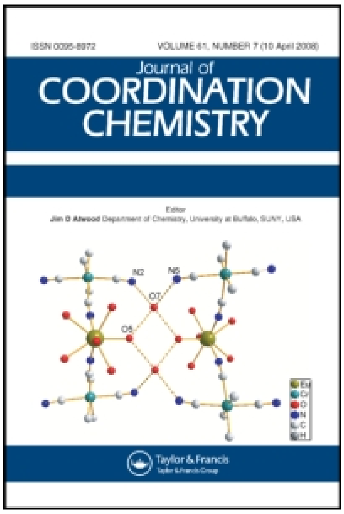

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INFRARED ASSIGNMENT OF BIS(GLYCOLATO)-BIS(PYRIDINE) METAL(II) COMPOUNDS AND CRYSTAL STRUCTURE OF *TRANS*-BIS(GLYCOLATO)-*CIS*-BIS(PYRIDINE)NICKEL(II) DIHYDRATE

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INFRARED ASSIGNMENT OF BIS(GLYCOLATO)-BIS(PYRIDINE) METAL(II) COMPOUNDS AND CRYSTAL STRUCTURE OF *TRANS*-BIS(GLYCOLATO)-*CIS*-BIS(PYRIDINE)NICKEL(II) DIHYDRATE

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Infrared spectra of the coordination compounds [$MG_2(py)_2$], M(II) = Co, Ni, Cu and Zn; G = glycolato, py = pyridine, have been fully assigned by means of py and py-d_5 and glycolato α—OH and α—OD (*G-d*) labelling as well as metal ion substitution in the 4000–70 cm^{-1} region. The crystal structure of the Ni(II) compound is presented and the spectra of the compounds are discussed on the basis of their structure and their bonding to the glycolato and pyridine ligands. Vibrational frequencies obtained for the Ni(II) compound are compared to those obtained by calculations carried out using the Gaussian 94 program package.

Keywords: Infrared spectra; Nickel complex; Glycolate; Deuterium substitution; Calculated frequencies

INTRODUCTION

The study of infrared spectra of coordination compounds with α-hydroxyacids has been limited to the assignment of the infrared spectra of bis(glycolato)metal (II) compounds [1,2] and the assignment of some of the bands appearing in the spectra of bis(lactato) and bis(mandelato) metal

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(II) compounds [2, 3]. As appears to be common with most of the work done in this field in the late 60's and early 70's, all bands appearing below the 500 cm^{-1} region were assigned as metal-ligand vibrations for all the compounds studied by the authors. In these cases, measurements in the far infrared region were limited by the instrumental facilities available and did not extend beyond 250 cm^{-1}. Pyridine adduct formation allows the compounds to be studied as monomeric units with octahedral coordination. It has been shown that the bis(glycolato) compounds form sheet polymers with octahedrally coordinated metal atoms in the solid state [4, 5] and it is only with Mn(II) and Zn(II) that the glycolato complexes also form discrete units with two water molecules bonded in a *cis* configuration [6, 7]. There has been no attempt to systematically study the infrared spectra of pyridine adducts for transition metal compounds with α-hydroxyacids. This seemed necessary as coordination of the glycolato ligands and the pyridine ligands may occur *cis* or *trans* (Fig. 1). Structural information regarding pyridine adducts of transition metal compounds with the glycolato ligand is also limited, and only the Cu(II) complex has been reported [8]. The spectra of $[MG_2(py)_2]$, M = Co, Ni, Cu and Zn, have been fully assigned in this work by means of isotopic labelling of the ligands and their spectra are discussed on the basis of the structural information for the Cu(II) complex [8] and the Ni(II) complex obtained in this work. This study was undertaken in order to establish the main M-L vibrations by ligand labelling and by metal ion substitution which has proven helpful in assignment of M-L vibrations [9–11]. Calculations carried out by Gaussian [15] of the $[NiG_2(py)_2]$

