As can be noted from Table I, the only products that were stable (as determined by hydrogen evolution) were those obtained from diethyl ether and tetrahydrofuran. The diethyl ether adduct is stable at room temperature in the absence of air and moisture, and the product from tetrahydrofuran is stable at 0°. Hydrogen, hydrogen sulfide, and ether were identified as decomposition products of the tetrahydrofuran and monoglyme adducts at room temperature.

A white solid pyridine adduct, $S_7NBH_2 \cdot C_5H_5N$, was isolated from the reaction of $S_7NBH_2 \cdot Et_2O$ with pyridine. Pure samples of this compound were stable indefinitely *in vacuo* at 0° and could be kept in an ordinary closed bottle at room temperature for as long as 5 days without decomposition. However, impure samples decomposed within 1 or 2 days.

When the reaction of heptasulfur imide and diborane is carried out with an excess of S_7NH in tetrahydrofuran at 0°, the reaction does not stop with the formation of S_7NBH_2, as evidenced by the continued slow evolution of hydrogen. Presumably the following subsequent reaction occurs: $S_7NH + S_7NBH_2 \rightarrow (S_7N)_2BH + H_2$. However, the reaction was incomplete after 1 month and was not further studied.

Experimental Section

Reagents and Procedure.—Heptasulfur imide was prepared by the usual method[3] and was purified by one recrystallization from methanol followed by repeated recrystallizations from carbon tetrachloride until the solutions were colorless and the solid melted at 113–114° (lit.[4] mp 113.5°). The infrared spectrum agreed with that reported in the literature.[4] Diborane was made by the reaction of potassium borohydride with phosphoric acid[5] and purified by vacuum distillation through a −112° trap. Tetrahydrofuran, diethyl ether, and dioxane were distilled from lithium aluminum hydride immediately before use. Monoglyme (1,2-dimethoxyethane) was distilled first from calcium hydride and then from lithium aluminum hydride. Pyridine was distilled from potassium hydroxide, and carbon tetrachloride was distilled from phosphorus pentoxide.

Approximately 10 ml of solvent was vacuum distilled into a 50-ml flask containing a known weight of heptasulfur imide. A known amount of diborane was condensed into the reaction vessel, and the vessel was allowed to warm to either room temperature or 0°. At various times the evolved hydrogen was collected using a Toepler pump, measured in a gas buret, and identified by mass spectroscopy. To isolate the crystalline product $S_7NBH_2 \cdot Et_2O$, an all-glass system was employed. The apparatus was sealed off after addition of the reactants and was provided with a break-seal for removal of hydrogen and a side arm for washing the product by decantation. The product was then removed in a drybox. *Anal.* Calcd for $S_7NBH_2 \cdot C_4H_{10}O$: C, 14.76; H, 3.69; N, 4.30; S, 69.01. Found: C, 14.86; H, 3.69; N, 4.45; S, 68.68.

A sample of S_7NBH_2 prepared in tetrahydrofuran was treated with a 500-fold excess of distilled water. The evolved hydrogen was collected and measured as described above. The precipitated S_7NH was collected by filtration, air-dried, and then weighed. It was identified by its infrared spectrum.[4] The boric acid formed was determined by a standard double-titration method.[6] *Anal.* Calcd for S_7NBH_2 prepared from 0.386 mmol of S_7NH: H_2, 0.772 mmol; $B(OH)_3$, 0.386 mmol; S_7NH, 0.386 mmol. Found: H_2, 0.773 mmol; $B(OH)_3$, 0.393 mmol; S_7NH, 0.31 mmol.

Raman Spectrum.—The following lines were observed for the diethyl ether adduct ($cm^{-1} \pm 3\ cm^{-1}$): 2969 (w), 2930 (w–m), 2419 (w), 2409 (sh), 1471 (w), 1452 (w–m), 1442 (sh), 1324 (w), 1181 (w–m), 1091 (w–m), 1005 (w), 870 (w–m), 851 (sh), 832 (w), 766 (w–m), 750 (w–m) 602 (m), 476 (vs), 458 (m), 437 (m), 292 (s), 251 (m), 213 (vs), 201 (s), 178 (m), 153 (s). The Raman spectrometer consisted of a Spectra-Physics 125 helium–neon laser with line filter (35 mW) and a Spex 1401 monochromator equipped with an ITT FW-130 photomultiplier tube.

