards, probably because of the amorphous condition of some of the sample caused by its very low solubility and rapid precipitation.

Calculated X-ray powder diffraction patterns were prepared using the structural parameters obtained from the single-crystal X-ray solutions of ngH [8] or [Ni(ng)$_2$]°. A nickel atom at increasing occupancy was successively added to the atom file at $1/2, 1/2, 1/2$ and the powder pattern calculated using DISPO from the NRCVAX [9] series of programs. Calculated ligand and nickel complex patterns were in good agreement with measured spectra.

2.1. *Computational methods*

In conjunction with the experimental study, ab initio conformational and configurational equilibrium structure preferences were calculated on the ligand [8] and its nickel complex at the MP2LAN1DZ level [10]. Restricted Hartree–Fock (RHF) calculations were performed with the ab initio quantum-mechanical program Gaussian98 [11] on a cluster of Alphaserver ES40 computers using direct methods. A non-relativistic effective core potential (ECP) was used for the basis set of Ni as described by Dunning and Hay [12] with the valence orbitals 3d, 4s and 4p. This Ni valence basis set is of the type [3s2p5d] and [2s2p3d] contracted, and was used in combination with the all-electron double-ζ basis sets on the main group atom and the resulting basis sets are commonly denoted LANL1DZ. The (3s2p)/[2s2p] bases for N, C and O were supplemented with single sets of six Cartesian d-type polarization functions and the exponents suggested by Hunzinaga [13] were used ($\zeta_d(C) = 0.600$, $\zeta_d(N) = 0.864$, $\zeta_d(O) = 1.154$) (see also Refs. [14,15]).

Infrared spectra were collected on a Nicolet 500 FT-IR spectrometer. The complexes in a very finely divided state were allowed to settle out on a AgCl plate from a water suspension, then dried over $CaCl_2$ before measurement.

The mass spectrum of the solid complex was attempted but neither electron-impact nor FAB produced any significant ions related to the structure. The substance has no measurable vapor pressure.

The 300 MHz ^1H NMR spectrum of the ligand was obtained in d^6-DMSO solution using TMS as standard. ^{13}C and ^{15}N NMR spectra of solid, diamagnetic, $[Ni(ng)_2]^\circ$ was recorded on a 300 MHz instrument in the "magic angle" mode spinning at 5500 Hz.

Magnetic susceptibility measurements were carried out on finely powdered solid using a Johnson Matthey balance standardized with liquid water and with $[Ni(en)_3]S_2O_3$ ($X = 11.03 \times 10^{-6}$ cgs g^{-1}).

2.2. Solid crystal structure

The X-ray crystal structure of [bis(nitrosoguanidate)nickel(II)] was investigated to find out which ligand atoms were coordinated to the metal ion, to which atoms the H-atoms were attached and whether there were metal–metal bonds in the lattice as suggested by the solid color and the similarity to $[Ni(dmg)_2]^\circ$. It was also of interest to find out if there were any intramolecular hydrogen bonds as is usually found in α-amineoxime complexes. For several years we were unable to obtain satisfactory crystals of the sparingly soluble substance and decided to try to predict the structure using MO-calculations. For this and other reasons we attempted both X-ray and ab initio MO-calculations on the ligand and its nitro analogue. These comparisons have been reported recently [8] and show the computed gaseous structure, distances and angles to be very close to those in the solid crystal structure. ngH and ngOH were chosen to compare a modern X-ray structure determination with the calculated Gausian98 parameters. The theoretical low-energy structure of the complex would help in the derivation of the complex structure from powder X-ray data. In fact, several unit-cell determinations from Ni and Pd powder data gave incorrect unit-cell symmetry. Ultimately it was not feasible, or necessary, to determine the complex structure from powder data. The theoretical–experimental comparison was in itself interesting and useful.

The crystal structure of $[Ni(ng)_2]^\circ$ was determined on an Enraf–Nonius FR571 Cad4 diffractometer using a rotating anode generator and Cu radiation. Because the crystals of the complexes were so small, special conditions were necessary. In particular, the complex crystals were mounted on a short, very thin (glasswool), fiberglass rod glued to the usual glass fiber to reduce scattering and background, the generator was operated at near its maximum rated power (45 kV, 90 mA anode current) and a hemisphere of data (doubly redundant) was taken with 4 min maximum time of collection per data point. It took about 75 h to collect the data, during which time some decay occurred (corrected for) and no absorption corrections were necessary.

After obtaining the structure of ngH and the unit cell of the first crystal of the nickel complex, it was apparent that they had essentially the same crystal structure. Powder diffraction patterns and single-crystal data, both observed and calculated, showed the unit cell of both the ligand and the complex to have the same symmetry, $P21/n$, and nearly the same dimensions but differing intensities. Inspection of the intermolecular arrangement of the ligand showed a cavity created by four coplanar nitrogen atoms from two ligands into which a nickel ion could easily fit at the $1/2, 1/2, 1/2$

unit-cell coordinates with nearly normal metal–nitrogen distances. When the structures of the complexes were completed, they were indeed found to be nearly the same as that of the free ligand with the metal ion replacing two nitrogen H-atoms.

