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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[14] V. Gutmann, referred to in "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, New York, N. Y., 1968.

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

BY BENNETT HUTCHINSON* AND ALAN SUNDERLAND

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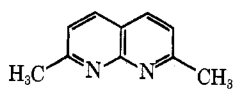
Several transition metal complexes with 2,7-dimethyl-1,8-naphthyridine have been prepared and characterized by Hendricker and Bodner.[1] These complexes are of special interest since they form four-member chelate ring systems. Hendricker and Bodner have measured the electronic and infrared spectra (4000–200 cm^{-1}). Based on metal–nitrogen stretching band assignments for $SnCl_4dmnapy$ (dmnapy = 2,7-dimethyl-1,8-naphthyridine, I), $SnCl_4phen$ (phen = 1,10-phenanthroline), and $SnCl_4bipy$[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.

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.



I

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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[1] D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, **9**, 273 (1970).

[2] W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, **4**, 284 (1967).

[3] (a) K. Nakamoto, K. Shobatake, and B. B. Hutchinson, *Chem. Commun.*, 1451 (1969); (b) B. B. Hutchinson, Ph.D. Thesis, Illinois Institute of Technology, 1970; (c) N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, **10**, 798 (1971).

[4] T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, **3**, 1805 (1964).

TABLE I[a]

OBSERVED FREQUENCIES (400–100 CM^{-1}) AND BAND ASSIGNMENTS FOR [Mn(dmnapy)$_3$](ClO$_4$)$_2$, [Co(dmnapy)$_3$](ClO$_4$)$_2$, [Ni(dmnapy)$_3$](ClO$_4$)$_2$, and [Zn(dmnapy)$_3$](ClO$_4$)$_2$

dmnapy	^{NA}Mn	^{NA}Co	^{NA}Ni	^{58}Ni	^{62}Ni	^{NA}Zn	^{64}Zn	^{68}Zn	Assignment
346 m	359 m	360 m	361 m	361.4	361.4	357 m	356.2	357.0	Ligand
	312 vw	317 vw	318 w	318.4	317.8	314 vw	[b]	[b]	Ligand
247 m	268 s	283 s	288 s	*288.4*	*285.6*	270 m	271.2	270.4	Ligand + Ni–N str (?)
	202 m	214 m	218 m	*219.9*	*217.4*	191 m	*193.0*	*188.5*	M–N str
	152 m	183 m	199 m	*201.3*	*197.7*	152 m	*152.0*	*149.5*	M–N str
154 m	163 m	165 m	176 m	176.2 m	177.0	170 m	169.5	168.5	Ligand

[a] Italic bands show isotopic shifts greater than 1.0 cm^{-1}. [b] Too weak to obtain accurate shift on milligram quantities.

TABLE II

M–N STRETCHING FREQUENCIES FOR MANGANESE-NA, COBALT-NA, NICKEL-62, AND ZINC-64 TRIS(2,2′-BIPYRIDINE) AND TRIS(2,7-DIMETHYL-1,8-NAPHTHYRIDINE) PERCHLORATE COMPLEXES

	Freq, cm^{-1}							
	Mn		Co		^{62}Ni		^{64}Zn	
bipy	240[a]	182	266[b]	228	277.5[c]	260.0	235.0[c]	186.0
dmnapy	202	152	214	183	217.4	197.7	193.0	152.0
% diff	15.8	16.5	19.5	19.7	21.6	24.0	17.9	18.3

[a] Reference 3b. [b] Y. Saitu, J. Takemoto, B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, in press. [c] Reference 6.

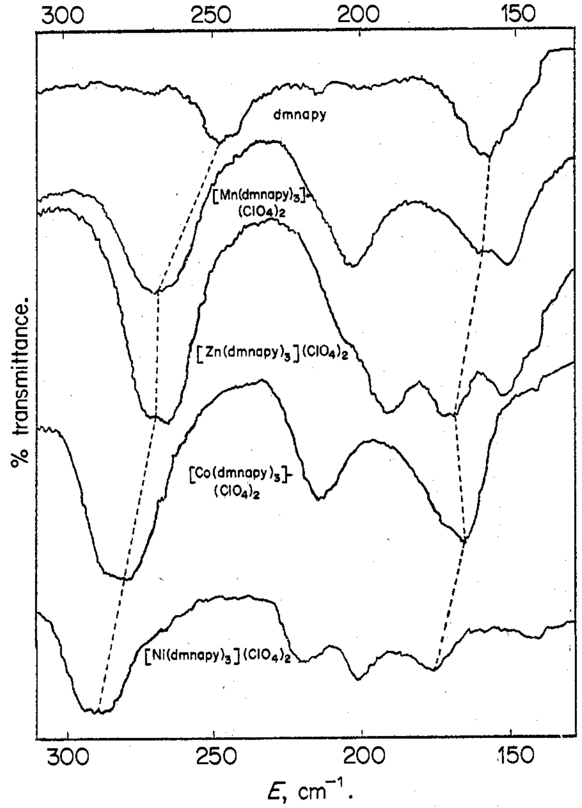

Figure 1.—The low-frequency infrared spectra of dmnapy, [Mn(dmnapy)$_3$](ClO$_4$)$_2$, [Zn(dmnapy)$_3$](ClO$_4$)$_2$, [Ni(dmnapy)$_3$](ClO$_4$)$_2$, and [Zn(dmnapy)$_3$](ClO$_4$)$_2$ from 310 to 130 cm^{-1}.

