This complex was prepared by the method of Curtis.[8] [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 $C_{16}H_{28}N_4NiCl_2O_8$: 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 $C_{16}H_{28}N_4NiCl_2O_8$: 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 $C_{16}H_{28}N_4Ni(NO_3)_2$: 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_2O 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)

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The nonbasic trimethylhydrazinium cation, $H_2NN^+(CH_3)_3$, coordinates to Ni(II) forming yellow, paramagnetic complexes $NiX_4\{H_2NN^+(CH_3)_3\}_2$ (X = Cl, Br) which have a tetragonally distorted octahedral stereochemistry. The crystalline yellow complex $NiCl_4\{H_2NN^+(CH_3)_3\}_2$, when heated to 145°, changes sharply to the blue salt $\{H_2NN^+(CH_3)_3\}_2[NiCl_4]$, 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, $H_2N(CH_2)_8NH_2$, decreases on monoprotonation by less than 0.8 unit (from 10.9 to 10.1),[13] but for hydrazine, H_2NNH_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, $H_2NN^+(CH_3)_3$, in which the site of the positive charge is immediately adjacent to the N-donor atom. The cat-

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ion ligand itself, $H_2NN^+(CH_3)_3$, does not have appreciable basic character—for example, it does not acetylate nor does it form a readily isolable protonated dication. In view of its extremely low basicity and of its similarity in structure and dimensions to the nearly spherical tetramethylammonium cation, it is very interesting that the $H_2NN^+(CH_3)_3$ cation will act as a ligand in metal complexes.

Experimental Section

Preparation of the Ligands. 1,1,1-Trimethylhydrazinium chloride, $[(CH_3)_3N^+NH_2]Cl^-$, was prepared in a manner similar to that described for the β-aminoethyltrimethylammonium cation.[2] 1,1-Dimethylhydrazine was treated with acetic anhydride to form the acetyl derivative, $(CH_3)_2NNHCOCH_3$, and this was quaternized with methyl iodide. The quaternized acetyl derivative, $[(CH_3)_3N^+NHCOCH_3]I^-$, was then cleaved with hydrochloric acid, and the product, a mixed iodide–chloride of the $(CH_3)_3N^+NH_2$ cation, was converted to the pure chloride salt by ion exchange on a chloride resin. The aqueous solution was concentrated to a syrup and recrystallized from ethanol. *Anal.* Calcd for $C_3H_{11}N_2Cl$: Cl, 32.1. Found: Cl, 32.2. The analogous bromide and iodide were obtained similarly, from the iodide–chloride product described above, by ion exchange on bromide or iodide resin. *Anal.* Calcd for $C_3H_{11}N_2Br$: Br, 51.5. Found: Br, 51.8. Calcd for $C_3H_{11}N_2I$: I, 62.8. Found: I, 63.2.

Preparation of the Complexes. Tetrachlorobis(trimethylhydrazinium)nickel(II), $NiCl_4\{H_2NN^+(CH_3)_3\}_2$.—An ethanol solution of anhydrous nickel(II) chloride was added to an ethanol solution of trimethylhydrazinium chloride ($Ni:L^+$ mole ratio = 1:2.5). A clear light green solution resulted, from which upon gentle warming the microcrystalline pinkish tan salt $(L^+)_n\{NiCl_3\}_n$ precipitated. *Anal.* Calcd for $C_3H_{11}N_2Cl_3Ni$: Ni, 24.4; Cl, 44.3. Found: Ni, 24.0; Cl, 44.6. This salt, when allowed to stand for several days in the presence of its mother liquor at room temperature, gradually reacted with the excess ligand present in solution to form the yellow crystalline complex $NiCl_4(L^+)_2$. This was filtered, washed with a 1:1 ethanol–ether solution, and dried *in vacuo*. *Anal.* Calcd for $NiC_6H_{22}N_4Cl_4$: Ni, 16.74; Cl, 40.49. Found: Ni, 16.7; Cl, 40.5. The magnetic moment, μ_{eff}, was 3.25 BM.