3. Results and discussion

Mass spectral analysis of the products of thermal decomposition of ngH in an atmosphere of argon showed dinitrogen to be the principal product along with traces of water. No N_2O was found. The solid residue consisted of urea along with traces of cyanamide as shown by IR analysis. By contrast, the nickel(II) complex was stable to temperatures greater than 200°C.

A summary of the X-ray unit-cell dimensions and symmetry, conditions used in data collection and the final solution output parameters for the two structures is given in table 1. D_{obs} for $[Ni(ng)_2]^\circ$ was 2.16 $Mg\,m^{-3}$ by flotation, in good agreement with the calculated value. ORTEP drawings with the atom numbering systems are presented in figure 1. Supplementary structural information has been deposited with the Cambridge Crystallographic Data Centre. In both cases the unit cell contains discrete non-ionic molecules with *trans*-ng ligands. The copper(II) analogue is solvated

Table 1. Crystallographic data and structure refinement details for $[Ni(ng)_2]^\circ$ and $[Cu(ng)_2]^\circ DMSO$.

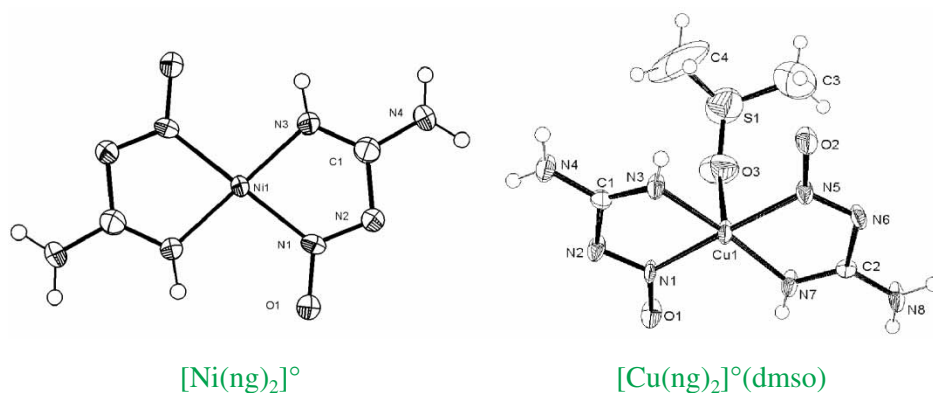|	$[Ni(ng)_2]^\circ$	$[Cu(ng)_2]^\circ DMSO$
Crystal shape/color	needle/red	needle/dark brown
Empirical formula	$C_2H_6N_8O_2Ni$	$C_4H_{12}N_8O_3SCu$
Formula weight	232.86	315.82
Temperature (K)	297(2)	173(2)
Wavelength (Å), type	1.54060, Cu $K\alpha$	0.71073, Mo $K\alpha$
Crystal system	monoclinic	monoclinic
Symmetry group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	3.597(2)	11.1938(17)
b (Å)	11.5500(4)	10.0579(15)
c (Å)	8.7070(4)	11.8249(18)
β (°)	100.14(1)	115.818(2)
Volume (Å^3)	356.1(2)	1198.4(2)
Z, D_{calc} ($Mg\,m^{-3}$)	2, 2.172(2)	4, 1.750(2)
Absorption coefficient (mm^{-1})	3.896	2.009
$F(000)$	236	644
Crystal size (mm)	$0.016 \times 0.0014 \times 0.0016$	$0.08 \times 0.07 \times 0.02$
θ range collection (°)	6.43 to 59.96	2.02 to 27.15
Limiting indices	$-4 \leq h \leq 3$	$-14 \leq h \leq 14$
	$0 \leq k \leq 12$	$-9 \leq k \leq 12$
	$0 \leq l \leq 9$	$-15 \leq l \leq 15$
Reflections collected/unique	1189/523, $R_{int} = 0.028$	8520/2630, $R_{int} = 0.122$
Completeness to $\theta =$	27.15°, 99.4%	59.96°, 99.0%
Max. and min. transmission	not measured	not measured
Refinement method	full-matrix LS on F^2	full-matrix LS on F^2
Data/restraints/parameters	448/0/62	2630/0/156
Goodness-of-fit on F^2	1.104	0.941
Final R [$I > 2\sigma(I)$]	$R1 = 0.0874$, $wR = 0.0971$	$R1 = 0.065$, $wR = 0.146$
R (all data)	$R1 = 0.216$, $wR = 0.227$	$R1 = 0.176$, $wR = 0.191$
Largest diff. peak and hole (e Å^{-3})	3.05, -0.413	1.06, -0.81

$[Ni(ng)_2]^\circ$ $[Cu(ng)_2]^\circ(dmso)$

Figure 1.   ORTEP drawings of $[Ni(ng)_2]^\circ$ and $[Cu(ng)_2]^\circ$DMSO with 50% elliptical probabilities.

by coordination with DMSO at the apex position, which only slightly displaces the metal atom about $0.06\,\text{Å}$ from the molecular plane.

The hydrogen atoms in the nickel complex were located in difference maps and the positional parameters allowed to vary in the least-squares calculation with the isotropic temperature factor held at 0.025. The final values gave reasonable bond distances and angles with the heavy atoms. With the copper complex the hydrogen atoms were calculated and allowed to ride on the heavy atoms in the least-squares analysis. The anisotropic temperature factors of the methyl carbon atoms in DMSO were somewhat larger than usual, which is attributed to thermal motion in the loosely bonded molecule. Other than that the thermal factors of all of the heavy atoms were in the usual range and nearly isotropic.