Nmr Spectra.—The samples for the ^{11}B nmr spectra were prepared and recorded in 12-mm o.d. tubes containing diethyl ether, in which the compound is only slightly soluble. For this reason the spectra were computer averaged over 10–150 scans. The spectrum consisted of a 1:2:1 triplet centered 33.5 ppm upfield from an external reference peak of boron trichloride, with $J_{B-H} = 136$ Hz. A Varian Model V4311 high-resolution nmr spectrometer operated at 8.134 MHz was used for the boron spectra. Proton spectra of samples prepared from monoglyme and diethyl ether were recorded in CS_2 using a Varian A-60 spectrometer. Although the samples decomposed in CS_2, the spectra did indicate the presence of the coordinated ether. For the sample from diethyl ether, a triplet at 1.98 ppm and a quartet at 4.75 ppm, relative to TMS, were observed, while from monoglyme two singlets at 4.63 and 4.67 ppm and a complex pattern centered at 4.87 ppm were noted. The complexity of the latter spectrum indicates that only one of the oxygen atoms of monoglyme was coordinated to S_7NBH_2.

X-Ray Diffraction.—Some preliminary X-ray diffraction data on a single crystal of $S_7NBH_2 \cdot C_4H_{10}O$ correspond to the space group *Pnma* and the unit cell dimensions (Å) $a = 15.80$, $b = 13.16$, and $c = 6.75$.

Preparation and Characterization of $S_7NBH_2 \cdot C_5H_5N$.—The pyridine adduct was prepared by addition of excess, dry pyridine to the solid $S_7NBH_2 \cdot Et_2O$. The solution was evaporated to a volume of 0.2–0.3 ml, and dry CCl_4 was then added. A white solid was precipitated and was washed with a small amount of chilled CCl_4. The infrared spectrum of a Nujol mull recorded with a Perkin-Elmer Model 137B Infracord spectrophotometer consisted of the following peaks ($cm^{-1} \pm 10\ cm^{-1}$): 2415 (m), 2353 (sh), 1618 (m), 1186 (m), 1157 (w), 1139 (sh), 1131 (s), 1100 (m–s), 1025 (w), 1013 (w), 977 (w), 961 (sh), 953 (m), 943 (s), 929 (w), 917 (m), 775 (m), 768 (m), 751 (s), 687 (s). A sample melting at 87.5–88° was analyzed. *Anal.* Calcd for $S_7NBH_2 \cdot C_5H_5N$: C, 18.17; H, 2.14; N, 8.48; S, 67.92; B, 3.3. Found: C, 18.97, H, 2.08; N, 8.62; S, 67.98; B, 3.2 (as a B_2O_3 residue). A proton nmr spectrum showed the protons on the pyridine ring, but we were unable to see the protons attached to boron.

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Niobium(IV) Halide Complexes of *N*,*N*-Dimethylformamide. Synthesis and Spectra

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N,*N*-Dimethylformamide resembles water and methanol in its solvent properties, but unlike these it is a nonhydroxylic solvent. With anhydrous halides such as TiX_4 (X = Cl, Br, I)[1] and $ZrCl_4$[2] it reacts to form

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[1] J. Archambault and R. Rivest, *Can. J. Chem.*, **38**, 1331 (1960).