Tetrabromobis(trimethylhydrazinium)nickel(II), $NiBr_4\{H_2N-N^+(CH_3)_3\}_2$.—This complex was obtained by dissolving nickel(II) bromide and trimethylhydrazinium bromide (mole ratio, exactly 1:2) in a very small volume of water. Slow evaporation of the resulting green solution under reduced pressure at room temperature yielded the dark yellow product $NiBr_4(L^+)_2$, in an anhydrous form. *Anal.* Calcd for $NiC_6H_{22}N_4Br_4$: Ni, 11.11; Br, 60.49. Found: Ni, 11.0; Br, 59.9. Attempts to prepare this bromo complex in ethanol solution, similarly to the chloro complex, yielded instead the tan $(L^+)_n\{NiBr_3\}_n$, identified by analyses and infrared and d–d electronic spectra.[15]

N-Deuterated derivatives were obtained by dissolving the N–H analogs in the minimum volume of D_2O and evaporating to dryness at room temperature under continuous mechanical pumping with a Dry Ice–acetone cold trap. The procedure, repeated three times, yielded compounds whose infrared spectra were completely free of $-NH_2$ or $-NHD$ absorptions.

Attempted Preparation of Other Complexes of the Trimethylhydrazinium Cation Ligand.—The reaction between trimethylhydrazinium chloride and the corresponding salts of Mn(II), Co(II), and Cu(II), carried out under a variety of experimental conditions, consistently yielded compounds in which the trimethylhydrazinium cation was present as a noncoordinated entity. The salts obtained were pink $(L^+)_n\{MnCl_3\}_n$, light yellow $(L^+)_2[MnCl_4]$, blue $(L^+)_2[CoCl_4]$, bright yellow $(L^+)_2[CuCl_4]$, and white $(L^+)_2[ZnCl_4]$. They were characterized by analyses and infrared and d–d electronic spectra.[16] Similar results were obtained with the bromide salts of these metal ions.

Attempts to prepare complexes of trimethylhydrazinium nitrate with the nitrates of Co(II), Ni(II), and Cu(II) yielded the tetranitratometalates(II) $(L^+)_2[M(NO_3)_4]$, strictly similar in their properties to the corresponding tetranitratometalates of the tetramethylammonium cation. Attempts to form complexes of trimethylhydrazinium perchlorate with the perchlorates of Co(II), Ni(II), and Cu(II) failed—the original, white, crystalline $[(CH_3)_3N^+NH_2]ClO_4^-$ being recovered unchanged from the reaction mixture.

Physical Characterization of the Complexes.—Infrared spectra (4000–250 cm^{-1}) were recorded on a Perkin-Elmer Model 521 spectrophotometer equipped with a dry-air purge. Samples were examined as hexachlorobutadiene and Nujol mulls. **d–d electronic spectra** (25,000–5000 cm^{-1}) were recorded on a Cary Model 14 spectrophotometer. Spectra of the finely powdered solid samples were obtained both by diffuse reflectance and by transmission of hexachlorobutadiene mulls. **Magnetic susceptibilities** of the powdered samples at room temperature were measured with a Gouy balance. Diamagnetic corrections from Pascal's tables were used in the calculation of μ_{eff}. For **thermal measurements**, the temperatures and ΔH values for the solid-state transformation $NiX_4(L^+)_2 \rightarrow (L^+)_2[NiX_4]$ were determined with a Du Pont differential thermal analyzer, Model 950, equipped with a differential scanning calorimeter cell.

Results and Discussion

The reaction between the dihalides of the first-row transition metals and the trimethylhydrazinium halides yields different products depending on the metal and on the experimental conditions. In general, crystalline salts containing the uncoordinated $H_2NN^+(CH_3)_3$ cation (abbreviated as L^+) and a halometalate(II) complex anion are obtained. With the chlorides and bromides of Mn(II), Co(II), Cu(II), and Zn(II) and in the presence of an excess of trimethylhydrazinium halide, the anions formed are the tetrahedral tetrahalometalates(II), MCl_4^{2-}, which can be identified by their characteristic d–d electronic spectra,[17] magnetic moments, and M–Cl infrared stretching frequencies.[18] In the presence of an excess of metal halide, however, Ni(II) and also Mn(II) give rise to salts containing polymeric, halogen-bridged, octahedral anions of the type $\{MX_3^-\}_n$. For example the Ni(II) salt thus formed, $(L^+)_n\{NiCl_3\}_n$, has magnetic and d–d electronic spectral properties very similar to those of the polymeric octahedral $Rb_n\{NiCl_3\}_n$ species.[19]

Of these halometalate(II) salts of the trimethylhydrazinium cation, the pinkish tan $(L^+)_n\{NiCl_3\}_n$ reacts, very slowly, with ethanol solutions of trimethylhydrazinium chloride to yield bright yellow crystals, which on the basis of the analytical composition, magnetic properties, and electronic and vibrational spectra can be identified as the high-spin, pseudooctahedral nonionic complex $NiCl_4(L^+)_2$. An analogous bromo complex, $NiBr_4(L^+)_2$, was obtained as a deep yellow crystalline powder. No similar iodo complex could be isolated.