Bonding of ngH occurs with the ionization of one H^+ from an amine-nitrogen and chelation occurs between the resulting imine-nitrogen and the nitroso-nitrogen. This is in agreement with the ab initio-MO calculations, where it was found that conversion to the *cis*-configuration or to a *trans*-six-membered ring and oxygen atom coordination resulted in a destabilization of 10.19 and $4.79\,\text{kcal mol}^{-1}$, respectively. Invariably the nitroso-nitrogen is farther from the metal ion than the imine-nitrogen atom. In all structures studied thus far, including $[Co(ng)_2(py)_2]^+$, the ng ligand takes the *trans*-configuration. There appears to be no observable tendency to form the *cis* structure even with the stabilization provided by an intramolecular hydrogen bond. However, both *mer*- and *fac*-$[Co(ng)_3]^\circ$ have been isolated and characterized (CCDC 184937 and CCDC 184936, respectively) and thus ng ligands are capable of occupying *cis* positions in an octahedral complex, in contrast to the dmg and α-amineoxime ligands. This result is substantiated by the ab initio calculations where the free energy of formation of the five-membered *cis*-chelate with an intramolecular hydrogen bond is destabilized by $27.05\,\text{kcal mol}^{-1}$. ngH and its complexes show little differences in ligand planarity, bond distances and angles. In fact, all bond distances are invariant within $0.02\,\text{Å}$, in contrast to the difference between the X-ray values and the large calculated value for the C1–N4 distance ($0.14\,\text{Å}$). We suggest that the ab initio calculations do not adequately account for the conjugation of this amine group.

The planar nickel complex molecules stack with a linear array of the metal ions. The ligand groups are tilted with respect to this line by about 30°. The bond distance

between the metal ions is 3.65(1) Å, which represents a weak metal–metal bond. This behavior is exactly analogous to that in $[Ni(dmg)_2]^\circ$, where the distance is 3.24 Å [6], and probably results in the similar color and solubility characteristics of these complexes. In the solid ligand structure, pairs of ligands occupy similar positions to that in the complex and the distance between the planes is 3.645(8) Å. Thus in the crystalline ligand a cavity exists between two *trans*-ligands that could be occupied by a metal ion.

In the structure of $[Ni(ng)_2]^\circ$ there is a residual peak of significant magnitude lying between the Ni atoms at a distance approximating to an Ni–O bond; it is about the size of half an oxygen atom. Considering the symmetry of the unit cell, this would amount to a +4 oxidation state for the metal. Because the crystal was prepared in DMSO, which is a potential oxidizing agent, it was originally thought that oxidation had occurred. The observed near-diamagnetism, $X_m = +84 \times 10^{-6} \, cgs \, mol^{-1}$, would not distinguish between the alternatives because both d^6 (octahedral) and d^8 (planar) would be low spin. The small paramagnetism is presumed to be temperature independent. A plausible paramagnetic impurity, i.e. $Ni(OH)_2$, is considered unlikely because extraction with 1 M NH_3 solution did not change the magnetism. Our conclusion that it is low-spin Ni(II) comes from the Ni–N distances, which are normal for the +2 state, and the fact that the residual peaks are not directly between the metal atoms but in one dimension are on either side of the line between them. Thus we tentatively attribute this residual peak to a defect in the structure of unknown cause. However, this conclusion should be subject to further investigation.

Unit-cell atomic coordinates, intramolecular bond distances and angles, least-squares planes and selected torsion angles for these molecules are given in tables 2 and 3.

Ab initio-MO optimized structures of the six potential configurations selected for the nickel(II) complex are shown in figure 2. All molecules remained planar during the optimization and stabilized with no imaginary frequencies. Calculated thermodynamic quantities for formation are given in table 4. The most stable molecule in the gaseous state was the 5-*trans* model with five-membered chelate rings and *trans*-ng ligands. While there are significant differences in the entropy of formation, they do not significantly modify the Gibbs free energy relationships. The most stable 5-*trans* form is the same as that found in the solid state by X-ray crystallography. The six-membered chelate in the *trans* geometry is in fact fairly stable while the five-membered chelate in the *cis* form is considerably less stable. Remarkably, the 6-*cis*, NH and OH forms are very unstable compared to the 5-*trans* model. A comparison between the two methods with regard to bond distances and angles is given in table 5. Clearly, in addition to predicting the correct geometrical arrangement of the molecule, the MO-calculations closely approximated the molecular parameters found in the solid structure. We came to the same conclusion previously [8] when comparing the structural methods of the two related organic molecules, ngH and ngoH.

Hydrogen bonding, crystal lattice effects and metal–metal bonding do not cause significant changes in the bonding parameters of the nickel(II) complex. However, there does appear to be a consistent difference between some calculated and observed bond distances. The ligand bond distances and angles are nearly the same in the two X-ray structures and the calculated except for the C1–N4 distance. The calculated C1–N4 value is 0.14 Å longer, a much greater difference than the estimated error.

Table 2. Structural parameters for $[Ni(ng)_2]°$.