[2] A. Clearfield and E. J. Malkiewick, *J. Inorg. Nucl. Chem.*, **25**, 237 (1963).

addition compounds, $MX_4 \cdot n$DMF. The relative ease with which the metal–metal bonded cluster compound Mo_6Cl_{12} is solvated[3] attests to the high donor properties of this solvent. With $MoCl_5$ oxygen abstraction occurs to yield a molybdenyl (MoO^{3+}) complex.[4] Another report[5] suggests that DMF is a good solvent for polymeric $NbCl_4$ with which it yields deep blue solutions. The color suggests that coordinated oxoniobium(IV) (NbO^{2+}) may have been formed *via* an oxygen abstraction. Since niobium(IV) halide reactions with Lewis bases are dominated by simple addition uncomplicated by other reactions, we decided to reinvestigate this system. A further motive for the study was to explore the feasibility of DMF as a medium for studying reactions of niobium(IV). Such studies have been hindered, in part, by the low solubility of the anhydrous halides and their complexes in most solvents. The study was extended to include the series NbX_4 (X = Cl, Br, I) of which all are diamagnetic solids with metal atoms bonded in pairs *via* metal–metal bonds.[6]

Experimental Section

Due to the oxygen and water sensitivity of the compounds, all were handled under high vacuum or in a Vacuum Atmospheres Corp. nitrogen-filled drybox, maintained *ca.* 1 ppm water and oxygen.

Materials.—Niobium pentachloride and high-purity niobium metal were purchased from Alfa Inorganics. $NbBr_5$, NbI_5, and NbX_4 (X = Cl, Br, I) were prepared by using procedures previously described.[7]

N,N-Dimethylformamide (DMF), purchased from Eastman Kodak, was purified by the method of Leader and Gormley[8] with the following modification. The DMF was purged with dry nitrogen before being distilled under dry nitrogen onto a mixture of KOH and CaO.

Analytical.—Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The elements determined were C, H, X (X = Cl, Br, I), and Nb. Molecular weight was determined for the bromide complex osmometrically in DMF.

Spectra.—All esr spectra were obtained on solutions and powders at ambient temperature and 77°K by use of a Varian Model E-4 spectrometer with an operating frequency range of 8.8–9.6 GHz.

Electronic spectra were recorded by using a Cary Model 14 spectrophotometer. Cylindrical fused silica cells, of 0.5-cm path length, adapted for use at low pressure, were used.[7a] Powdered samples and saturated solutions were loaded in the drybox. The cell assembly was then evacuated to *ca.* 10^{-5} Torr. After sealing off the cell assembly, solutions of various concentrations could be obtained by distilling solvent through a medium-porosity frit into more concentrated solutions in the cell.

Solid-state infrared spectra were obtained by use of a Perkin-Elmer 457 (4000–250 cm^{-1}) spectrophotometer. Samples were prepared in the drybox and were mounted as Nujol mulls between sodium chloride plates. Mulls were prepared immediately before measuring the spectra.

Far-infrared spectra were obtained by using a Block Engineering Co. Model-FTS 16 (3900–20 cm^{-1}) far-infrared spectrophotometer. High-density polyethylene was used for windows.

Synthesis.—The preparative procedure varied only slightly from one halide to the other. The appropriate halide (2–3 g), 50–100 ml of DMF, and a magnetic stirring bar were introduced into a round-bottomed flask. This flask was evacuated to *ca.* 10^{-5} Torr and, after extensive outgassing, was isolated from the vacuum system. The mixture was stirred for several days at room temperature.

A yellow saturated solution and a brown-yellow precipitate were obtained with $NbCl_4$. The precipitate was recovered by filtration, extracted with DMF, filtered again, washed with dry pentane, and dried *in vacuo*. *Anal.* Calcd for $NbCl_4 \cdot 2C_3H_7NO$: Nb, 24.4; Cl, 37.2; C, 18.9; H, 3.7. Found: Nb, 24.7; Cl, 37.0; C, 19.3; H, 3.7; mp 139–142°.

An opaque green solution was obtained with $NbBr_4$. A bright green solid was present in the mixture. *Anal.* Calcd for $NbBr_4 \cdot 2C_3H_7NO$: Nb, 16.6; Br, 57.2; C, 12.9; H, 2.5. Found: Nb, 16.8; Br, 54.0; C, 12.8; H, 3.0; mp 230–233°. Molecular weight in DMF: calcd for $NbBr_4 \cdot 2DMF$, 558; found, 506.