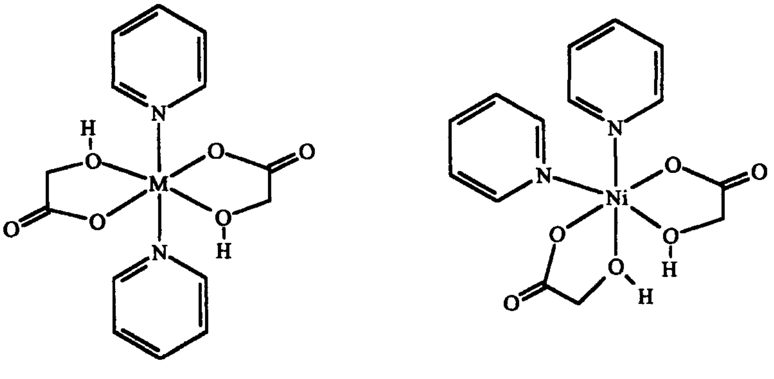

FIGURE 1 Structure of bis(pyridine)bis(glycolato)M(II) compounds. Compounds with M = Co and Zn have *trans* configuration. The compound with M = Cu is tetragonally distorted along the Cu—OH bonds. The compound with Ni(II) has *cis* configuration.

complex have further confirmed the assignment done on the infrared spectra of these compounds.

EXPERIMENTAL

All chemicals were from Aldrich Chemical Co. and used without further purification. Co, Ni and Zn (II) compounds were prepared by the addition of an excess of pyridine to 1 mmol of the anhydrous bis(glycolato) compounds which were prepared by reported methods [1]. The heterogeneous mixture was left stirring for a period of two to three hours and the mixture dissolved totally after the addition of one mL of distilled water. This solution was precipitated with acetone and the solid was vacuum filtered and dried. Purity was established by microanalysis:

Anal. Calcd. for $MC_{14}H_{16}O_6N_2 \cdot 1/2H_2O$(%): M = Co: C, 44.69; H, 4.55; N, 7.45. Found: C, 44.62; H, 4.58; N, 7.27. Calcd. for M = Ni: C, 44.71; H, 4.56; N, 7.45. Found: C, 44.91; H, 4.61; N, 7.48. Calcd. for M = Cu: C, 44.15; H, 4.50; N, 7.36. Found: C, 44.09; H, 4.54; N, 7.41. Calcd. for M = Zn: C, 43.95; H, 4.51; N, 7.23. Found: C, 43.94; H, 4.48; N, 7.32.

Compounds with py-d_5 were prepared as described above using py-d_5 99% isotopic purity. The py-d_5 isotopomers were identified by means of their infrared spectra.

Compounds with α—OD were prepared as described above by adding D_2O 99.99% isotopic purity to the [MG_2] and py or py-d_5 mixture under N_2. The compounds were identified by means of their infrared spectra due to the rapid interchange of the α—OD to α—OH.

Crystalline [$NiG_2(py)_2$] • $2H_2O$

Crystals for the title compound were obtained by adding an excess of py (5 mL) to 1 mmol of [NiG_2]. The mixture was left stirring for approximately two hours. Distilled water was added dropwise to this mixture until a blue solution was formed. Light blue crystals were obtained by diffusion of acetone. The crystals tend to become opaque if left out of solution probably by loss of water in the crystal lattice, which could explain the difference in water content obtained by microanalysis. The infrared spectra of the blue crystals obtained this way are identical to the spectra in the mid and far infrared regions of the Ni(II) complex precipitated by acetone.

A single crystal of the title complex was used to collect data [13] at 298 K on a Siemens P4/PC diffractometer with Mo-$K\alpha$ radiation

($\lambda = 0.71073$ Å) in the $\theta/2\theta$ scan mode at variable scan speed (4 to 60°min^{-1} in ω).

