is impossible to assign infrared bands explicitly to the monodentate nitrate when an ionic nitrate is also present. We attach more significance to the uni-univalent conductance and the electronic spectral similarity with the halide complexes. Thus, we assign the formulation [Ni(stars)$_2$NO$_3$]NO$_3$ to this complex, which implies a monodentate nitrate and a pentacoordinate cation.

These five-coordinate complexes of stars have electronic spectra (Figure 1) that are very similar to the
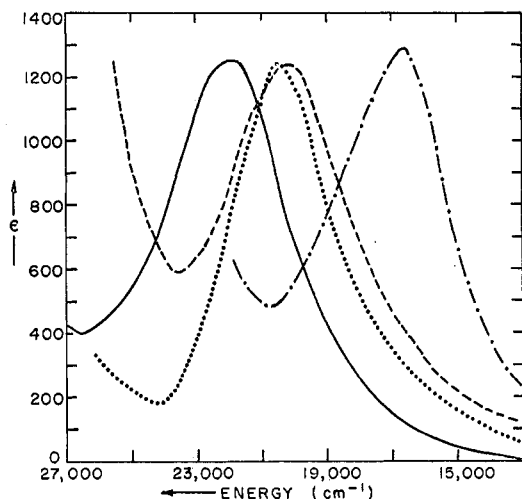

Figure 1.—The visible portions of the electronic absorption spectra: [Ni(stars)$_2$](ClO$_4$)$_2$, ————; [Ni(stars)$_2$I]I, – – – – –; [Ni(diars)$_2$I]I, ·······; Ni(DSP)I$_2$, –·–··–··–··–··–.

spectra of [Ni(SP)$_2$X]X and Ni(DSP)X$_2$, where SP and DSP are (o-methylthiophenyl)diphenylphosphine and bis(o-methylthiophenyl)phenylphosphine, respectively.[28] The latter complex is known to have a square-pyramidal structure,[29] so square-pyramidal Ni(stars)$_2$X$^+$ cations are proposed on the basis of the electronic spectra. The energy of the $^1A_1 \rightarrow$ ^1E electronic transition (d$_{zz,yz} \rightarrow$ d$_{z^2-y^2}$) in each of our Ni(stars)$_2$X$^+$ complexes is almost identical with the corresponding peak in the square-pyramidal Ni(diars)$_2$X$^+$ complexes.[25]

A comparison of the ligand properties of antimony with those of arsenic and phosphorus was the primary impetus for this study. The electronic spectral maxima in Table I show that stars exerts a ligand field that is *slightly* lower than for the analogous diarsine, B. The lower field is more prominent in the square-planar complex Ni(stars)$_2$$^{2+}$, where the absorption is $\sim$500 cm^{-1} below that of Ni(diars)$_2$$^{2+}$.[25]

Conclusions.—This study shows that the bidentate antimony–arsenic ligand forms stable five-coordinate nickel(II) complexes and that the apparent spectrochemical effect of the phenyldimethylstibine group is slightly lower than for the corresponding arsine. The latter observation perhaps reflects the disparity in the size of the donor and acceptor orbitals.

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# A Proton Magnetic Resonance Study of Some Tetraimine Complexes of Nickel

By VIRGIL L. GOEDKEN and DARYLE H. BUSCH*

A series of salts of the nickel complexes with the isomeric tetraimine ligands 1,4,8,11-CT and 1,3,7,11-CT has been prepared and characterized and the pmr spectra of these species have been studied in detail. Selective deuteration facilitated the assignment of the various pmr resonances. The ligands are 14-membered macrocycles each having 4 imine donor atoms and 6 methyl substituents. Although the complexes are particularly resistant to attack by either strong acid or strong chelating agents, the chelate rings appear to undergo rapid flexing, thereby causing pairs of gem methyls to become equivalent.