A similar opaque green solution was found with NbI_4. There was no solid present in solution. The iodide solution was filtered, and a green crystalline solid was recovered from the filtrate by removal of excess DMF *in vacuo*. This product was then washed with dry pentane and dried *in vacuo*. *Anal.* Calcd for $NbI_4 \cdot 8C_3H_7NO$: Nb, 7.8; I, 42.8; C, 24.3; H, 4.8. Found: Nb, 7.4; I, 43.4; C, 24.0; H, 5.0; mp 130–132°.

Results and Discussion

Solid-State Studies.—The solubility of the halides in DMF was in the order I > Br ≫ Cl. The chloride solutions were also yellow rather than deep blue as reported earlier.[5] Data for the chloride and bromide complexes suggest that they are simple diadducts (either cis or trans). The iodide composition, however, is identical with that found for $TiI_4 \cdot 8DMF$,[1] which has been discussed as a simple adduct with six additional ligands bonded in a secondary coordination sphere, *e.g.*, $TiI_4(DMF)_2 \cdot 6DMF$.

The important ir frequencies and their assignments are presented in Table I. The ir spectrum of DMF has been discussed in a number of reports, but the most detailed study has been that of Kaufmann and Leroy[9] which included a normal-coordinate analysis. This study revealed that ν(CO), ν(CN), and ν(CH) in DMF are extensively coupled rendering less significant (as an indicator of coordination *via* the carbonyl oxygen) the observed shift $\Delta\nu$(CO) in the carbonyl band at 1682 cm^{-1}. Jungament and Curran[10] however reported that in complexes δ(N—C=O) at 657 cm^{-1} shifts to higher frequency upon coordination, and the results of normal-coordinate analysis indicated that it does not interact with other modes of vibration. In $Pd(DMF)_4{}^{2+}$[11] $\Delta\delta$(N—C=O) is +60 cm^{-1}, the same value found for $Al(DMF)_6{}^{3+}$.[12]

TABLE I

RELEVANT DATA FROM INFRARED SPECTRA (IN CM^{-1}) OF NUJOL MULLS[a]

Complex	ν(CO)	$\Delta\nu$-(CO)	δ(N—C=O)	$\Delta\delta$(N—C=O)	ν(Nb—X)	ν(Nb—O)
$NbCl_4(DMF)_2$	1647 (s)	−35	700 (s)	+40	318 (s)	428 (s)
$NbBr_4(DMF)_2$	1647 (s)	−35	700 (s)	+40	248 (s)	425 (s)
$NbI_4 \cdot 8DMF$	1645 (s)	−37	700 (s)	+40		435 (s)

[a] s = strong intensity.

As shown in Table I, $\Delta\nu$(CO) for the complexes and $\Delta\delta$(N—C=O) are reasonably constant at −35 and +40 cm^{-1}, respectively. We consider this to be indicative of coordination of DMF *via* the carbonyl oxygen. Bands attributable to uncoordinated DMF were not observed in any of the spectra.

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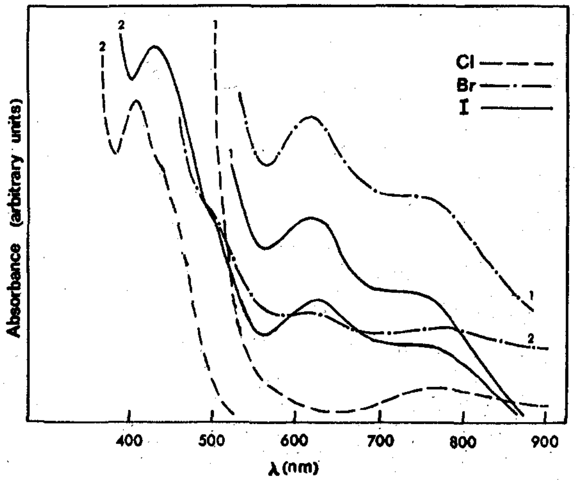

Figure 1.—Electronic spectra of $NbX_4 \cdot n$DMF in DMF. Molar concentration: Cl, (1) 7.27×10^{-2}, (2) 6.65×10^{-3}; Br, (1) 1.19×10^{-2}, (2) 1.87×10^{-3}; I, (1) 2.1×10^{-2}, (2) 1.44×10^{-2}.

