

Vibrational spectra and normal coordinate analysis of bis(glycino) complexes with Ni(II), Cu(II) and Co(II)

JAMES R. KINCAID and KAZUO NAKAMOTO

Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233 U.S.A.

(Received 23 January 1975)

Abstract—The i.r. and Raman spectra of bis(glycino) complexes of Ni(II), Cu(II) and Co(II) are reported. In order to aid band assignments, isotope substitutions such as H/D, $^{14}\text{N}/^{15}\text{N}$, $^{68}\text{Ni}/^{62}\text{Ni}$ and $^{63}\text{Cu}/^{65}\text{Cu}$ have been carried out. Normal coordinate analyses on trans-bis(glycino) complexes of Ni(II) and Cu(II) have been made based on these data. The results provide definitive band assignments of the metal–nitrogen and metal–oxygen stretching modes which have been controversial.

INTRODUCTION

For many years the assignments of low-frequency i.r. spectra of bis(glycino) complexes with transition metals have been controversial. For example, NAKAMURA [1] empirically assigned the $M-N$ (metal–nitrogen) stretching bands of cis-Cu and trans-Ni complexes at 576 and 596 cm^{-1} , respectively. On the other hand, LANE *et al.* [2] assigned these modes at 332 and 275 for cis-Cu and 283 cm^{-1} for trans-Ni complex. CONDRADE and NAKAMOTO [3] were the first to assign both $M-N$ and $M-O$ stretching modes based on normal coordinate analysis of a 1:1 (metal/ligand) model. However, their assignments were different from either of previous investigators; the $M-N$ stretching at 460 (cis-Cu) and 439 (trans-Ni), and the $M-O$ stretching at 360 (cis-Cu) and 290 cm^{-1} (trans-Ni). Later, WALTER and HOOPER [4] assigned the Cu–N stretching bands at 333 and 279 cm^{-1} and the Cu–O stretching bands at 160 and 130 cm^{-1} from an approximate normal coordinate analysis of cis-Cu complex. Recently RAYNER CANHAM and LEVER [5] assigned the Cu–N and Cu–O stretching bands of cis-Cu complex at 379 and 334 cm^{-1} , respectively, based on the $^{64}\text{Cu}/^{65}\text{Cu}$ shift data (NA: natural abundance). The only Raman study on metal glycino complexes is that of KRISHNAN and PLANE [6] who assigned the Zn–N and Zn–O stretching bands of trans-Zn complex at 470 and 395 cm^{-1} , respectively, in aqueous solution. The main purpose of this investigation is to provide definitive band assignments of these and other low-frequency modes of bis(glycino) complexes based on normal coordinate analyses combined with isotope shift data due to the H/D, $^{14}\text{N}/^{15}\text{N}$, $^{68}\text{Ni}/^{62}\text{Ni}$ and $^{63}\text{Cu}/^{65}\text{Cu}$ substitutions.

EXPERIMENTAL

Preparation of complexes

Trans-Ni(gly)₂·2H₂O. This complex was prepared by the method previously described in the literature utilizing nickel carbonate [7]. The nickel isotopes (^{68}Ni (98%) and ^{62}Ni (95–99%), Oak Ridge National Laboratories) were obtained as the free metal and converted to the carbonate by the following procedure. The metal was dissolved in concentrated hydrochloric acid and the solution was evaporated to dryness. The residue, nickel chloride, was dissolved in water and added dropwise to an aqueous solution containing excess sodium hydrogen carbonate. The gelatinous green precipitate, nickel carbonate, was isolated and washed several times with distilled water by centrifugation.

Cis-Cu(gly)₂·H₂O. Although a simple preparation of this compound has previously been reported [8], an alternative procedure was used for the preparation of the isotopically substituted compounds. It was found that heating stoichiometric amounts of copper chloride and glycine in 95% ethanol gives a nearly quantitative yield of a light blue amorphous powder which is insoluble in 95% ethanol. Recrystallization from water–ethanol mixture (1:1 volume ratio) yields light blue needles whose i.r. spectrum is identical to the published spectrum of an analytical sample of cis-Cu(gly)₂·H₂O [9]. The copper isotopes [^{63}Cu (98%) and ^{65}Cu (90%)] (Oak Ridge National Laboratories) were obtained as cupric oxide and converted to the chloride by treatment with concentrated hydrochloric acid and heating to dryness.