The pmr spectra of a number of isomers of the diimine complexes derived from the condensation of ethylenediamine and acetone have been studied in detail.[1] These complexes exist as noninterconvertible isomeric forms which are related by the position of the imine functions which are located in either the 1(14) and 7 positions of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-dienenickel(II) (structure I, Ni(1,7-CT)$^{2+}$) or the 1 and 4 positions of 5,7,7,12,12,-14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),-4-dienenickel(II) (structure II, Ni(1,4-CT)$^{2+}$).[2] The

I   II
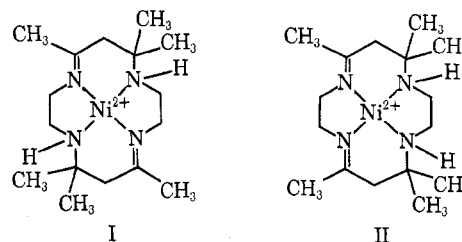
Ni(1,7-CT)$^{2+}$ species exists as interconvertible meso and *dl* isomers depending on the configuration of the two asymmetric nitrogen atoms, whereas the Ni(1,4-CT)$^{2+}$ species has only been observed in the *dl* form.[1]

Each of these complexes undergoes oxidative dehydrogenation of the ligand in concentrated nitric acid to

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TABLE I
PROTON MAGNETIC RESONANCE SPECTRA OF THE COMPLEXES[a,b]

Complex	Solvent	Imine CH	Methylene protons of five-membered rings	Methylene protons of six-membered rings	Imine methyl protons	Geminal dimethyl protons
[Ni(1,4,8,11-CT)](ClO₄)₂	C₃D₆O	7.92 (2)	4.70 (4)	2.85 (4)	2.19 (6)	1.28 (12)
[Ni(1,4,8,11-CT)](PF₆)₂	CD₃CN	7.70 (2)	4.55 (4)	2.84 (4)	2.22 (6)	1.37 (12)
[Ni(1,4,8,11-CT)](NO₃)₂	D₂O	7.83 (2)	4.76 (4)	2.92 (4)	2.29 (6)	1.40 (12)
[Ni(1,4,8,11-CT)](PF₆)₂[c]	C₆D₅N				1.55 (6)	1.27 (12)
[Ni(1,4,8,11-CT)](ClO₄)₂[d]	C₃D₆O	8.00 (2)	4.75 (4)			1.32 (12)
[Ni(1,3,7,11-CT)](ClO₄)₂	C₃D₆O	9.25 (2)	4.10 (4)	2.78 (4)	2.21 (6)	1.38 (12)
[Ni(1,3,7,11-CT)](ClO₄)₂	CD₃CN	8.42 (2)	3.70 (4)	2.99 (4)	2.30 (6)	1.43 (12)
[Ni(1,3,7,11-CT)](NO₃)₂	D₂O	8.42 (2)	3.77 (4)	3.00 (4)	2.36 (6)	1.45 (12)
[Ni(1,3,7,11-CT)](ClO₄)₂[d]	C₃D₆O	9.26 (2)	3.90 (4)			1.34 (12)

[a] Chemical shifts are in ppm relative to TMS standard. [b] Chemical shifts relative to DSS internal standard. [c] Basic nature of solvent facilitated the exchange of all labile protons with the solvent within the time required to take pmr spectrum. Imine CH was obscured by the proton impurities in the deuterated solvent. [d] Deuterated sample.

give the respective tetraimine complexes (structures III and IV).[3] Although there are no asymmetric atoms

III   IV
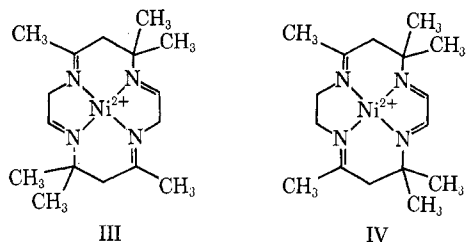
in these oxidized compounds, there exists the possibility of isomers by virtue of the conformation of the six-membered chelate rings. Stereochemical models, as well as an X-ray structural determination,[4] indicate that the geminal dimethyl groups have axial and equatorial orientations in the solid state. The energy barrier for the interconversion of the axial and equatorial methyl groups in these tetraimine derivatives is expected to be small as interconversion is expected to be rapid in solution. The nmr spectra of these complexes yield valuable information on the properties and solution behavior of the complexed ligands as a function of the degree of saturation and conjugation of the ligand, especially in light of the detailed studies of the related diimine complexes[1] and their fully saturated counterparts.[5]