In the region below *ca.* 600 cm^{-1} one expects both internal ligand bands and bands due to metal-ligand vibrations. For the series of complexes reported here, both metal-oxygen and metal-halogen bands should be observed. A single strong band observed for the chloride at 428 cm^{-1} and for the bromide at 425 cm^{-1} was assigned as ν(Nb-O). Only a weak band at 405 cm^{-1} was present in the spectrum of pure DMF. Bands were also reported in this region for $SnX_4 \cdot 2$DMF (X = Cl, Br),[13] but they were not assigned to ν(Sn-O). On the other hand Wayland and Schramm[11] so assigned bands at 420 and 463 cm^{-1} for $Pd(DMF)_2Cl_2$ and $Pd(DMF)_4^{2+}$, respectively. For the iodide complex $NbI_4 \cdot 8$DMF a single, very broad band is observed in this region.

Single bands of high intensity observed at 318 and 248 cm^{-1} in the spectrum of $NbCl_4 \cdot 2$DMF and $NbBr_4 \cdot 2$DMF, respectively, are assigned as ν(Nb-X). The shift to lower frequency is as expected for complexes having the same stereochemistry but differing only in the nature of the halide. These results—only one ν(Nb-X) band and the appearance of only one ν(Nb-O)—are consistent with trans six-coordinate complexes rather than cis complexes.

The ir spectrum of the iodide showed no bands attributable to ν(Nb-I). This suggests extensive ionization of Nb-I bonds in the solid state to form the species $Nb(DMF)_nX_{4-m}^{m+}$. Such a formulation contrasts with that reported for $TiI_4 \cdot 8$DMF.[1] There have been no earlier reports of well-characterized cationic niobium(IV) complexes.

The esr spectrum for the chloride complex at 77°K was a broad symmetric resonance with $\langle g \rangle = 1.660$. The bromide exhibited similar resonances at both 298 and 77°K having respective $\langle g \rangle$ values of 1.696 and 1.740. The fact that esr spectra were observed for these d^1 complexes suggests that the electron resides in an orbital singlet ground state as expected for a trans complex. The iodide exhibited spectra at both 298 and 77°K which contained hyperfine lines arising from ^{93}Nb ($I = {}^9/_2$, 100% abundance). The occurrence of resolved hyperfine structure is not inconsistent with the earlier formulation, $Nb(DMF)_n^{4+}$, since these centers would be well separated in the ionic lattice by halide ions and extra DMF molecules. At 298°K the spectrum was isotropic with $\langle g \rangle = 1.953$ and $\langle A \rangle_{Nb} = 0.0185$ cm^{-1}. At 77°K the spectrum was slightly anisotropic.

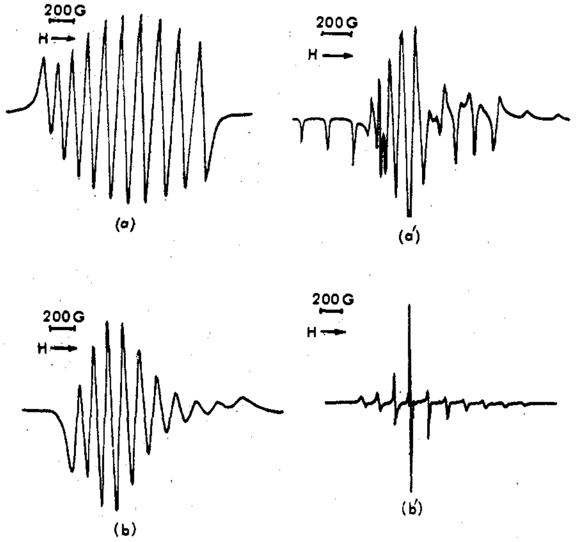

Figure 2.—Solution esr spectra: at ambient temperature, (a) $NbCl_4$, (b) NbX_4 (X = Br, I); at 77°K, (a') $NbCl_4$, (b') NbX_4 (X = Br, I).