Trans-Cu(gly)₂·2H₂O. This complex was prepared from the cis analog by the method reported by HERLINGER *et al.* [9], although it was somewhat difficult to apply to very small quantities.

Trans-Co(gly)₂·2H₂O. This complex was prepared by a method previously described by NAKAMURA [1]. Some difficulty (oxidation to Co(III)) was encountered for the preparation of very small quantities resulting in the failure of the synthesis of the ^{15}N -substituted analog. The ^{15}N -glycine (99%) used in this study was purchased from Stohler Isotope Chemical Company.

Spectral measurements

The i.r. spectra of all these compounds were recorded on a Perkin Elmer FIS-3 Far-i.r. spectrophotometer from 410–33 cm^{-1} as nujol mulls spread on a polyethylene plate. The compounds were also run on a Beckman IR-12 i.r. spectrophotometer from 4000–300 cm^{-1} either as nujol mulls on CsI plates or using the CsI pellet technique. In both cases the spectra were obtained at room temperature and in cold cells adaptable to the two instruments. Liquid nitrogen was used as the coolant and no attempt was made to measure the temperature at the sample. Isotopic shifts were measured from multiple scans over metal isotope sensitive bands. In all cases the shift values were reproducible to $\sim 0.2 \text{ cm}^{-1}$ in the 400–33 cm^{-1} region and $\sim 0.4 \text{ cm}^{-1}$ in the 700–400 cm^{-1} region.

The Raman spectra were recorded on a Spex Model 1401 double monochromator equipped with an ITT FW-130 phototube. A Coherent Radiation Laboratories Model 52 Argon Ion Laser (5145 Å (green)) was used as the excitation source whose power at the sample was approximately 300 mw. The samples were pressed into a stainless steel cell and rotated at about 3000 rpm to prevent extensive decomposition by the laser beam. The premonochromator optical system is described by CLAASSEN *et al.* [10]. A maximum band pass of 5 cm^{-1} with a 10 mm slit height was used for all spectra.

RESULTS AND DISCUSSION

Table 1 lists the observed i.r. and Raman frequencies and band assignments of the four bis-

(glycino) complexes in the 1600–500 cm^{-1} region. Figure 1 illustrates the i.r. and Raman spectra of trans-Ni(gly)₂·2H₂O. Previously, CONDRADE and NAKAMOTO [3] assigned these high frequency bands based on normal coordinate analysis and deuteration data. Their results are also supported by the present normal coordinate analysis which will be described later. Since these assignments are not controversial, no further discussion will be given on the high-frequency spectra.

Table 2 lists the observed i.r. and Raman frequencies, isotopic shifts and empirical assignments for the bands below 600 cm^{-1} . Figure 2 illustrates the low-frequency i.r. spectra of the four complexes studied in this work. In order to aid in assigning these bands, we have carried out three types of isotope substitution. First, the metal isotope substitution (⁵⁸Ni/⁶²Ni and ⁶³Cu/⁶⁵Cu) is expected to shift all the metal-ligand stretching (*M*-N, *M*-O and *M*-W(aquo)) modes by more than 2.0 cm^{-1} [11]. Secondly, the ¹⁴N/¹⁵N substitution should shift only the *M*-N stretching among these three modes. Finally, the H/D substitution at the amino and aquo groups is expected to cause the shifts of the *M*-N and *M*-W stretching modes while the *M*-O stretching mode remains unshifted. By combining these criteria, three bands at 442, 289

Table 1. Vibrational spectra of *M*(gly)₂·*X*H₂O complexes (1600–500 cm^{-1})