(a) *Atomic coordinates and equivalent isotropic displacement parameters*

Atom	x	y	z	U(eq)
Ni	1/2	1/2	1/2	0.0190(8)
O1	0.2754(21)	0.4770(5)	0.7889(8)	0.041(3)
N4	0.5630(30)	0.1602(6)	0.5441(9)	0.041(3)
N2	0.4041(23)	0.3143(5)	0.6859(8)	0.020(3)
N1	0.3812(21)	0.4252(5)	0.6767(8)	0.029(3)
N3	0.5769(24)	0.3482(6)	0.4451(8)	0.033(3)
C1	0.5213(23)	0.2736(7)	0.5502(10)	0.029(3)
H1N4	0.580(24)	0.133(7)	0.470(10)	0.025
H2N4	0.485(24)	0.120(7)	0.630(10)	0.025
HN3	0.656(24)	0.327(7)	0.380(10)	0.025

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(b) *Bond distances (Å) and angles (°)*

Ni–N1	1.879(7)	N2–N1	1.285(9)
Ni–N3	1.851(6)	N2–C1	1.404(11)
O1–N1	1.260(9)	N3–C1	1.297(11)
N4–C1	1.321(11)	N3–HN3	0.72(9)
N4–H1n4	0.73(9)	N4–H2N4	0.96(9)
N1–Ni–N1a	180.0(0)	N1–N2–C1	107.8(7)
N1–Ni–N3	80.9(3)	Ni–N1–O1	124.0(5)
N1–Ni–N3a	99.1(3)	Ni–N1–N2	119.2(5)
N1a–Ni–N3	99.1(3)	O1–N1–N2	116.8(7)
N1a–Ni–N3a	80.9(3)	Ni–N3–C1	113.4(6)
N3–Ni–N1a	180.0	N4–C1–N2	114.7(7)
C1–N4–H1N4	119.0(7)	N4–C1–N3	126.7(8)
C1–N4–H2N1	113.0(5)	N2–C1–N3	118.6(7)
H1n1–N1–H2N4	124.0(9)	Ni–N3–HN3	128.(6)
C1–N3–HN3	117.(6)		

(c) *Least-squares plane*
Equation of the plane: $3.193(4)x + 0.875(20)y + 2.530(18)z = 3.299(14)$
Distances (Å) to the plane from the atoms in the plane

Ni	0.0000	O1	−0.007(10)
N4	0.015(12)	N2	0.002(9)
N1	0.002(8)	N3	−0.026(10)
C1	−0.003(10)		

χ^2 for this plane 9.361
Distances (Å) to the plane from other atoms

H1N4	−0.14(11)	H2N4	−0.05(10)	HN3	0.04(10)

(d) *Selected torsion angles (°)*

N3–Ni–N1–O1	−178.6(6)	N3–Ni–N1–N2	0.7(4)
N1–Ni–N3–C1	−1.3(4)	C1–N2–N1–Ni	−0.1(3)
C1–N2–N1–O1	179.3(9)	N i–N3–C1–N4	−178.5(9)
N1–N2–C1–N4	179.1(10)		
N1–N2–C1–N3	−1.0(4)		
Ni–N3–C1–N2	1.7(2)		

The calculated M–N distances are also 0.10 Å longer than the observed values. In fact, one Ni–N calculated distance is greater than that observed for the copper analogue. The large change between the Ni and Cu coordination is due to the large change in the M1–N1 distance. Copper ion retains its affinity for the imine-nitrogen while lowering its ability to coordinate to the nitroso-nitrogen. This is in keeping with the general concept that it prefers the softer ligand atom. Comparison of the X-ray bonding parameters in $[Ni(ng)_2]°$ and ngH [8] shows little change upon coordination. However, the calculated values differ to a considerable extent. Again, this may be the result of improperly handling the metal orbitals.

Table 3.   Structural parameters for [Cu(ng)$_2$]°(DMSO).

(a) *Atomic coordinates and equivalent isotropic displacement parameters*

Atom	x	y	z	U(eq)
Cu(1)	0.8379(1)	0.5005(1)	0.0097(1)	0.026(1)
S(1)	0.4842(3)	0.4224(4)	−0.1804(3)	0.077(1)
N(7)	0.8460(6)	0.5538(6)	0.1696(6)	0.028(2)
N(2)	0.8247(6)	0.6786(6)	−0.1835(6)	0.026(2)
N(5)	0.8539(6)	0.3219(6)	0.0961(6)	0.026(2)
N(6)	0.8577(6)	0.3225(6)	0.2058(6)	0.027(2)
O(2)	0.8527(6)	0.2105(5)	0.0469(5)	0.043(2)
N(1)	0.8293(6)	0.6793(6)	−0.0727(5)	0.024(2)
N(8)	0.8651(7)	0.4650(6)	0.3588(6)	0.038(2)
N(4)	0.8247(7)	0.5359(6)	−0.3335(6)	0.035(2)
O(1)	0.8224(6)	0.7913(5)	−0.0292(5)	0.041(2)
N(3)	0.8583(6)	0.4484(6)	−0.1383(6)	0.028(2)
C(2)	0.8561(7)	0.4545(7)	0.2445(7)	0.021(2)
C(1)	0.8384(7)	0.5453(7)	−0.2169(7)	0.023(2)
O(3)	0.5996(6)	0.5119(7)	−0.1028(7)	0.067(2)
C(3)	0.4894(11)	0.2850(13)	−0.0849(12)	0.101(5)
C(4)	0.5270(15)	0.344(2)	−0.2920(14)	0.195(12)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(b) *Bond distances* (Å) *and angles* (°)