The yellow complex $NiCl_4(L^+)_2$ is stable in the crystalline state at room temperature but at 145° undergoes a very sharp solid-state transformation to a deep blue crystalline substance, without change in composition. This high-temperature blue form is identified from its d–d electronic and vibrational spectra as the salt $(L^+)_2[NiCl_4]$, containing the tetrahedral tetrachloronickelate(II) anion. The blue $(L^+)_2[NiCl_4]$ reverts completely to the original yellow complex $NiCl_4(L^+)_2$ on cooling below 120°, but the transformation is rather slow. The interconversion yellow $NiCl_4(L^+)_2 \rightleftarrows$ blue $(L^+)_2[NiCl_4]$ can be carried out repeatedly without sample decom-

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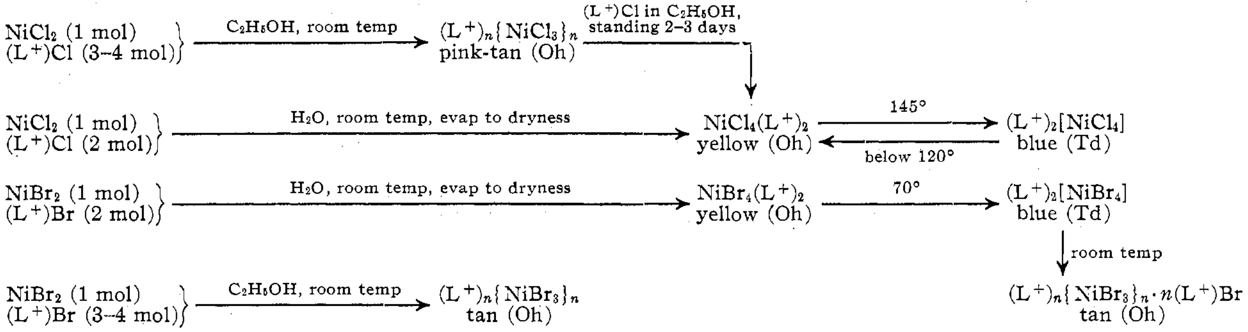
SCHEME I

INTERRELATIONS OF NICKEL(II) HALIDE COMPLEXES CONTAINING THE TRIMETHYLHYDRAZINIUM CATION, L^+



position, provided the blue form is not heated far above 145°. Samples of $(L^+)_2[NiCl_4]$, heated between 220 and 250° for 0.5 hr and then cooled to room temperature, formed microscopically homogeneous mixtures of the pinkish tan octahedral salt $(L^+)_n\{NiCl_3\}_n$ and of the free $(L^+)Cl$ (identified by their electronic and vibrational spectra). On standing for a period of days in the presence of a low-moisture atmosphere, these mixtures almost completely reverted to the original yellow complex, $NiCl_4(L^+)_2$. Thus the yellow $NiCl_4(L^+)_2$ may indeed be considered to be the stable low-temperature form of the system $NiCl_2 + 2(L^+)Cl$. In fact, the transformation $NiCl_4(L^+)_2 \rightarrow (L^+)_2[NiCl_4]$ is endothermic, its ΔH having the relatively large value of $+15.5$ (± 0.5) kcal/mol. This value, even though it includes other factors beside the breaking of two Ni–N coordinate bonds, agrees very closely with those observed in solution for reactions of the type[20]

$$[NiCl_2(C_2H_5OH)_4]_{octahedral} + Cl^- \rightleftarrows [NiCl_3(C_2H_5OH)^-]_{tetrahedral} + 3C_2H_5OH$$

Although there are many well-established examples of octahedral–tetrahedral equilibria for complexes of Ni(II) in solution, the interconversion between the yellow, octahedral $NiCl_4(L^+)_2$ and the blue, tetrahedral $(L^+)_2[NiCl_4]$ represents an almost unique example of a reversible change in coordination number and stereochemistry, taking place in the solid state at a relatively low temperature.