Solution Studies.—The solubility of the niobium(IV) halides in DMF afforded an opportunity to investigate their electronic spectra and esr spectra. Figure 1 gives the electronic spectra and Figure 2 shows typical esr spectra.

The visible spectra of the chloride, bromide, and iodide in DMF exhibited low-intensity bands at 775, 446, and 437 nm; 752, 633, and 485 nm; and 741, 621, 490, and 450 nm, respectively. We are reluctant to assign these bands as due to d-d transitions until further studies of niobium(IV) halides in DMF have been completed.

The solution esr spectra in DMF exhibited the typical ten-line hyperfine splitting. The experimental $\langle g \rangle$ values were 1.900, 1.960, and 1.966 while the experimental isotropic hyperfine splittings were 0.0164, 0.0161, and 0.0165 cm^{-1} for the chloride, bromide, and iodide, respectively. Esr spectra recorded at Q-band frequencies for $NbCl_4(DMF)_2$ exhibited no unexpected bands. Both $\langle g \rangle$ and $\langle A \rangle$ were the same as found for X-band spectra. At low temperature, the chloride exhibited the asymmetry expected for a tetragonally distorted octahedral complex. The esr parameters obtained were $g_\perp = 1.910$, $g_\parallel \simeq 1.885$, $A_\parallel = 0.0239$, and $A_\perp \simeq 0.0119$ cm^{-1}.

Esr spectra at 77°K for both the bromide and iodide were unexpectedly isotropic and identical with $\langle g \rangle = 1.913$ and $\langle A \rangle = 0.0176$ cm^{-1}. This congruence was also evident in the spectra at 298°K. It is recalled that a similar congruence was noted for the electronic spectra of these complexes in DMF. While spectra of complexes of similar stereochemistry differing only in halide are expected to be more similar for X = Br and I than for X = Cl, a virtually one-to-one correspondence is totally unexpected. At this point it is proposed that identical complexes are present in the solu-

(13) M. F. Farona and J. G. Graselli, *Inorg. Chem.*, **6**, 1675 (1967).

tions. The only possible class of complexes (alluded to earlier) is $Nb(DMF)_nX_{4-m}{}^{m+}$. While as yet it has not been possible to isolate such complexes, preliminary conductance measurements for DMF solutions of the iodide indicate these solutions are 10^3 times more conducting than the pure DMF used in this study. Ionization is expected to be favored in the order I $\approx$ Br $\gg$ Cl.[14]

While our results for the chloride differ in one respect from those of Gut,[5] we have confirmed the polarographic wave at −890 mV *vs.* sce observed by him and have observed another wave of similar height at −1.37 V *vs.* sce. Further studies of these interesting solutions by normal chemical methods and electrochemical techniques are in progress.

Acknowledgment.—The authors wish to thank Dr. Robert E. McCarley for obtaining duplicate far-infrared spectra for solid complexes reported in this paper. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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The Effect of Chelate Ring Size on Metal–Ligand Stretching Frequencies

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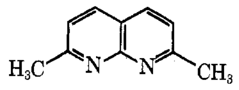
Several transition metal complexes with 2,7-dimethyl-1,8-naphthyridine have been prepared and characterized by Hendricker and Bodner.[1] These complexes are of special interest since they form four-member chelate ring systems. Hendricker and Bodner have measured the electronic and infrared spectra (4000–200 cm^{-1}). Based on metal–nitrogen stretching band assignments for $SnCl_4$dmnapy (dmnapy = 2,7-dimethyl-1,8-naphthyridine, I), $SnCl_4$phen (phen = 1,10-phenanthroline), and $SnCl_4$bipy[2] (bipy = 2,2′-bipyridine), they suggested that the metal–nitrogen stretching bands for $[M(dmnapy)_3](ClO_4)_2$, where M is the metal, occur below 200 cm^{-1} and were not detected in their study. Using the infrared spectra of 1,8-naphthyridine as a model, they assigned and discussed ligand bands for the metal complex spectra.



I

In this paper we have studied the low-frequency infrared spectra (400–100 cm^{-1}) of the manganese, nickel, cobalt, and zinc tris(2,7-dimethyl-1,8-naphthyridine) perchlorate complexes and assigned the metal–nitrogen stretching bands based on the metal isotope technique.[3] The metal–nitrogen stretching vibrations are discussed in terms of strain in the four-member chelate ring.