Cu(1)–N(1)	2.027(6)	N(6)–C(2)	1.407(8)
Cu(1)–N(3)	1.934(6)	N(7)–C(2)	1.307(9)
Cu(1)–N(5)	2.035(6)	N(2)–N(1)	1.289(7)
Cu(1)–N(7)	1.929(6)	N(5)–N(6)	1.279(7)
Cu(1)–O(3)	2.410(6)	N(1)–O(1)	1.255(7)
S(1)–O(3)	1.513(7)	N(5)–O(2)	1.260(7)
S(1)–C(3)	1.770(12)	N(8)–C(2)	1.314(9)
S(1)–C(4)	1.774(13)	N(4)–C(1)	1.323(9)
N(2)–C(1)	1.425(9)	N(3)–C(1)	1.298(9)
N(7)–Cu(1)–N(3)	171.5(3)	O(2)–N(5)–N(6)	117.4(6)
N(7)–Cu(1)–N(1)	101.4(3)	O(2)–N(5)–Cu(1)	125.0(5)
N(3)–Cu(1)–N(1)	78.8(2)	N(6)–N(5)–Cu(1)	117.5(5)
N(7)–Cu(1)–N(5)	78.3(2)	N(5)–N(6)–C(2)	109.6(6)
N(3)–Cu(1)–N(5)	101.3(3)	O(1)–N(1)–N(2)	116.0(6)
N(1)–Cu(1)–N(5)	177.9(3)	O(1)–N(1)–Cu(1)	126.7(4)
N(7)–Cu(1)–O(3)	95.5(2)	N(2)–N(1)–Cu(1)	117.2(5)
N(3)–Cu(1)–O(3)	93.0(3)	C(1)–N(3)–Cu(1)	113.1(5)
N(1)–Cu(1)–O(3)	83.3(2)	N(7)–C(2)–N(8)	125.5(6)
N(5)–Cu(1)–O(3)	98.8(2)	N(7)–C(2)–N(6)	120.6(6)
O(3)–S(1)–C(3)	107.2(5)	N(8)–C(2)–N(6)	113.8(6)
O(3)–S(1)–C(4)	106.3(5)	N(3)–C(1)–N(4)	126.8(7)
C(3)–S(1)–C(4)	100.5(9)	N(3)–C(1)–N(2)	121.0(7)
C(2)–N(7)–Cu(1)	113.9(5)	N(4)–C(1)–N(2)	112.2(6)
N(1)–N(2)–C(1)	109.0(6)	S(1)–O(3)–Cu(1)	138.9(4)

(c) *Least-squares plane*

Equation of plane: $10.2097x + 0.5466y − 0.3714z = 8.8823$

Deviation from plane in Å

−0.0577	Cu1	−0.0459	N4
−0.0426	O1	−0.0237	N5
−0.0792	O2	−0.0172	N1
−0.0256	N6	0.1773	N3
−0.0053	N7	0.0229	N2
0.0714	N8	0.0558	C1
0.0156	C6		

(d) *Selected torsion angles* (°)

N7–Cu1–N5–N6	2.0(5)	N3–Cu1–N5–N6	173.3(3)
O3–Cu1–N5–N6	90.2(6)	O3–Cu1–N5–N6	−91.9(6)
Cu1–N5–N6–C2	−2.9(8)	N3–Cu1–N1–O1	−175.4(7)
N3–Cu1–N1–N2	7.8(5)	N5–N6–C2–N8	−177.4(7)

5-*trans*   **5-*cis***

6-*trans*   **6-*cis***
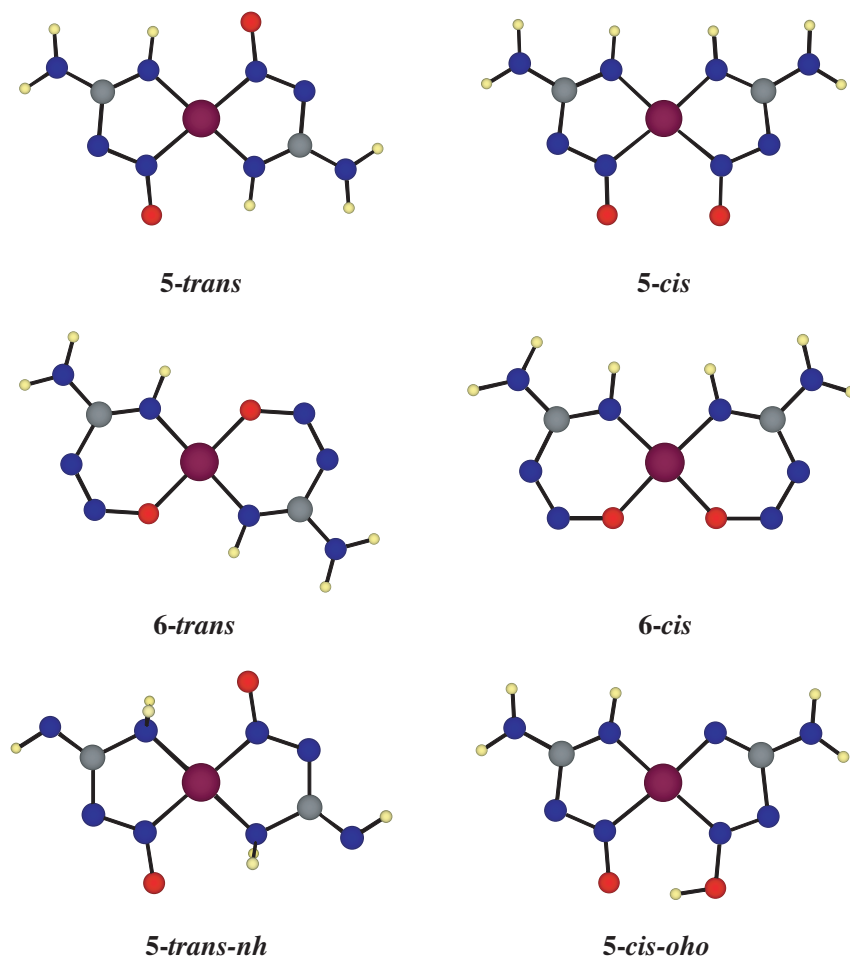
5-*trans*-nh   **5-*cis*-oho**