trans-Ni(gly) ₂ ·2H ₂ O		Cu(gly) ₂ · <i>X</i> H ₂ O				trans-Co(gly) ₂ ·2H ₂ O		Assignment
IR	R	cis-X = 1		trans-X = 2		IR	R	
1589s	1563w	1609vs	1604 1586vw 1570	1593vs	1570m	1570s	1554m	$\nu_a(\text{CO}_2)$
1438m	1436m	1428w	1430m	1435w	1429s	1445m	1445m	$\delta(\text{CH}_2)$
1413s	1410s 1398sh	1391s	1395s	1392s	1398s 1392sh 1354s	1408s	1409s	$\nu_s(\text{CO}_2)$
1348m 1305m	1346m 1305w 1299W	1326w	1322s	1331m	1315sh	1333sh 1323s	1326m	$\rho_w(\text{CH}_2)$
1186w	1185w-m	1200vw 1185vw 1170vw 1121m-s 1060w	1196w 1175w 1116w	1199w,sh	1175w-m	1188w		$\rho_t(\text{CH}_2)$
1041s 945m-s 916w 793m br 740s	1037m 945w 915s 785vw 727w	1038m 949vw 922w-m	1058w 952vw 919s	1058s 942w 909m-s	1055w 943w 912s	1091s 1022s	1019m	$\nu(\text{C-N})$
672s 625s 600s	648vw 594s 553w 512m-s	673w br 570w br 557m	570s 558s 549s	580w br	570s	579s 545s 536s	596m	$\pi(\text{CO}_2)$ $\rho_r(\text{CO}_2)$
								$\nu(\text{C-C})$ $\rho_r(\text{H}_2\text{O})$ $\delta(\text{CO}_2)$ $\rho_r(\text{NH}_2)$

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; ν_a , antisymmetric stretching; ν_s , symmetric stretching; δ , bending; π , out-of-plane bending; ρ_t , twisting; ρ_w , wagging; ρ_r , rocking.

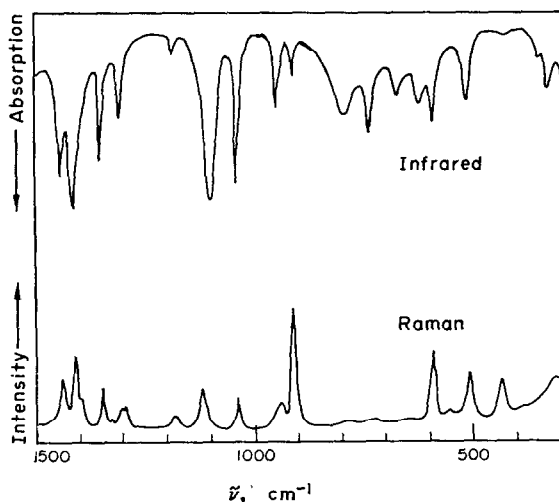


Fig. 1. Infrared and Raman spectra of $\text{trans-Ni}(\text{gly})_2 \cdot 2\text{H}_2\text{O}$.

and 365 cm^{-1} of $\text{trans-Ni}(\text{gly})_2 \cdot 2\text{H}_2\text{O}$ have been assigned to the Ni-N, Ni-O and Ni-W stretching modes, respectively (Table 3). The assignment of the Ni-N stretching band is also supported by WATT and KNIFTON [12] who observed that the

442 cm^{-1} band is shifted to 486 cm^{-1} upon deprotonation of the amino group which strengthens the Ni-N bond.

The i.r. and Raman selection rules provide another criteria in making band assignments. In the case of bis(glycino) Cu(II) complex, we have obtained the spectra of both cis and trans isomers. It is anticipated that the cis isomer exhibits two M-N and two M-O stretching while the trans isomer exhibits only one for each mode both in i.r. and Raman spectra. Based on this rule together with isotope shift data, we have assigned the Cu-N and Cu-O stretching bands of the cis isomer at 478 and 457 cm^{-1} and 334 and 284 cm^{-1} , respectively, and those of the trans isomer at 483 and 337 cm^{-1} , respectively. Table 2 gives the corresponding Raman frequencies. Previous workers [5] assigned the 380 cm^{-1} (i.r.) of the cis isomer to the Cu-N stretching band since it exhibits a relatively large shift (2.3 cm^{-1}) by the $^{63}\text{Cu}/^{65}\text{Cu}$ substitution. However, this band has no counterparts in this region. On the other hand, two bands at 478 and 457 cm^{-1} are sensitive to the $^{14}\text{N}/^{15}\text{N}$ substitution. As will be shown later, the band at 380 cm^{-1} of cis-Cu complex has been assigned to a skeletal