Discussion

General Properties.—The perchlorate salts of these two isomeric tetraimines are square planar and diamagnetic in most solvents. The Ni(1,4,8,11-CT)²⁺ species has a d–d electronic absorption band at 22.7 kK with an ϵ_{max} of 75 and an absorption at 34.2 kK (ϵ_{max} 6630) associated with the isolated imine functions. The Ni(1,3,7,11-CT)²⁺ species, which contains a conjugated α-diimine chromophore, has an absorption with a shoulder at 23.52 and 25.51 kK (ϵ_{max} 1403 and 1704). In the presence of axial ligands having moderate field strength, both complexes form paramagnetic species in solution and some have been isolated in the solid state.[6] The α-diimine species Ni(1,3,7,11-CT)²⁺ is especially prone to form paramagnetic species; it does so even with halide ions. This behavior contrasts markedly with that observed for the Ni(1,7-CT)²⁺ and Ni(1,4-CT)²⁺ which have little tendency to form paramagnetic complexes.

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The tetraimine complexes [Ni(1,4,8,11-CT)](ClO4)₂ and [Ni(1,3,7,11-CT)](ClO4)₂ are particularly resistant to attack by strong acids and are resistant to displacement reactions with strong chelates such as 1,10-phenanthroline or α,α'-dipyridyl. They are susceptible to attack by base with the Ni(1,4,8,11-CT)²⁺ moiety yielding deprotonated species[6] whereas Ni(1,3,7,11-CT)²⁺ apparently yields a solvolyzed product.[7] Aqueous solutions of [Ni(1,3,7,11-CT)](ClO₄)₂ display a darkening of color after 24 hr and the pmr spectra of these solutions indicate the presence of paramagnetic species.

Proton Magnetic Resonance Spectra of the Complexes.—The assignment of the proton resonances for the Ni(1,4,8,11-CT)²⁺ and Ni(1,3,7,11-CT)²⁺ isomers are given in Table I and typical spectra are shown in Figure 1. The pmr spectrum of each complex, when recorded on a Varian A-60 spectrometer, consists of five singlets which are found between 1.3 and 10.0 ppm.

The highest field resonance for the Ni(1,4,8,11-CT)²⁺ isomer occurs at 1.28 ppm and is assigned to the geminal dimethyl protons on the basis of the integrated intensity of 12. The resonance, at 2.19 ppm with relative intensity of 6, is assigned to the imine methyl groups. These occur at virtually the same position as found in the parent diene complex[1] and are deshielded because of their proximity to the electron-withdrawing imine function.

The next two peaks occur at 2.85 and 4.70 ppm and each has an integrated intensity of 4. These belong to the methylene protons of the five- and six-membered chelate rings. Their unambiguous assignment was based on the results of deuteration experiments.

Deuteration of the parent complex Ni(1,7-CT)-(ClO₄)₂ by recrystallization from basic D₂O selectively deuterates the methylene protons of the six-membered rings and the protons of the methyl group attached to the imine function.[1] Oxidation of the complex with nitric acid to the tetraimine species Ni(1,4,8,11-CT)²⁺ preserves the deuteration, and the nmr of the deuterated, oxidized species contains only three absorptions (Table I and Figure 1). These are the geminal dimethyl resonances at 1.28 ppm, the imine CH at 7.92 ppm, and the absorption at 4.68 ppm. Since the methylene positions of the six-membered rings are deuterated, the 4.68-ppm resonance can only be due to the methylene protons of the five-membered chelate ring. Thus the absorption at 2.85 ppm in the nondeuterated spe-