The octahedral bromo complex $NiBr_4(L^+)_2$ is thermally less stable than the chloro complex and at 70° transforms sharply into the blue salt $(L^+)_2[NiBr_4]$, containing the tetrahedral tetrabromonickelate(II) anion, which is then stable up to 260°. As expected, the ΔH of the transformation is also lower than for the corresponding chloro complex—its value being approximately $+9$ kcal/mol. (An accurate determination was prevented by the tendency of the yellow bromo complex to "jump" and spatter during the transformation.) When the blue $(L^+)_2[NiBr_4]$ cools to room temperature, it slowly changes to a microscopically homogeneous mixture of the tan octahedral $(L^+)_n\{NiBr_3\}_n$ and of L^+Br^-. The interrelations of the various salts and complexes formed by nickel(II) chloride and bromide with the trimethylhydrazinium halides are summarized in Scheme I (where Oh signifies octahedral complexes and Td tetrahedral). It should be mentioned that all the solid species included in this scheme—the complexes $NiX_4(L^+)_2$ as well as the salts $(L^+)_n\{NiX_3\}_n$ and $(L^+)_2[NiX_4]$—apparently are stable only in the solid state. In fact, all these compounds are insoluble in nonpolar solvents and dissolve in good donor solvents with complete solvation.

d–d Electronic Spectra.—The d–d electronic spectra of the complexes $NiCl_4(L^+)_2$ and $NiBr_4(L^+)_2$ clearly indicate a tetragonally distorted octahedral stereochemistry. The energy values of the absorption maxima are listed in Table I, together with those of some structurally similar complexes for comparison. In general, the extent of the tetragonal distortion of an octahedral complex can be related to the difference in the field strengths of the ligands occupying the axial and equatorial positions. The field strengths of the chloro and bromo ligands are well known, and thus the observed splitting of the ${}^3T_2(F) \leftarrow {}^3A_2(F)$ transition can be used as a criterion for placing the trimethylhydrazinium cation ligand in the spectrochemical series. For $NiCl_4(L^+)_2$ this splitting is about 1.15 kK, very close to that observed for the tetragonal $NiCl_4(H_2O)_2{}^{2-}$ anion.[21] In fact, the entire spectra of the two complexes $NiCl_4(L^+)_2$ and $NiCl_4(H_2O)_2{}^{2-}$ are virtually superimposable, indicating that the field strength of the trimethylhydrazinium cation ligand must be very similar to that of water ($10Dq = 9$ kK)[22] and therefore appreciably lower than that of uncharged primary aliphatic amines ($10Dq = \sim 10$ kK)[23] or of heterocyclic N-donor ligands such as pyridine ($10Dq = 9.8$ kK).[24] For the pseudo-

TABLE I

d–d ELECTRONIC SPECTRA[a] AND ASSIGNMENTS

Complex[b]	${}^3A_2(F) \rightarrow$				
	${}^3T_2(F)$		${}^3T_1(F)$		${}^3T_1(P)$
$(L^+)_n\{NiCl_3\}_n$	6.25	7.15	11.3, 12.6	18.7 sh[c]	21.3
$NiCl_4(L^+)_2$	6.15	7.30	12.6	19.05 sh[c]	22.6
$(L^+)_n\{NiBr_3\}_n$	6.65		10.8	17.4 sh[c]	20.05
$NiBr_4(L^+)_2$	6.15	7.14	11.95	18.4 sh[c]	21.6
$(C^{2+})[NiCl_4(H_2O)_2]$[d]	5.7	7.0	12.1		22.6
$\{NiCl_2(py)_2\}_n$[e]	6.00	8.40	12.2, 13.9		Not reported
$\{NiBr_2(py)_2\}_n$[e]	5.8	8.00	11.6, 13.7		Not reported

[a] Reported values (kilokaysers) are absorption maxima from diffuse reflectance spectra. Transmission spectra of hexachlorobutadiene mulls gave nearly coincident values but the lower energy bands were not well resolved. [b] L^+ = trimethylhydrazinium, $H_2NN^+(CH_3)_3$. [c] Shoulder assigned to spin-forbidden transition to one of the ${}^1D$ states. [d] C^{2+} = diprotonated 1,4-dimethylpiperazinium, $(CH_3)HN^+(CH_2CH_2)_2N^+H(CH_3)$.[19] [e] py = pyridine; values from D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