nickel, and zinc complexes, respectively. The 247-cm^{-1} ligand spectrum band occurs at 268 cm^{-1} in the manganese complex, 283 cm^{-1} in the cobalt complex, 288 cm^{-1} in the nickel complex, and 270 cm^{-1} in the zinc complex. We assign the 163-, 165-, 176-, and 170-cm^{-1} bands in the manganese, cobalt, nickel, and zinc complexes, respectively, as the 154-cm^{-1} ligand band in the complexes. The nickel and zinc isotopic spectra show these ligand bands do not shift more than 1.0 cm^{-1} upon isotope substitution with one exception. This exception is the 288-cm^{-1} band in the nickel complex. This strong, broad band is centered at 288.4 cm^{-1} in the ^{58}Ni complex and at 285.6 cm^{-1} in the ^{62}Ni complex. This shift may indicate that this ligand band is overlapping a metal–ligand stretching band, but careful study of this band has shown but one band maximum. We tentatively assign this band as a ligand band.

A weak band about 315 cm^{-1} is observed in concentrated mull spectra of the metal complexes. This absorption does not appear in the pure ligand spectrum; it is too weak to be observed in the zinc isotope spectra but shows no shift in nickel isotope spectra. These data and the consistent band position are the bases for assigning this band as a complex-activated ligand band. The dotted lines in Figure 1 follow the wave number increases of the ligand bands upon complexation.

M–N Stretching Bands.—Table I lists two nickel isotope sensitive bands below 220 cm^{-1} in the nickel complex spectra and two zinc isotope sensitive bands below 200 cm^{-1} in the zinc complex spectra. Zinc–nitrogen stretching bands are expected to occur at lower wave number than the Ni–N stretching bands due to the absence of crystal field stabilization energy in the zinc complex and the slightly larger mass of zinc ion. Nickel isotope sensitive bands occur at 217.4 and 197.7 cm^{-1} in the ^{62}Ni complex and at 193.0 and 152.0 cm^{-1} in the ^{64}Zn complex spectrum. Only these two bands are assigned as stretching bands, although group theory predicts three infrared-active metal–nitrogen stretching bands (A_2 + 2 E) for complexes with D_3 symmetry. A similar situation occurs in several (bipy)$_3$ complexes and in some (acac)$_3$ complexes.[5,6] For example, Shimanouchi, *et al.*, have carried out a normal-coordinate analysis of M(acac)$_3$ (M = Cr, Fe, Co) and have suggested that one E and the A_2 mode of the metal–ligand stretching vibrations overlap so that only two metal–oxygen stretching bands are observed.[5] This may also be the case here. Raman data from these complexes are needed to complete the symmetry mode assignments.

Using the above assignments of Ni–N and Zn–N stretching vibrations, we are able to make reasonable

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(5) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta.*, *Part A*, **23**, 1037 (1967).

(6) B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3335 (1970).

assignments for Co– and Mn–dmnapy complexes even though metal isotope studies are not possible. The Mn–dmnapy spectra are quite similar to the Zn–dmnapy spectra in that three medium-intensity bands occur below 210 cm^{-1}. By comparison with the zinc complex spectra we assign the 203- and 152-cm^{-1} bands to manganese–nitrogen stretching vibrations. The cobalt complex spectrum has one medium-strength band at 214 cm^{-1} and another broad, asymmetric band with a minimum at 165 cm^{-1}. Gaussian analysis indicates this band envelope contains two medium-strength bands at 183 and 165 cm^{-1}. We assign the 183-cm^{-1} band to the Co–N stretching vibration.

Discussion

In order to compare the M–N stretching frequencies for four- and five-member chelate ring systems, the M–N stretching bands for $(dmnapy)_3$ and $(bipy)_3$ complexes are listed in Table II. The M–N stretching frequencies are of particular interest since they provide direct information about the coordinate bond. The following factors may affect the frequency of metal–ligand stretching modes: mass of ligand and metal, symmetry of the complex, nature and size of the anion, basicity of ligand, oxidation state and coordination number of the metal, and nature of the coordinate bond.

The comparisons made in this work examine ligands of closely similar mass (a difference of 2 amu), complexes of similar symmetry (D_3), complexes containing similar anions, and metals of similar oxidation state and coordination number. The type of M–N bonding in these cases is expected to be essentially σ bonding since π back-bonding is important primarily in cases where a transition metal is in a low oxidation state.[7] The basicity of the two ligands is similar and molecular models indicate no steric hindrance due to ligand–ligand crowding.[1] The principal difference in the two types of complexes is the chelate ring size.