Experimental Section

Materials.—The ligand 2,7-dimethyl-1,8-naphthyridine was prepared by the method of Paudler and Kress.[2] Nickel and zinc isotopes were obtained from the Oak Ridge National Laboratories, Oak Ridge, Tenn. All other materials used were of reagent grade.

Preparations.—The complexes $[Mn(dmnapy)_3](ClO_4)_2$, $[Co(dmnapy)_3](ClO_4)_2$, $[Ni(dmnapy)_3](ClO_4)_2$, and $[Zn(dmnapy)_3](ClO_4)_2$ were prepared by the method of Hendricker and Bodner.[1] ^{58}Ni and ^{62}Ni were obtained as the metal while ^{64}Zn and ^{68}Zn were purchased as the oxide. The isotopic purity of the metals used was as follows: ^{58}Ni, 99.98%; ^{62}Ni, 98.75%; ^{64}Zn, 99.60%; ^{68}Zn, 98.50%. An aqueous metal solution was obtained by dissolving the isotopic metal species in dilute perchloric acid. The isotopic metal complexes were also prepared by the method of Hendricker and Bodner.[1]

Instrumentation.—The low-frequency spectra of the isotopic metal species were recorded as Nujol mulls on a Hitachi Perkin-Elmer FIS-3 far-infrared spectrophotometer using polyethylene plates and on a Beckman Ir-12 spectrophotometer using CsI plates. Calibrations were performed using polystyrene and water vapor. The frequencies of the bands measured for isotopic species are reproducible to ±0.5 cm^{-1}.

Analysis.—Analytical results are given for the naturally abundant (NA) metal complexes. The infrared spectra of the isotopic metal complexes corresponded to the naturally abundant metal complexes. *Anal.* Calcd for $[Mn(C_{10}H_{12}N_2)_3](ClO_4)_2$: C, 49.46; H, 4.16; N, 11.54. Found: C, 49.61; H, 3.98; N, 11.31. Calcd for $[Ni(C_{10}H_{12}N_2)_3](ClO_4)_2$: C, 49.20; H, 4.14; N, 11.48. Found: C, 49.29; H, 4.22; N, 11.60. Calcd for $[Zn(C_{10}H_{12}N_2)_3](ClO_4)_2$: C, 48.76; H, 4.22; N, 11.60. Found: C, 48.64; H, 4.33; N, 11.19. Calcd for $[Co(C_{10}H_{12}N_2)_3](ClO_4)_2$: C, 49.19; H, 4.14; N, 11.48. Found: C, 49.61; H, 3.90; N, 11.32. Carbon, nitrogen, and hydrogen analyses were performed by M-H-W Laboratories, Garden City, Mich.

Results

The 400–100-cm^{-1} region of the spectrum is assigned using the metal isotope technique.[3] This technique allows us to assign directly metal–ligand stretching bands. Absorptions due to ligand vibrations are assigned based on comparison with the free-ligand spectrum and the metal isotope data. Metal–ligand bending vibrations occur much lower than the metal–ligand stretching and do not appear in the region studied.[4] The infrared spectra obtained by Hendricker and Bodner are very similar to the spectra we have measured. We observed a very weak band about 315 cm^{-1} in the metal complexes not previously reported; this band is assigned as a complex-activated ligand band. Only one significant change in band position was found: the band at 361.1 cm^{-1} for the nickel complex in our work is reported at 376 cm^{-1} by Hendricker and Bodner.[1] We have no explanation for this difference, and it does not affect our discussion. The low-frequency spectral bands for the four complexes are presented in Table I. The actual tracing of the region containing the M–N stretching bands is shown in Figure 1.

Ligand Bands.—The free-ligand spectrum contains three bands below 400 cm^{-1}. These three bands are shifted to higher wave number upon complexation. The 346-cm^{-1} ligand spectrum band is observed at 359, 360, 361, and 357 cm^{-1} in the manganese, cobalt,

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