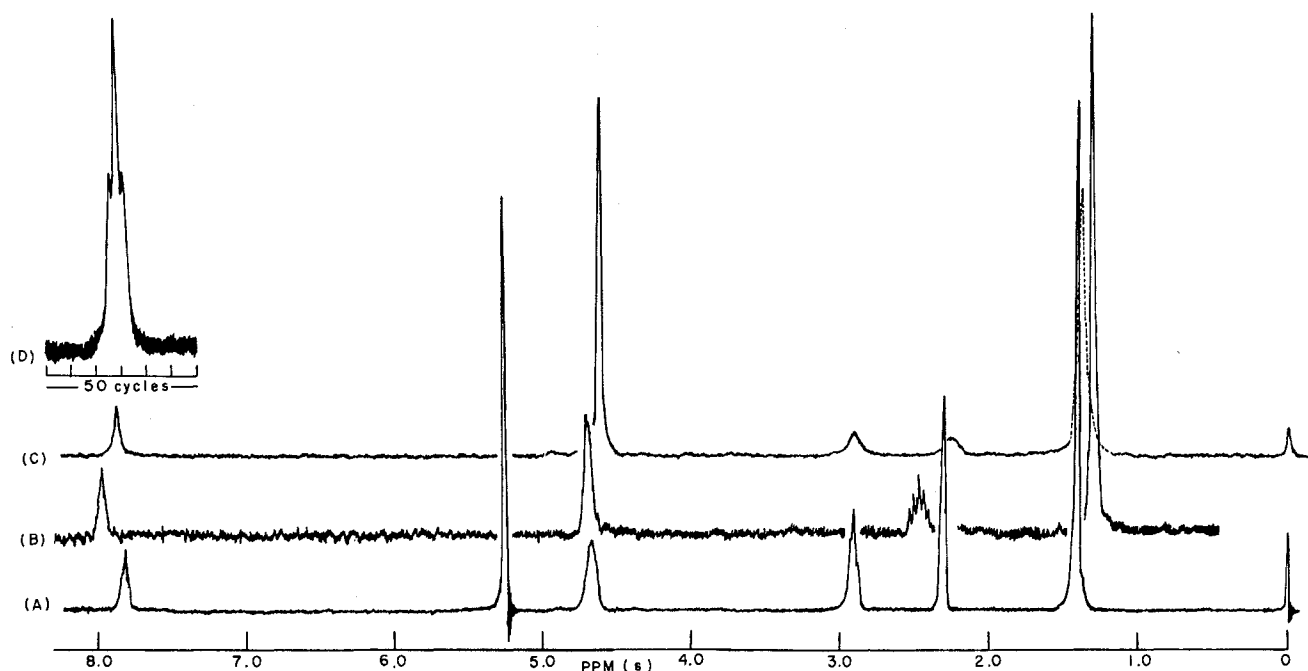(7) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

Figure 1.—Pmr spectra of Ni(1,4,8,11-CT)$^{2+}$ under varying conditions: (A) [Ni(1,4,8,11-CT)](NO$_3$)$_2$ in D$_2$O acidified with HNO$_3$ to move the HOD peak off the 4.76-ppm resonance; (B) [Ni(1,4,8,11-CT)](ClO$_4$)$_2$-d_{10} in DMSO with deuterium atoms substituted for the imine methyl protons and the methylene protons of the six-membered rings; (C) [Ni(1,4,8,11-CT)](NO$_3$)$_2$ in basic D$_2$O, pH 10, 5 min after sample preparation; (D) inset—expanded and amplified imine CH resonance with 250 cps sweep width and 1000 sec sweep time.

cies belongs to the methylene protons of the six-membered rings.

The remaining absorption at 7.95 ppm, which has a relative intensity of 2, is assigned to the imine CH of the five-membered ring. The pronounced deshielding observed for the imine CH and the methylene protons of the five-membered ring can be ascribed to a number of factors. The proximity of these protons to both of the electron-withdrawing imine groups and the electronegative nitrogen atoms undoubtedly accounts for most of the deshielding effects. However, the divalent nickel ion, as a concentrated center of positive charge, certainly accounts for part of the observed effects.

The protons α to the imine functions are acidic and can be exchanged for deuterium atoms.[8,9] Aqueous solutions of [Ni(1,4,8,11-CT)](NO$_3$)$_2$ show a loss of the methylene protons of the five-membered rings after 24 hr. The addition of base to elevate the pH to 10 facilitates this proton exchange and all of the protons α to an imine function exchange within minutes. The pmr spectrum then consists of only two absorptions, one due to the imine CH and the other due to the geminal dimethyl protons (Figure 1).