The structure was solved by direct methods and difference Fourier maps and subjected to full matrix least-squares refinement [13, 14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for OH groups (O1 and O11) and water molecules (O41 and O42) were found on difference maps and refined using a riding model with fixed isotropic U. Computations were carried out using the SHELXTL 5.03 and SHELX97-2 program packages. Crystal and refined experimental data are listed in Table I. Complete data are available from the deposited CIF file CCDC-142221. Infrared spectra were recorded on a FTIR Nicolet 740 spectrometer as KBr pellets in the 4000–400 cm^{-1} region and as polyethylene pellets in the 700–70 cm^{-1} region.

Theoretical Calculations

Full geometry optimization without symmetry constraints was performed using Gaussian 94 at the B3LYP level [15]. The bases used were 3–21G**. Optimized geometries were verified performing frequency calculations. For the infrared spectrum, we have used a value of 0.95 for the scale factor.

TABLE I Crystal data

Empirical	$(C_5H_5N)_2(C_2H_3O_3)_2Ni(OH_2)_2$
Crystal size	$0.4 \times 0.3 \times 0.1$ mm^3
Crystal System	Triclinic
Space group	$p\bar{1}$
Unit cell dimensions	$a = 8.142(2)$ $b = 9.070(2)$ $c = 12.374(3)$Å $\alpha = 77.832(6)$ $\beta = 84.89(5)$ $\gamma = 81.807(13)$°
Volume	882.5(4) Å^3
Z	2
Formula weight	403.03
Density(calc.)	1.517 g·cm^{-3}
Absorption coefficient	1.143 mm^{-1}
2θ Range	4.64–55.02°
Reflections collected	4665
Independent reflections$^{(a)}$	3852($R_{\mathrm{int}} = 2.37\%$)
Reflections with $F_o > 4\sigma(F_o)$3257	
Absorption correction	46ψ-scans with χ close to 90°
Transmission factors	min = 0.696, max = 0.932
Final R indices ($I > 2\sigma(I)$)$^{(a)}$	$R_1 = 3.52\%$, $wR_2 = 8.28\%$
Final R indices (all data)$^{(a)}$	$R_1 = 4.57\%$, $wR_2 = 8.80\%$
Goodness-of-fit$^{(a)}$	1.048
Data-to-parameters ratio	3852/227
Largest difference peak,hole	0.257, -0.280 e·Å^{-3}

(a) $R_{int} = (\sum |F_o^2 - \langle F_o^2 \rangle| / \sum F_o^2)$, $R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|)$, $wR_2 = \sqrt{(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)}$, $S = \sqrt{(\sum w(F_o^2 - F_c^2)^2)/m - n}$.

RESULTS AND DISCUSSION

Crystal Structure of *Trans*-bis(glycolato)-*cis*-bis(pyridine) Nickel(II) Dihydrate

The Ni(II) ion lies in an octahedral environment in which the two pyridine nitrogen atoms bind to the metal center *cis* and the glycolato ligands are coordinated as chelates to the Ni atom with the carboxy oxygen atoms *trans* to each other, as depicted in Figure 2, where the structure of the compound and atom labelling is shown. The bite angles around the Ni atom arise, as expected, from the glycolato ligands, 78.39(6)° and 79.53(7)° for O1—Ni1—O2 and O11—Ni1—O12 respectively. The Ni(II) compound differs significantly from the Cu(II) complex reported by Prout *et al.* [8] in that the Cu(II) complex has both the pyridine ligands and the glycolato ligands in *trans* configuration (Fig. 1). The coordination environment observed for the Ni(II) compound is closer to octahedral than that observed for the Cu(II) complex where tetragonal distortion results in a lengthening of the two Cu—α—OH bonds. Selected bond lengths for both the Ni(II) and