Table 2. Far i.r. and Raman spectra of $M(\text{gly})_2 \cdot X\text{H}_2\text{O}$ ($600\text{--}90\text{ cm}^{-1}$)^a

trans-Ni(gly) ₂ ·2H ₂ O		trans-Cu(gly) ₂ ·2H ₂ O		cis-Cu(gly) ₂ ·H ₂ O		trans-Co(gly) ₂ ·2H ₂ O		Approximate Assignments
IR	R	IR	R	IR	R	IR		
<i>In-Plane Modes</i> ^b (A _g , B _u)								
521s(0,6)	512s(-;2.9)	545w	517s	557m(0;6)	558s 549s	545s 536s		ρ _r (CO ₂)
442vw(2.1;8.0)	441s(-;6.1)	483w(0.8;4.9)	462s	478w(<1;7)	477s	410w		v _{as} (M-N)
342m(3.5;1.5)	282s(-;3.8)	377m(1.7;0.4)	-	457s(0;5)	455s			v _s (M-N)
289s(5.0;1.0)		337s(4.0;1.2)		380m(2.3;1.0)	-	331s		δ(skeletal)
194m(0.5;1.7)	227m		230vs	334s(3.0;0)	330m	322sh		v _{as} (M-O)
				284s(0;1.7)	-	286s		v _s (M-O)
				258w	239vw			
		201wsh		205wsh	-	194vw		
				198m	195vw			
164m(0.5;0.5)		157m(0.7;1.0)		172mbr		179s		
114m(0.8;0)		113m(1.4;1.2)		165mbr		175s		
				113w		126m		
<i>Out-of-Plane Modes</i> (A _u , B _g)								
600s	594s	580wbr	570s	570wbr	570s	579s		ρ _w (CO ₂)
365w(1.7;1.0)	313vw	-	-	-	-	386vw		v(M-W)
239w-m(0.3;1.3)	192s	225m(0;0.8)	-	235w	-	252m		
212m(0.8;0.8)	180s	209m(0;0.8)	-	219m	-	228m		
	152m					219sh		
148mbr(0.8;0.7)	143w	145m(0;0)	-	138m		145wsh		
97m-s(0;0)	97s			92w		118mbr		

a) The isotope shifts are given in parentheses; the first number gives the metal isotope shift and the second number denotes the ^{14}N - ^{15}N shift. Assignments of the bands below 250 cm^{-1} should be regarded as only tentative.

b) The following bands exhibit the shifts given in parentheses upon deuteration of the amino and aquo groups: 442 cm^{-1} (18 cm^{-1}), 365 cm^{-1} (11 cm^{-1}), 341.5 cm^{-1} (5 cm^{-1}), 289 cm^{-1} (2 cm^{-1}).

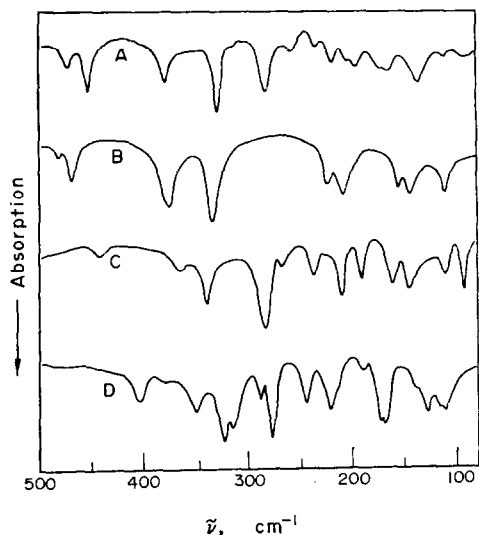


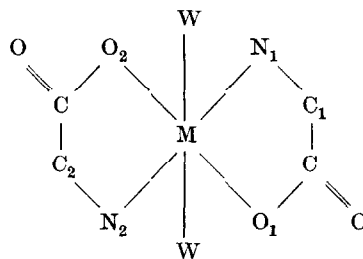
Fig. 2. Far-i.r. spectra of glycino complexes: A, *cis*-Cu(gly)₂·2H₂O; B, *trans*-Cu(gly)₂·2H₂O; C, *trans*-Ni(gly)₂·2H₂O; D, *trans*-Co(gly)₂·2H₂O.

bending mode since it corresponds to the 377 cm⁻¹ band of *trans*-Cu complex for which normal coordinate analysis was carried out.