The imine CH proton is predicted to be split into a triplet and the methylene protons of the five-membered rings are expected to exist as a doublet on the basis of simple spin–spin coupling arguments. The pmr spectrum of aqueous solutions of Ni(1,4,8,11-CT)(NO$_3$)$_2$ obtained on a P-60-A Varian spectrometer does reveal some splitting of the resonances. The imine proton signal can be obtained as a well-resolved triplet with a coupling constant of 1.25 cps. This triplet structure collapses into a singlet in basic D$_2$O. The dihedral angle between the imine CH and the methylene protons

is expected to be about 60°. Coupling constants of about 1.5 cps are predicted for substituted ethanes when the dihedral angle is 60°.[10] The resonance due to the methylene of the five-membered rings, although broad, could not be resolved into its component peaks. It exhibited a number of shoulders at high resolution, as did the methylene protons of the six-membered ring. This broadening is apparently due to transoid homoallylic coupling which was also observed in the pmr spectrum of the NiCT–diene complexes.[1]

The pmr spectrum of the Ni(1,3,7,11-CT)$^{2+}$ isomer consists of a five-line spectrum similar to that of the Ni(1,4,8,11-CT)$^{2+}$ isomer. The absorption at 1.38 ppm (relative intensity 12) is attributed to the geminal dimethyl protons, and the absorption at 2.21 ppm (relative intensity 6) is assigned to the imine methyl protons. The imine CH protons of the α-diimine function are found at 9.05 ppm and reflect the deshielding effects of this conjugated system. The two remaining resonances, each of relative intensity 4, are at 4.10 and 2.78 ppm and are assigned to the methylene protons of the five- and six-membered rings, respectively, on the basis of deutration experiments similar to that described for the Ni(1,4,8,11-CT)$^{2+}$ isomer.

Experimental Section

Physical Measurements.—Infrared spectra were determined from Nujol and hexachlorobutadiene mulls using a Perkin-Elmer Model 337 spectrophotometer. Visible spectra were measured using a modified Cary 14 recording spectrophotometer. Proton magnetic resonance spectra were obtained from a Varian A-60 nmr spectrometer and the spectra of selected samples were obtained from a Varian A-60A spectrometer. Concentrations were generally 20–30% by weight and spectra were determined at 37°. Elemental analyses for carbon, hydrogen, and nitrogen were performed by Galbraith Laboratories, Inc.

Preparation of the Complexes. [Ni(1,3,7,11-CT)](ClO$_4$)$_2$.—

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(10) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 117.

This complex was prepared by the method of Curtis.[3] [Ni-(1,4-CT)](ClO$_4$)$_2$ was prepared by the metal-promoted condensation of tris(ethylenediamine)nickel(II) perchlorate with acetone. The product was subsequently oxidized to [Ni-(1,3,7,11-CT)](ClO$_4$)$_2$ with concentrated nitric acid. The final product was precipitated with an acetone–ether solution, recrystallized from a 1:4 acetonitrile–ethanol solution, and dried *in vacuo*. *Anal.* Calcd for C$_{16}$H$_{28}$N$_4$NiCl$_2$O$_8$: C, 35.97; H, 5.24; N, 10.49; Cl, 13.30. Found: C, 36.18; H, 5.44; N, 10.29; Cl, 13.50.

[Ni(1,4,8,11-CT)](ClO$_4$)$_2$.—This complex was also prepared by the method of Curtis by first obtaining [Ni(1,7-CT)](ClO$_4$)$_2$ from the reaction of nickel acetate with the dihydrogen perchlorate salt of the ligand. The [Ni(1,7-CT)](ClO$_4$)$_2$ was subsequently oxidized to the bis-β-diimine compound [Ni(1,4,8-CT)](ClO$_4$)$_2$ with concentrated HNO$_3$. The yellow product was recrystallized from a 1:4 ethanol–acetonitrile solution, filtered, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for C$_{16}$H$_{28}$N$_4$NiCl$_2$O$_8$: C, 35.97; H, 5.24; N, 10.49; Cl, 13.30. Found: C, 36.05; H, 5.40; N, 10.54; Cl, 13.09.