Figure 2.   Optimized MO structures for bis-ng-Ni(II) complexes.

Table 4.   Thermodynamic energies of formation of Ni(II)-ng complexes.

Complex	MP2(full)/ LANL1DZ	Erel (kcal mol^{-1})	VZPE (kcal mol^{-1})	TE (cal K^{-1} mol^{-1})	S (kcal mol^{-1})	Hrel (kcal mol^{-1})	Grel (kcal mol^{-1})
5-*trans*	−704.7050032		80.55	88.47	110.20		
5-*cis*	−704.6865111	11.60	79.87	88.04	113.49	11.17	10.19
6-*trans*	−704.6944934	6.60	79.20	87.25	112.15	5.37	4.79
6-*cis*	−704.6709499	21.37	78.93	87.17	114.54	20.06	18.77
5-*trans*-nh	−704.6503216	34.31	79.69	87.66	116.09	33.50	31.75
5-*cis*-oho	−704.6592442	28.71	78.77	86.81	110.19	27.05	27.05

The ^{13}C NMR spectrum of [Ni(ng)$_2$]°, taken in the solid state at the "magic angle" and 5500 Hz, shows only one sharp absorption at 164.2 ppm *vs.* the external standard glycine at 176.03 ppm. The ^{15}N "magic angle" spectrum was obtained using nitromethane at 0.00 ppm as the standard. It comprised four sharp singlets

Table 5. Comparison of bond distances (Å) and angles (°) obtained by
ab initio-MO calculation or X-ray crystallography.

| | | X-ray crystallography | |
	Ab initio-MO(Ni)	Nickel(II)	Copper(II)
M1–N1	1.974	1.879	2.207
M1–N3	1.956	1.851	1.934
N1–O1	1.209	1.260	1.255
N1–N2	1.266	1.285	1.289
N2–C1	1.388	1.404	1.425
N3–C1	1.250	1.297	1.298
C1–N4	1.469	1.321	1.323
N1–M–N3		80.9	78.8
M–N3–C1	109.2	113.4	113.1
N3–C1–N2		114.7	121.0
C1–N2–N1	116.8	107.8	109.0
M–N1–O1		124.0	126.7

at $+74$, -15, -280 and -284 ppm, ascribed to N2, N1, N4 and N3, respectively (figure 1). These results confirm the diamagnetism of the complex and suggest significant multiple bonding to the nitrogen atoms.

Splitting of the ^{1}H NMR signal of nitrosoguanidine was observed only if the solution was free of water. Then three peaks were found at 7.783, 7.657 and 7.124 ppm *vs.* TMS, attributed to nitrogen coupling and averaged by H-exchange when water is present. The IR spectrum of $[Ni(ng)_2]°$ was not very definitive. It was useful initially because it showed no OHO stretch usually found in the $1620 \, cm^{-1}$ region, suggesting that the complex was not the 5-*cis*-oho type (figure 2). Other absorption peaks were at 1583, 1370, 1300, 1089, 1026 and $711 \, cm^{-1}$. The electronic spectra were all obtained in anhydrous DMSO. The finely divided solid dissolved slowly (hours) in DMSO at about 100°C and remained in solution when cooled. All of the complexes had similar spectra and are presumed to have nearly the same structures. Absorption peaks in order of decreasing intensity are: Ni 300, 396, 460, 540; Cu 318, 408; Pd 316, 380; Co 318, 480 mμ. The cobalt(II) complex oxidized over a long period of time when suspended in water, forming $[diaquoCo(ng)_2]^+$.