NORMAL COORDINATE ANALYSIS

In the preceding section, we have given empirical band assignments of the metal-ligand vibrations based on the observed isotopic shifts. However, such a simple approach fails to account for many other bands which appear in the low-frequency region. Furthermore, it cannot provide any infor-

mation about vibrational coupling which is expected to occur among various modes. Previously, we have assigned the 442 cm⁻¹ band of *trans*-Ni(gly)₂·2H₂O to the Ni-N stretching mode based on the ¹⁴N-¹⁵N isotope shift data although its ⁵⁸Ni/⁶²Ni shift (2.1 cm⁻¹) is smaller than the 342 cm⁻¹ band (3.5 cm⁻¹). In order to give complete band assignments and to estimate theoretical isotope shifts, we have carried out normal coordinate analyses on the thirteen-atom *trans*-isomer model shown below:



Since our main interest is in the skeletal vibrations, all the hydrogen vibrations were neglected in our calculations. This approximation does not cause appreciable errors in our calculations because hydrogenic frequencies are too high to couple with skeletal modes.

The molecular parameters used for *trans*-Ni(gly)₂·2H₂O were taken from X-ray analysis [13]. The same parameters were assumed for *trans*-Cu(gly)₂·2H₂O. The potential energy was expressed by a modified Urey-Bradley Force field [14] with the addition of four interaction constants associated with the metal-ligand bonds. In this paper, we

Table 3. Metal-ligand frequencies and isotope shifts for *trans*-Ni(gly)₂·2H₂O (cm⁻¹)

Band at Substitution	442 cm ⁻¹ (Bu)	365 cm ⁻¹ (Au)	342 cm ⁻¹ (Bu)	289 cm ⁻¹ (Bu)
⁵⁸ Ni- ⁶² Ni	2.1 (2.6)	1.7 (n.c.)	3.5 (4.0)	5.0 (5.2)
¹⁴ N- ¹⁵ N	8.0 (8.9)	1.0 (n.c.)	1.5 (0.5)	1.0 (0.8)
H-D	18 (n.c.)	11 (n.c.)	5 (n.c.)	2 (n.c.)
Assignment	Ni-N str.	Ni-W str.	Skeletal bend.	Ni-O str.

The number in the brackets indicates the calculated isotope shift (n.c. - not calculated)

Table 4. Calculated force constants (mdyn/Å)

Force Constant	trans-Ni(η^1) ₂ ·2H ₂ O	trans-Cu(η^1) ₂ ·2H ₂ O
<i>Stretching</i>		
K(M-N)	0.85	1.05
K(M-O)	0.60	0.80
K(C-N)	3.90	4.10
K(C-C)	2.3	2.10
K(C-O)	7.6	7.50
K(C=O)	7.7	7.66
K(M-W)	0.75	0.75
<i>Bending</i>		
H(NMW)	0.25	0.25
H(OMW)	0.15	0.15
H(N ₁ MO ₁)	0.15	0.15
H(N ₁ MO ₂)	0.20	0.20
H(MNC)	0.10	0.10
H(NCC)	0.45	0.45
H(C ₁ CO ₁)	0.23	0.23
H(C ₁ CO)	0.60	0.60
H(OCO)	0.50	0.50
H(MOC)	0.10	0.10
<i>Repulsive</i>		
F(M...C ₁)	0.20	0.35
F(M...C)	0.05	0.20
F(N ₁ ...O ₁)	0.12	0.12
F(N ₂ ...O ₁)	0.30	0.30
F(N ₁ ...W)	0.10	0.10
F(N ₁ ...C)	0.25	0.20
F(O ₁ ...W)	0.15	0.15
F(C ₁ ...O ₁)	0.67	0.67
F(O ₁ ...O)	2.50	2.50
F(C ₁ ...O)	.90	0.90
<i>Interaction</i>		
MN ₁ str-N ₁ MO ₁ bend	0.00	0.10
MN ₁ str-MN ₂ str	0.10	0.10
MO ₁ str-MO ₂ str	0.10	0.15
MOstr-N ₁ MO ₁ bend	0.00	0.10