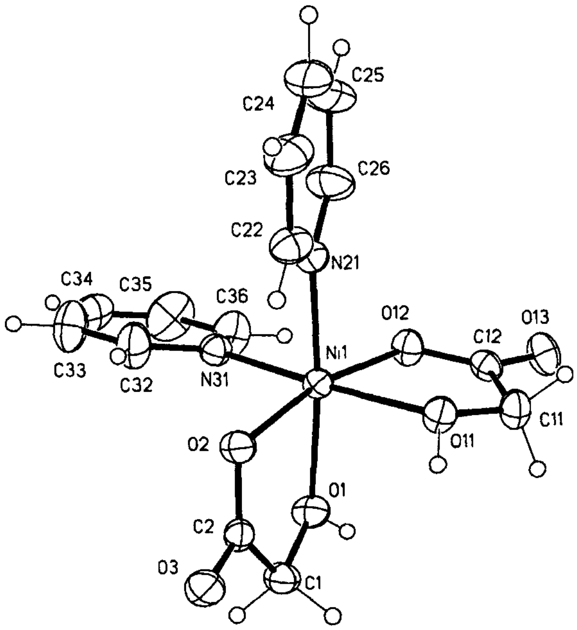

FIGURE 2 "ORTEP" drawing of the title compound *cis*-Ni(glycolato)$_2$(pyridine)$_2$. Water molecules were omitted for clarity and thermal ellipsoids for non-H atoms are at 30% probability level.

the Cu(II) compounds are shown in Table II. In both compounds the shortest bonds occur for the carboxy oxygen coordinated to the metal ion. Bond lengths between the pyridine N atoms and the α—OH oxygen atoms are very much alike in the Ni(II) complex, as opposed to the Cu(II) complex in which the bonds to the α—OH groups are the longest. Molecules of the title compound form dimers in the solid state through a strong hydrogen bond involving the non-coordinated carboxylic group O3···H11 of 1.88 Å. Finally, the crystal lattice is stabilized by the inclusion of two water molecules, which give a number of hydrogen bonds with the glycolato ligands, with O···H separations ranging from 1.81 to 2.62 Å. Due to the presence of water of crystallization and to the low crystallographic symmetry, no interactions between the pyridine rings are observed in the packing of the crystal; the shortest distance between the centroids of the two aromatic rings being 6.33 Å.

Infrared Spectra

Assignments for the [$MG_2(py)_2$] compounds are shown in Table III and have been done according to the assignments carried out by Nakamoto *et al.* [1] for the [MG_2] compounds on the basis of deuteration of the G ligand, by the ν_D/ν_H ratio on py and py-d_5 substitution [20] and glycolato α—OH and α—OD substitution. The proposed assignments are consistent with those done on the pyridine adduct of Ni(II) and glycine [20], except for differences arising from the different configuration of these complexes. It is interesting to note that there exist several bands that are sensitive to the geometry of the different compounds studied and that splitting is observed in the Ni(II) complex which is apparently the only one with py ligands in *cis* configuration as well as *cis* Ni—α—OH bonds. Bands ν_{21}, ν_{29} and ν_{30} on Table III for νC—OH and γC—H(py) appear as a single band on all compounds except that of Ni(II). Bands more likely to split in *cis*- py

TABLE II Selected bond lengths (Å) observed in bis(glycolato) bis(pyridine) complexes with Ni(II) and Cu(II)

Bond	*Ni*	*Cu*
M—O^a	2.0279(16)	1.994(3)
M—OH^a	2.0924(16)	2.299(3)
M—O^b	2.0301(16)	1.994(3)
M—OH^b	2.0997(18)	2.299(3)
M—N	2.0897(19)	2.017(4)
M—N	2.092(2)	2.017(4)

a and b indicate oxygen atoms on glycolato ligands.