The calculated and observed X-ray powder patterns of ngH and $[Ni(ng)_2]°$ were similar as shown in figure 3. After it was shown that the solid structures were essentially the same except for the replacement of two H^+ for a Ni^{2+}, the powder patterns for solid solutions of various compositions were calculated by changing the occupancy factor for the metal ion. As the hydrogen atoms being substituted did not contribute significantly to the diffraction, this was a good approximation. The results are shown in figure 4, where the changes in intensity of the main peaks are plotted as a function of metal occupation. As the structures are the same no new peaks are observed, only changes in intensity. Indeed the first crystal of the complex was deficient in metal, 18% occupancy, and the diffraction peaks showed the expected intensities for this composition. Attempts have been made to prepare uniform powders containing a deficiency of metal ion by precipitating from solutions with a large excess of alkaline ligand solution. Some success has been obtained but because the solubility decreases as the metal ion occupancy increases, there is a strong tendency toward high occupancy in the precipitate formed. As shown in figure 5, the complexes stack in a linear array with parallel faces. The position of the residual peak is shown in the lower portion. A very similar
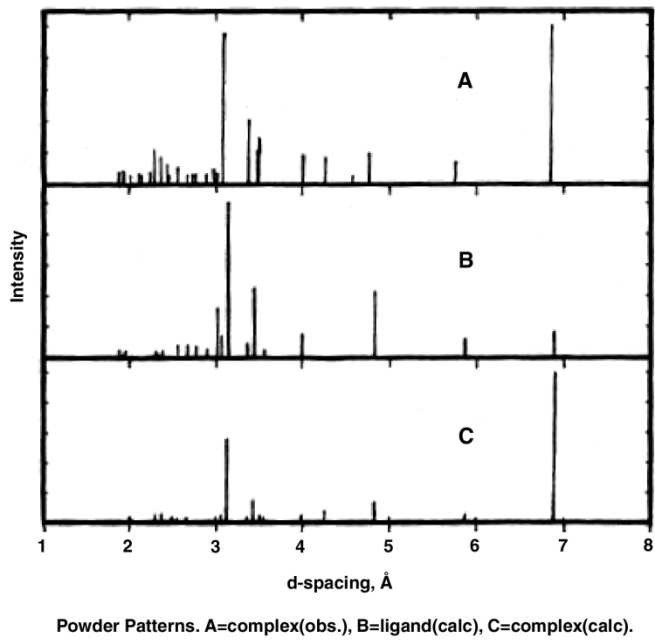
Powder Patterns. A=complex(obs.), B=ligand(calc), C=complex(calc).

Figure 3. X-ray powder patterns for ngH and $[Ni(ng)_2]°$: (a) complex (obs.); (b) ligand (calc.); (c) complex (calc.).
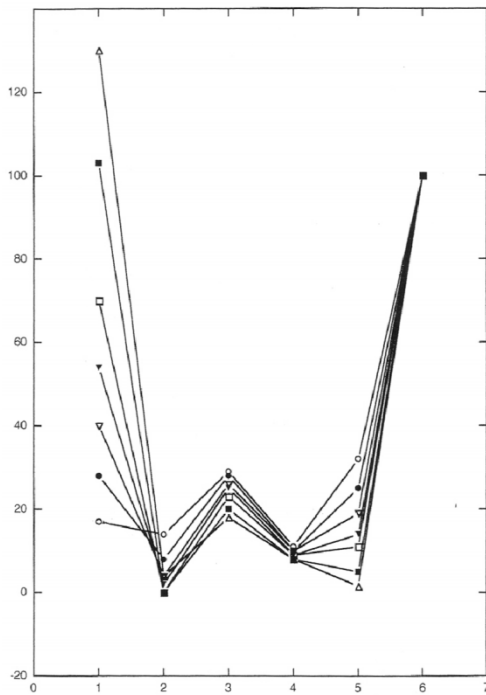

Figure 4. Relative X-ray powder intensities calculated versus % nickel occupancy of cavity. $1 = 011$, $2 = 012$, $3 = 002$, $4 = 020$, $5 = 110$, $6 = 200$. For 0, 10, 20, 30, 40, 70, 100% occupancy. Standard is the 101 plane.

Figure 5. [Ni(ng)₂]°: relative packing of complex in a unit cell, also showing the position of the residual peak between the planes of the complex.

arrangement exists in the crystalline ligand and the unit cell is directly comparable in both dimensions and angles [8]. There is a cavity in the ligand structure between *trans*-facing ligands that is at the center of four nitrogen atoms and the plane of this grouping stacks with a separation of 3.645 Å (3.597 Å in [Ni(ng)₂]°). The similarity of the unit cells is readily apparent (complex, ligand) ($a = 3.597$, 3.645; $b = 11.550$, 11.746; $c = 8.707$, 8.648 Å; $\beta = 100.14$, 99.17°). Within the cavity the distances between the potential coordinating nitrogen atoms are given in figure 6, where they are compared with the analogous values in the Ni(II) complex.