Table 5. Comparison of observed and calculated frequencies and isotope shifts (cm⁻¹)

	trans-Ni(η^1) ₂ ·2H ₂ O						trans-Cu(η^1) ₂ ·2H ₂ O						
	Obs.			Calc.			Obs.			Calc.			
	$\tilde{\nu}$	$\Delta\nu^a$	$\Delta\nu^b$	$\tilde{\nu}$	$\Delta\nu^a$	$\Delta\nu^b$	$\tilde{\nu}$	$\Delta\nu^a$	$\Delta\nu^{b,d}$	$\tilde{\nu}$	$\Delta\nu^a$	$\Delta\nu^b$	
A _g (R)	1563	-	0	1577	0	0	1570	-		1573	0	0	
	1410	-	0	1314	0	0	1398	-		1307	0	0	
	1037	-	13	1034	0	10.4	1055	-		1055	0	11.3	
	915	-	1.1	941	0	1.7	912	-		929	0	0.7	
	727	-	-	723	0	0	725	-		737	0	0.2	
	512	-	2.9	502	0	6.3	517	-		506	0	7.6	
	441	-	6.1	452	0	8.6	462	-		478	0	8.1	
	313	-	2.5	302	0	0.4	-c	-		315	0	2.8	
	282	-	3.8	275	0	2.4	-c	-		302	0	0.3	
	227	-	-	220	0	0.7	230	-		249	0	0.8	
	B _u (IR)	1589	0	0	1577	0	0	1593			1572	0	
		1413	0	0	1314	0	0	1392			1307	0	
		1041	0	10	1037	0	10	1058	0	10	1057	0	11
945		0	0	933	0	1.9	909	0	0	922	0	0	
740		0	0	722	0	0.3	737	0	0	734	0	0.3	
521		0	6.0	513	0	5.8	545	-c	-c	513	0	6.0	
442		2.1	8.0	442	2.6	8.9	483	0.8	4.9	476	1.4	9.8	
342		3.5	1.5	341	4.0	0.5	377	1.7	0.4	380	2.1	0.7	
289		5.0	1.0	293	5.2	0.8	337	4.0	1.2	334	2.6	0.7	
194		0.5	1.7	179	2.0	0.4	201	0.7	0.7	177	0.9	0.4	
164		0.5	0.5	159	0	0	157	0.7	1.0	159	0	0	
114		0.8	0	117	0.3	0.2	113	1.4	1.2	116	0	0.2	

a) Metal isotope shift: $\tilde{\nu}(^{58}\text{Ni}) - \tilde{\nu}(^{62}\text{Ni})$ or $\tilde{\nu}(^{63}\text{Cu}) - \tilde{\nu}(^{65}\text{Cu})$. The metal isotope shift should be zero for all A_g modes.

b) Nitrogen isotope shift, $\tilde{\nu}(^{14}\text{N}) - \tilde{\nu}(^{15}\text{N})$.

c) Not observed

d) The nitrogen isotope shift was not measured for Raman spectra.

Table 6. Potential energy distribution for trans-Ni(gly)₂·2H₂O

	Freq. (cm ⁻¹)	% potential Energy Distribution
A _g	1563	ν(C-O)(49) + ν(C=O)(41)
	1410	ν(C-O)(33) + ν(C=O)(45) + ν(C-C)(7)
	1037	ν(C-N)(73) + ν(C-C)(11) + δ(C-C=O)(9)
	915	ν(C-C)(48) + δ(OCO)(24)
	727	δ(OCO)(30) + δ(CCO)(18) + δ(MOC)(13) + δ(MNC)(10) + ν(C-C)(11)
	512	δ(C-C=O)(28) + δ(MNC)(21) + δ(MOC)(15) + δ(CCO)(10) + δ(N ₁ MO ₁)(8)
	441	ν(M-N)(35) + δ(MNC)(26) + δ(MOC)(9)
	313	ν(M-W)(86) + ν(M-N)(8)
	282	ν(M-N)(32) + ν(M-O)(18) + δ(CCN)(20) + δ(N ₁ MO ₁)(14)
	227	δ(N ₁ MO ₁)(31) + ν(M-O)(32) + δ(MNC)(20) + δ(N ₁ MO ₂)(6)
	B _u	1589
1413		ν(C-O)(33) + ν(C=O)(45) + ν(C-C)(7)
1041		ν(C-N)(69) + ν(C-C)(15)
945		ν(C-C)(44) + δ(OCO)(23) + δ(C-C=O)(10) + ν(C-N)(10)
740		δ(OCO)(31) + δ(C-C=O)(17) + δ(MOC)(12) + δ(MNC)(11) etc
521		δ(C-C=O)(33) + δ(MNC)(14) + δ(MOC)(12) + δ(CCO)(13) etc
442		ν(M-N)(60) + δ(MNC)(22) + δ(MOC)(9)
342		δ(N ₁ MO ₁)(38) + δ(CCN)(22) + ν(M-N)(12) + δ(MNC)(9)
289		ν(M-O)(46) + δ(NMO ₁)(27) + δ(MNC)(16)
194		δ(WMN)(34) + δ(WMO)(31) + δ(N ₁ MO ₂)(29)
164		δ(WMN)(36) + δ(WMO)(47) + δ(N ₁ MO ₁)(8)
114		δ(N ₁ MO ₂)(67) + δ(WMN)(16) + δ(WMO)(11)