TABLE III Infrared assignments[§] (4000–70 cm^{-1}) for [MG$_2$(py)$_2$] complexes, M = Co, Ni, Cu and Zn

Band	[*CoG$_2$(py)$_2$*]	† ν_D/ν_H	[*NiG$_2$(py)$_2$*]	† ν_D/ν_H	‡ ν_D/ν_H	[*CuG$_2$(py)$_2$*]	† ν_D/ν_H	‡ ν_D/ν_H	[*ZnG$_2$(py)$_2$*]	† ν_D/ν_H	*Assignment*
ν_1	–[a](2299)		3107 (2290)	0.74		3106 (2304)	0.74		–[a](2291)		{νC—H(py)
ν_2	3070 (2278)	0.74	3070 (2280)	0.74		3074 (2287)	0.74		3071 (2278)	0.74	
ν_3	3049 (–)					3063 (2276)	0.74		3045 (–)		
ν_4			3026 {2206}		0.73	2996 {2231}		0.74			{νO—H
			3002								
ν_5	–[c]		2949			2894			–[c]		{νC—H(G)
ν_6	2920		2922						2921		
	2795		2871 {2105}		0.73	2793 {2160}		0.77	2798		{νO—H + νO—H- - -O
	2747		2800 {2033}		0.73	2730 {2116}		0.78	2745		
	2704		2751 {1964}		0.71						
	2640					2704			2713		
	2573					2641 {2076}		0.79	2646		
						2573 {2042}		0.79	2574		
ν_7	–[a](1560)		1602 (1561)	0.97		1605 (1560)	0.97		–[a](1560)		ν ring (py)
ν_8	1590		1586			1588			1594		{νC=O
						1581					
ν_9	1570 (1537)	0.98	1569 (1539)	0.98		1567 (1539)	0.98		1570 (1537)	0.98	ν ring (py)
ν_{10}	1504		1494[b]			1472			1504		
ν_{11}	1484 (1315)	0.89	1485 (1314)	0.88		1487 (1315)	0.88		1485 (1315)	0.88	{ν ring (py)
ν_{12}	1444 (–)[a]		1445 (–)			1448 (–)[a]			1445 (–)[a]		
ν_{13}	1410		1414			1397			1410		νC—O + νC—C(G)

TABLE III (Continued)

Band	[$CoG_2(py)_2$]	$^{\dagger}\nu_D/\nu_H$	[$NiG_2(py)_2$]	$^{\dagger}\nu_D/\nu_H$	$^{\ddagger}\nu_D/\nu_H$	[$CuG_2(py)_2$]	$^{\dagger}\nu_D/\nu_H$	$^{\ddagger}\nu_D/\nu_H$	[$ZnG_2(py)_2$]	$^{\dagger}\nu_D/\nu_H$	Assignment
ν_{14}	1382		1388		0.78				1382		δC—OH
			{1089}								
ν_{15}	$-^{a}$ (1330)		$-^{a}$			1361 (1331)	0.98		$-^{a}$ (1331)		ν ring (py)
			(1346)								
ν_{16}	1300		1304		1.02	1291 {1294}		1.00	1299		δC—OH + CH_2 wag
			{1330}								
ν_{17}	1236		1236			1239			1238		{CH_2 twist
ν_{18}	1223^{b}					1226^{b}			1226^{b}		
ν_{19}	1215 (888)	0.73	1217	0.73		1219 (852)	0.70		1216 (889)	0.73	{δC—H (py)
			(891)								
ν_{20}	1152 (832)	0.72	1151	0.72		1149 (837)	0.73		1153 (832)	0.72	
			(831)								
ν_{21}	1068		1071		1.02	1084 {1086}		1.00	1071		{νC—OH
			{1089}								
			1056								
						1069 (827)	0.77		$-^{a}$ (828)		νC—H (py)
ν_{22}	1039 (1021)	0.98	1040	0.98		1044 (1014)	0.97		1039 (1022)	0.98	{ν ring (py)
			(1022)								
ν_{23}	1011 (978)	0.97	1012	0.97		1017 (981)	0.96		1012 (979)	0.97	
			(979)								
ν_{24}	986		986			997			987		νC—C(G)
			951 (–)^{a}			952 (–)^{a}					ν ring (py)
ν_{25}	933								932		{νC – C(G) + CH_2 scissor
ν_{26}	920		925			925			920		
						895					CO_2 scissor
ν_{27}	883 (–)^{f}		884	0.79							γC—H (py)
			(695)								
ν_{28}	866		908^{e}		0.73	839 {611}		0.73	854		π OH
			{661}								
ν_{29}	760 (–)^{f}		767	0.71		758 (562)^{f}	0.74		760 (–)^{a}		{γC—H (py)
			(543)								
			759								