The data in Table II show a sizable and consistent decrease in M–N stretching vibrations when metal–bipy complex spectra are compared with metal–dmnapy complex spectra. We feel these decreases are the result of strain in the four-member chelate ring. The per cent change for each M–N stretching band is also given in Table II. The per cent decrease ranges from 24% for Ni–N stretching bands to about 16% for Mn–N. The per cent M–N stretching change as well as the M–N stretching vibrations follow the Irving–Williams order, Mn < Co < Ni > Zn, for high-spin transiton metal complexes. The 10*Dq* value of $Ni(bipy)_3^{2+}$ is 12.65 kK, while the 10*Dq* value for the $Ni(dmnapy)_3^{2+}$ is 9.56 kK.[1,8] This represents a 24.4% decrease and agrees very well with the per cent decreases found from the infrared data. A similar comparison of cobalt complexes shows a slightly smaller decrease in 10*Dq* values,[8] and this is also reflected in the infrared data. Bands due to d → d transitions for Mn^{2+} and Zn^{2+} are not observed, but infrared data reflect the absence of ligand field stabilization energy through the low frequency of the M–N stretching bands. The strain effect in these complexes should be similar to that which occurs in the non-transition-metal complexes of $(dmnapy)_3$.

Acknowledgment.—We wish to thank Texas A & M University for the use of their infrared instruments and Dr. James Takemoto for running some of the spectra. This work was supported in part by the Robert A. Welch Foundation, Grant No. R-483.

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[7] R. Fitzgerald, B. B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, **9**, 2618 (1970); M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6946 (1968).

[8] R. A. Palmer and T. J. Piper, *Inorg. Chem.*, **5**, 864 (1966).

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Tungstovanadate Heteropoly Complexes.
III. The Ion $V_5W_8O_{40}^{7-}$

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In a recent publication[1] we described the preparation and characterization of the ions $V_4W_9O_{40}^{6-}$ and $V_3W_{10}O_{40}^{5-}$. These were considered to be derivatives of the unknown 12-tungstovanadate(V) with partial replacement of tungsten(VI) by vanadium(V), *i.e.*, $V(W_{12-n}V_n)O_{40}^{(3+n)-}$ with $n = 2$ or 3. In this communication we describe the ion $V_5W_8O_{40}^{7-}$ which appears to be the member $n = 4$ of this series.

Experimental Section

The preparations of KVO_3, $Na_4V_2O_7 \cdot 18H_2O$, and K_2WO_4 were described previously.[2,3]

Potassium 8-Tungsto-5-vanadate(V).—Potassium metavanadate (KVO_3, 3.45 g, 25 mmol) was dissolved with heating in 12 ml of water. The solution was cooled to room temperature and added to 40 ml of 1.0 *F* K_2WO_4, giving a medium-yellow solution. Formic acid (25 ml of 10 *F* solution) was added immediately and rapidly to this solution. The resulting red-orange mixture was heated quickly almost to boiling to dissolve the solid which had precipitated. The hot, clear red solution was then poured into a large preheated crystallizing dish, covered, and set aside. The next day, the first crop of product had crystallized as a red-orange crust. After the solution was decanted, the product was washed with a little water, then with ethanol–water (1:4 by volume) until the washings were nearly colorless, and finally with 95% ethanol, and air-dried at room temperature. The decanted reaction solution was filtered and allowed to stand in a large open dish to obtain further crops of product during the next 2–3 days. The last crop isolated contained chunky orange-yellow crystals ($V_2W_4O_{19}^{4-}$ salt), which were dissolved out in the ethanol–water washing. The crops were kept separate for analyses. The total yield was 4–5 g of red-orange crystalline powder consisting of small orange to red-orange square blocks (microscope). (If the reaction solution was allowed to stand longer, more of the product separated, but the crystals were brown colored and were mixed with much $V_2W_4O_{19}^{4-}$ salt.) Attempted recrystallization led to much decomposition. *Anal.* Calcd for $K_7V_5W_8O_{40} \cdot 12H_2O$: K, 9.59; V, 8.92; W, 51.5; H_2O, 7.57. Found: K, 9.73–9.75; V, 8.91–8.95; W, 51.4–51.5; H_2O, 7.60–7.67 (for different crops of product). The mean material sum was 100.2%. Experimental mole ratios are W/V = 1.598 and K/W = 0.889. In the water determination, the weight loss was 1.92 ± 0.15% at 110° and 7.14 ± 0.03% at 200°. These data correspond to loss of 3.0 ± 0.2 and 11.2 ± 0.1 mol of H_2O/mol of salt, respectively. The salt heated at 200° was brown. Instability of the anion in solution precluded recrystallization tests. (The product of the final 500° ignition was black.)

When the preparation was carried out with less formic acid than stated above, the yield of 5:8 complex was lower. When more acid was used, the product was contaminated with a light

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[1] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2745 (1971).

[2] C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970).

[3] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2524 (1971).