[Ni(1,4,8,11-CT)](NO$_3$)$_2$.—The nitrate salt of the Ni(1,4,8,11-CT)$^{2+}$ cation could not be prepared by metathetical displacement because of the very insoluble nature of [Ni(1,4,8,11-CT)](ClO$_4$)$_2$ starting material in hydroxylic solvents. Therefore the nitrate complex was prepared by a direct method similar to that described by Curtis to prepare the perchlorate salt. *Anal.* Calcd for C$_{16}$H$_{28}$N$_4$Ni(NO$_3$)$_2$: C, 41.49; H, 6.91; N, 18.15. Found: C, 41.47; H, 6.40; N, 18.51.

The nitric acid salt of the diimine ligand was prepared by the condensation of ethylenediamine and acetone using equimolar portions of nitric acid and ethylenediamine in acetone. The substance was isolated with an excess of HNO$_3$ of crystallization and allowed to react with an equimolar ratio of nickel acetate in methanol to form [Ni(1,7-CT)](NO$_3$)$_2$. This was then oxidized to the tetraimine [Ni(1,4,7,11-CT)](NO$_3$)$_2$ with concentrated nitric acid and isolated by the addition of 1:1 acetone–ether mixture. The nitrate salt is very soluble in water.

Deuteration Experiments.—Selective sites on [Ni(1,4,8,11-CT)](ClO$_4$)$_2$ and [Ni(1,3,7,11-CT)](ClO$_4$)$_2$ were deuterated by first recrystallizing the parent [Ni(1,4-CT)](ClO$_4$)$_2$ and [Ni-(1,7-CT)](ClO$_4$)$_2$ complexes several times from hot, basic D$_2$O in a manner already reported.[1] The infrared spectra of the deuterated diene complexes indicated the absence of any N–H and the presence of N–D as well as C–D stretching absorptions. The pmr spectra were very similar to those of the reported deuterated analogs,[1] indicating the complete exchange of the imine methyl protons and the methylene protons of the six-membered ring for deuterons. These deuterated sites remain intact when the complexes are oxidized to their respective tetraimine derivatives with HNO$_3$ and the products are isolated under acidic conditions.

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Cationic Ligands. Coordination of the 1,1,1-Trimethylhydrazinium Cation to Nickel(II)

BY V. L. GOEDKEN, L. M. VALLARINO,* AND J. V. QUAGLIANO

The nonbasic trimethylhydrazinium cation, H$_2$NN$^+$(CH$_3$)$_3$, coordinates to Ni(II) forming yellow, paramagnetic complexes NiX$_4${H$_2$NN$^+$(CH$_3$)$_3$}$_2$ (X = Cl, Br) which have a tetragonally distorted octahedral stereochemistry. The crystalline yellow complex NiCl$_4${H$_2$NN$^+$(CH$_3$)$_3$}$_2$, when heated to 145°, changes sharply to the blue salt {H$_2$NN$^+$(CH$_3$)$_3$}$_2$[NiCl$_4$], containing the tetrahedral tetrachloronickelate(II) anion; the original yellow octahedral complex re-forms upon cooling. This transformation represents a unique example of change in coordination number and stereochemistry of a Ni(II) complex, occurring reversibly in the solid state at a relatively low temperature.

Introduction

It has been shown that the presence of a positive charge in the vicinity of a potential donor atom in a cationic ligand does not prevent coordination to appropriate metal ions,[1–12] even though the basicity may be

markedly lowered. In general, the effect of a positive charge on the basicity of a donor atom depends upon their electronic interaction and, other factors being equal, upon their bonded distance within the ligand. Thus, the pK_a of 1,8-diaminooctane, H$_2$N(CH$_2$)$_8$NH$_2$, decreases on monoprotonation by less than 0.8 unit (from 10.9 to 10.1),[13] but for hydrazine, H$_2$NNH$_2$, the pK_a decreases by 9 units (from +7.93 to −2.95).[14] Whatever their basicity in aqueous solution, however, positively charged amines—whether primary, secondary, or tertiary—coordinate to transition metal ions forming stable and unusual complexes.[2–6]

In most examples of such complexes so far reported, the positive charge of the amine ligand is localized on a site at least two carbon atoms removed from the N-donor atom. This paper reports complexes of Ni(II) with the 1,1,1-trimethylhydrazinium cation ligand, H$_2$NN$^+$(CH$_3$)$_3$, in which the site of the positive charge is immediately adjacent to the N-donor atom. The cat-

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