ν_{30}	700		707 700			697			700		{CO_2 rock + γC—H (py)
ν_{31}	629 (–)^{a}		631 (537)	0.85		642 (535)	0.83		629 (537)^{a}	0.85	δ ring (py)
ν_{32}	599		595						599		{CO_2 wag + ring def. (MG)
ν_{33}	548		557			561			548		
ν_{34}	510 (–)^{g}		517 {512}		[5]				–		
ν_{35}	440^{a}	0.91	453 {439}^{d}						435^{b}		νM—OH
ν_{36}	424 (385)	[3]	435 (396)	0.91		444 (406)	0.91		422 (383)	0.91	γ ring (py)
ν_{37}	496 (403)		414								{ring def. (MG)
ν_{38}	390 (–)^{a}		387						391 (–)^{g}		
ν_{39}	294		324			381 {377}		[4]	269 (268)		νM—OH + νM—O
ν_{40}	258		300 (299)			311 {308}		[3]	237 (234)	[3]	{νM—O + νM—OH+ νM—N
		[2]	276 {274}		[2]						
ν_{41}	220 (218)		239			270			209 (208)		νM—O + def. G
ν_{42}	198^{b}		214 (210)	[4]		232 (225)^{h}	[7]	[4]	183 (175)	[8]	νM—N + δO—M—OH
						{228}					{δO—M—N + δN—M—N + def. G
			184 (177)	[7]		199					
ν_{43}	161	[2]	163 {158}		[5]	177					
ν_{44}	146 (144)		133 (129)	[4]	[5]	133 {131}		[2]	146 (144)	[2]	

TABLE III (Continued)

Band	*[CoG$_2$(py)$_2$]*	† ν_D/ν_H	*[NiG$_2$ (py)$_2$]*	† ν_D/ν_H	‡ ν_D/ν_H	*[CuG$_2$(py)$_2$]*	† ν_D/ν_H	‡ ν_D/ν_H	*[ZnG$_2$ (py)$_2$]*	† ν_D/ν_H	*Assignment*
			{128}								
			115			114 (107)	[7]		115 (113)	[2]	
			86			96 (88)	[8]		81		

§ Values in parenthesis are the observed frequencies in the [MG$_2$(py-d_5)$_2$] isotopomers. Values in braces are the observed frequencies in the [M(G-d)$_2$(py)$_2$] isotopomers. In the far infrared region, only shifts greater than 1 cm^{-1} are considered.

† ν_D/ν_H is the ratio of the frequency obtained for the py-d_5 complex over the frequency obtained for the py complex. Values in brackets in the far infrared region correspond to the ν[MG$_2$(py)$_2$] − ν[MG$_2$(py-d_5)$_2$] difference.

‡ ν_D/ν_H is the ratio of the frequency obtained for the [MG$_2$(py)$_2$] complex over the frequency obtained for the [M(G-d)$_2$(py)$_2$] complex. Values in brackets in the far infrared region correspond to the ν[MG$_2$(py)$_2$] − ν[M(G-d)$_2$(py)$_2$] difference.

[a] Band overlapped by a higher intensity band.

[b] Band taken from the spectrum of the complex with py-d_5.

[c] Band obscured by OH vibrations occurring in this region.