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TABLE II

INFRARED ABSORPTIONS[a] ARISING FROM VIBRATIONS OF THE NH_2 GROUP OF THE $H_2NN^+(CH_3)_3$ CATION LIGAND

	$(L^+)I$		$(L^+)_2[CoCl_4]$[b]		$(L^+)_n\{NiCl_3\}_n$[c]		$NiCl_4(L^+)_2$		$NiBr_4(L^+)_2$
NH_2–ND_2 antisym str	*d*	2465 vs 2445 vs	3290 vs	2470 vs 2453 vs 2382 m	3315 vs 3275 sh, m	2474 s 2452 s	3210 vs	2400 vs 2343 sh, m 2318 m	3190 vs
NH_2–ND_2 sym str	*d*	2350 m 2310 s 2285 m	3180 vs	2330 s 2310 sh	3200 m	2370 m 2330 m	3115 vs	2290 sh, m 2276 s	3100 vs
NH_2–ND_2 bend	1615 s	1168 s	1620 s	1178 s	1605 s	1170 s	1592 m	1164 m	1582 m
NH_2–ND_2 twist	1278 s	995 s	1280 m	1010 m	1278 m	1020 m	1299 m	1010 w	1290 m
NH_2–ND_2 wag	1055 vs, b	780 vs	1065 vs, b	800 vs, b	1083 vs 1075 vs	832 sh 828 vs	1190 vs	886 vs	1190 vs
NH_2–ND_2 rock	. . .	. . .	. . .	. . .	. . .	. . .	640 m	500 m	600 w
NH_2–ND_2 torsion	475 m	370 w	484 m	370 m	490 m 482 m	373 m	480 m[e]	363 w	475 m

[a] Values are in cm^{-1}. Samples were examined as mulls in hexachlorobutadiene and Nujol. [b] The spectra of $(L^+)_2[CoBr_4]$, $(L^+)_2[MnCl_4]$, $(L^+)_2[CuCl_4]$, and $(L^+)_2[ZnCl_4]$ are virtually identical with that of $(L^+)_2[CoCl_4]$. [c] The spectra of $(L^+)_n\{NiBr_3\}_n$ and $(L^+)_n\{MnCl_3\}_n$ are virtually identical with that of $(L^+)_n\{NiCl_3\}_n$. [d] Very strong, broad, unresolved absorptions in the 3300–3100-cm^{-1} region. [e] An additional medium-weak band appears at 526 cm^{-1} in the spectrum of $NiCl_4(L^+)_2$ and is lowered to 434 cm^{-1} in the N-deuterated analog. This band was not observed in the bromo complex and was not assigned.

octahedral complex $\{NiCl_2(py)_2\}_n$, in which the pyridine molecules occupy the (trans) axial positions and the Cl^- ions are bridging at the equatorial sites,[25] the splitting of the ${}^3T_2(F) \leftarrow {}^3A_2(F)$ transition is 2.4 kK—twice as large as that observed for $NiCl_4(L^+)_2$. It is logical to attribute this lowering of the field strength of the NH_2 group of trimethylhydrazinium to the influence of the adjacent positive charge of the $(CH_3)_3N^+$ group. Finally, the energy of the ${}^3T_1(P) \leftarrow {}^3A_2(F)$ transition for $NiCl_4(L^+)_2$ is higher by about 1.3 kK than for the polymeric $\{NiCl_3^-\}_n$ species. This shows that the N-donor atom of the trimethylhydrazinium cation, despite the presence of the adjacent positive charge, still has a nephelauxetic effect appreciably lower than that of the chloro ligand.

Infrared Spectra.—The infrared spectra of several salts of the trimethylhydrazinium cation and of the two complexes $NiCl_4(L^+)_2$ and $NiBr_4(L^+)_2$ were determined in the 4000–250-cm^{-1} region (Table II). All absorptions arising from fundamental vibrations of the NH_2 group in these compounds were identified by comparison with the *N*-deuterio analogs and follow the pattern characteristic of "symmetrical top" primary aliphatic amines—such as methylamine,[26] H_2NCH_3, and *tert*-butylamine,[15] $H_2NC(CH_3)_3$. The observed frequency shifts may be attributed to the influence of the positive charge on the NH_2 group. In the salts of the $H_2NN^+(CH_3)_3$ cation the frequencies of the NH_2 modes are only very slightly affected by the counterion—whether it be monatomic such as the iodide or polyatomic consisting of discrete monomeric entities such as $CoCl_4^{2-}$ or even polymeric such as $\{NiCl_3^-\}_n$. Coordination of the $H_2NN^+(CH_3)_3$ cation to a metal ion, on the other hand, causes marked shifts in the characteristic NH_2 frequencies, and these shifts have the magnitude and direction usually observed for metal complexes of uncharged primary amines. Thus, the NH_2 stretching modes are lowered by about 100 cm^{-1}, the NH_2 bending mode is lowered by about 20–10 cm^{-1}, the NH_2 twisting mode is raised by about 20 cm^{-1}, and the NH_2 wagging mode is raised by about 100 cm^{-1}. In addition, the rocking mode arising from coordination of the NH_2 groups appears as a new, medium-strong band at about 600 cm^{-1}. Unfortunately, it was not possible to identify with certainty the N–Ni(II) stretching mode. This is not surprising, however, since this metal–ligand mode is often rather weak and the low-energy region of the spectra of these complexes is cluttered by many absorptions characteristic of the ligand itself.

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