The ligand is essentially insoluble in methanol, which makes it possible to attempt the diffusion of metal ions into the solid lattice. Using methanol solutions of nickel acetate and single crystals of the ligand, we have observed the slow formation of a red color in or on the crystals. Solely on the basis of microscopic examination the crystals appear to remain intact. It is not clear, however, whether metal ions diffuse into the lattice or if a small amount of ligand dissolves and then precipitates the complex on the crystal surface. As it is a unique occurrence for the ligand and its complex to have the same atomic positions in the crystal lattice, this presents an opportunity to learn about diffusion rates of metal ions into a solid lattice. Nickel(II) complexes with linear metal–metal contacts in the solid state have been partially oxidized with halogens resulting in electrically conducting solids. Coupled with the possibility of preparing mixed transition metal arrays there appears to be the possibility of a wide range of new materials having variable electrical and optical properties.
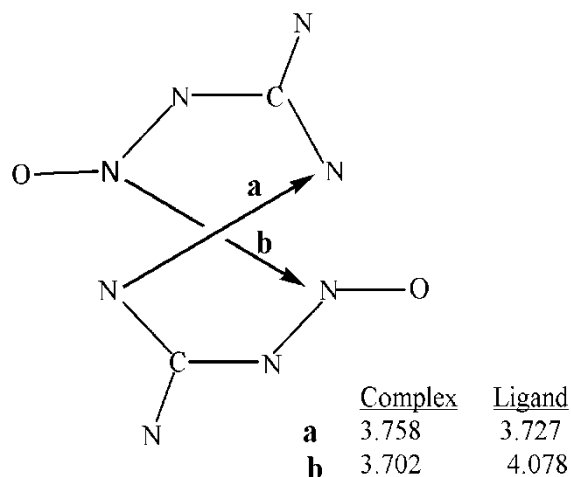
	Complex	Ligand
a	3.758	3.727
b	3.702	4.078

Figure 6.   Distances (Å) in crystal cavity of ngH and [Ni(ng)$_2$]°.

4. Conclusions

Nitrosoguanidine dissociates one H$^+$ on coordination to a transition metal ion and bonds to it through the imine and nitroso nitrogen atoms. It retains its planar nature on coordination and generally forms a planar *bis*-complex in the *trans* configuration. Structures of Ni(II), Cu(II) and Co(III) are now known and show the same bonding features. The red-colored nickel complex [Ni(ng)$_2$]° is very insoluble in most solvents and closely resembles [Ni(dmg)$_2$]°. In the solid state both have weak metal–metal bonds. Ab initio MO-calculations show the most stable structure to be identical to that found by single-crystal X-ray determination. Bond distances and angles are almost identical from the two independent determinations except for the terminal C–amine and metal–nitrogen atom distances, which are calculated to be slightly longer. [Cu(ng)$_2$]° is structurally identical to the Ni(II) complex except for solvation at the apex position and an elongation of the bond between the metal and the NO-nitrogen atom. In addition, there is no metal–metal bond in the solid state.

Crystals of the ligand have nearly the same unit-cell dimensions, angles and symmetry as crystals of [Ni(ng)$_2$]°. Within the solid ligand there are cavities surrounded by four nitrogen atoms at distances and angles exactly suited for coordination with Ni(II) ions. Insertion of a nickel ion in this cavity, with the loss of two H$^+$, gives the complex structure without significant changes in ligand atom positions. Furthermore, when placed in this cavity at the 1/2, 1/2, 1/2 unit-cell position it has a bonding distance to itself in both directions almost exactly that required for the metal–metal bond in the complex. These unique conditions provide an opportunity to study diffusion of metal ions into a lattice and to prepare single crystals with special electrical properties.

Supporting material

Atomic coordinates, structure factors, positional parameters, anisotropic thermal parameters, least-squares planes and dihedral angles for bis-nitrosoguanidatenickel(II),

CCDC 185117, and bis-nitrosoguanidatecopper(II), CCDC 221495, have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments

References

[1] V.J. Sabetta, D. Himmerfarb, G.B.L. Smith, *J. Am. Chem. Soc.* **57**, 2478 (1935).
[2] J. Thiele, *Liebigs Ann.* **273**, 133 (1893).
[3] G.B. Smith, V.J. Sabatta, *J. Am. Chem. Soc.* **54**, 1034 (1932).
[4] R.K. Murmann, *J. Am. Chem. Soc.* **80**, 4174 (1958).
[5] E.O. Schlemper, R.K. Murmann. Unpublished work.
[6] L.E. Godycki, R.E. Rundle, *Acta Cryst.* **6**, 487 (1953); R.E. Rundle, *J. Am. Chem. Soc.* **76**, 3101 (1954); S. Yamada, R. Tsuchida, *J. Am. Chem. Soc.* **75**, 6351 (1953); C.V. Banks, D.W. Barnum, *J. Am. Chem. Soc.* **80**, 3579 (1958).
[7] F. Feigl. In *The Chemistry of Specific, Selective, Sensitive Reactions*, R.E. Oesper (Ed.), p. 273, Academic Press, New York (1949).
[8] R.K. Murmann, R.E. Glaser, C.L. Barnes, *J. Crystallogr. Chem.*, accepted.
[9] E.J. Gabe, Y. LePage, J.P. Charland, F. Lee, P.S. White, *J. Appl. Cryst.* **22**, 384 (1969).
[10] J. Christopher, J. Cramer, *Computational Chemistry, Theories and Models*, John Wiley & Sons, Chichester, UK (2002).
[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas. J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Lahm, C.Y. Peng, A. Nanayakkara, M. Challacombe, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *Gaussian 98, Revision A.11.3*, Gaussian, Inc., Pittsburg, PA (2002).
[12] T.H. Dunning, P.J. Hay, *Modern Theoretical Chemistry*, Plenum, New York (1976).
[13] S.J. Hunzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
[14] R, Glaser, Y. Young-Hee, G.S. Chen, C.L. Barnes, *Organometallics* **13**, 2578 (1994).
[15] R. Glaser, P.E. Haney, C.L. Barnes, *Inorg. Chem.* **35**, 1758 (1996).