ν, stretching; δ, bending. The number in brackets indicates the percentage of contribution of the preceding internal coordinate.

have calculated only the A_g and B_u vibrations of the above model. The neglect of the A_u and B_g vibrations has no effect on our calculation since there is no coupling between them. The programs written by SCHACHTSCHNEIDER [15] were used in conjunction with a Xerox Sigma 9 computer at Marquette University.

Table 4 lists the force constants for each compound which were obtained by making minor changes in the force field transferred from our previous work [3]. Table 5 compares the observed frequencies and isotope shifts with those calculated by using the force constants given in Table 4. The agreement is satisfactory in view of the approximation used. It is particularly significant that the calculated shifts due to metal and nitrogen isotope substitutions are in good agreement with those observed.

Table 6 gives the percentage potential energy distribution for trans-Ni(gly)₂·2H₂O. In the preceding section, we assigned the bands at 442, 432 and 289 cm⁻¹ to the Ni-N stretching, skeletal bending and Ni-O stretching modes, respectively, based on the observed isotopic shifts. The results shown in Table 6 indicate that these assignment are essentially correct although they couple strongly with other modes. The potential energy distributions for the copper complex are not shown here since they are similar to those of the nickel complex. Although no calculations have been made for the cobalt complex, its structure is

concluded to be trans since its spectra are similar to those of the trans-nickel and copper complexes.

As stated in the introduction, band assignments made by previous workers have been conflicting and confusing. The present investigation, however, definitely supports earlier assignments of the M-N and M-O stretching bands made by Condrate and Nakamoto.

Acknowledgements—The authors wish to thank Dr. J. R. FERRARO and Argonne National Laboratory for the use of their Raman facilities. They are especially grateful to Dr. JAMES TAKEMOTO for the gift of several compounds and very helpful suggestions. During the course of this work, JAMES KINCAID was supported by an NDEA predoctoral fellowship.

REFERENCES

- [1] K. NAKAMURA, *J. Chem. Soc. Japan*, **80**, 113 (1959).
- [2] T. J. LANE, J. A. DURKIN and R. J. HOOPER, *Spectrochim. Acta*, **20**, 1013 (1964).
- [3] R. A. CONDRADE and K. NAKAMOTO, *J. Chem. Phys.*, **42**, 2590 (1965).
- [4] J. WALTER and R. J. HOOPER, *Spectrochim. Acta*, **25A**, 647 (1969).
- [5] C. W. RAYNER CANHAM and A. B. P. LEVER, *Spectroscopy Lett.* **6**, 109 (1973).
- [6] K. KRISHNAN and R. PLANE, *Inorg. Chem.*, **6**, 55 (1967).
- [7] J. STOSICK, *J. Am. Chem. Soc.*, **67**, 365 (1945).
- [8] E. ABDERHALDEN and E. SCHNITZER, *Z. Phys. Chem.*, **163**, 96 (1927).
- [9] A. HERLINGER, S. L. WENHOLD and T. V. LONG, *J. Am. Chem. Soc.*, **92**, 6474 (1970).

- [10] H. H. CLAASSEN, H. SELIG and J. SHAMIR, *Appl. Spectroscopy*, **23**, 8 (1969).
- [11] K. NAKAMOTO, *Angew. Chem. (Int. Ed.)*, **11**, 666 (1972).
- [12] G. WATT and J. KNIFTON, *Inorg. Chem.*, **6**, 1010 (1967).
- [13] H. FREEMAN, private communication.
- [14] T. SHIMANOCHI, *Pure Appl. Chem.*, **7**, 131 (1963).
- [15] J. H. SCHACHTSCHNEIDER, *Vibrational Analysis of Polyatomic Molecules*, Vol. V and VI, Technical Reports, No. 231-64 and 57-65, Shell Development Co., Emeryville, CA. U.S.A., 1964 and 65.