[d] Value taken from the spectrum of the [Ni(G-d)$_2$(py-d_5)$_2$] complex.

[e] Best estimate of shoulder band.

[f] Coupled to C=O vibrations.

[g] Value not determined due to poor shape of band.

[h] Mean of two bands occurring in this region.

complexes are bands 11, 4, 5 and 16b in the notation of Kline and Turkevitch [17]. Bands ν_{29} and ν_{30} are γC—H(11) and γC—H(4), respectively and split in the Ni(II) complex whereas band ν_{36} is γ(ring) 16b and appears as a single band. The γC—H(5) band is a weak intensity band in the py spectrum and is not observed in the complex. There is a band to band correspondence for the Co(II) and Zn(II) compounds which leads to the assumption that they are isostructural and bonded to both the glycolato and pyridine ligands in *trans* configuration as observed in the Cu(II) complex. However, the spectra of these complexes differs from that of the Cu(II) compound due to the structural difference that originates from the static Jahn-Teller distortion that exists for the latter [8]. The spectra of the complexes with py and py-d_5 from 1250–500 cm^{-1}, which appears to be the region most sensitive to geometry in these compounds is shown in Figure 3.

The infrared spectra of the compounds exhibit a complex band pattern in the 3250–2250 cm^{-1} region. In all cases, the bands associated to C—H vibrations from the pyridine ring may easily be assigned on the basis of their

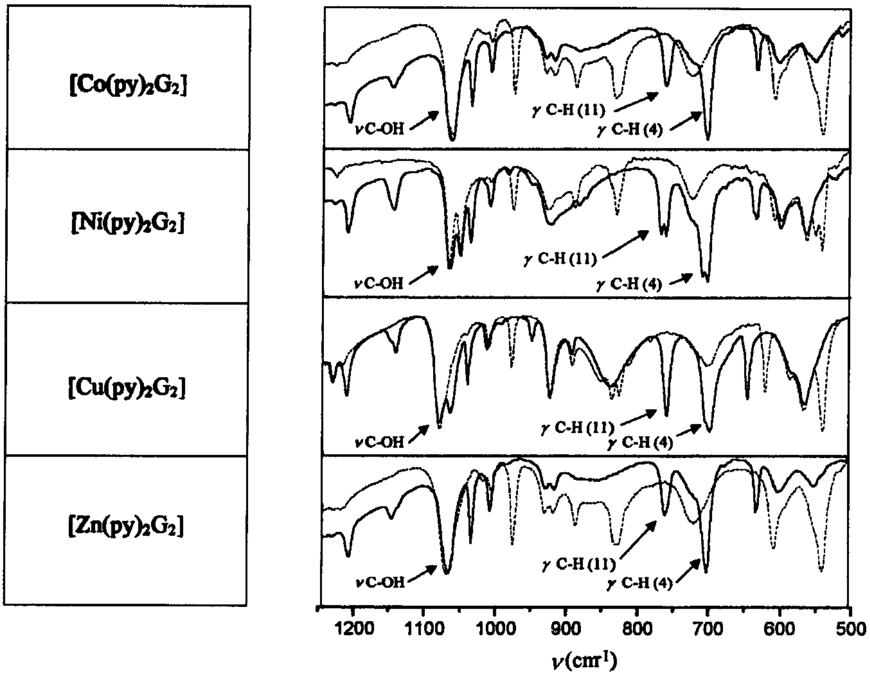

FIGURE 3 Infrared spectra of the [MG$_2$(py)$_2$] compounds, M = Co, Ni, Cu and Zn, in the 1250–500 cm^{-1} region. Dashed lines are the spectra of the [MG$_2$(py-d_5)] complexes.

800 cm^{-1} shift to lower energy on py-d_5 substitution. Weak intensity bands appearing in the 2900 cm^{-1} region have been assigned to the C—H vibrations in the glycolato ligand as they have been assigned by Nakamoto *et al.*, for the bis(glycolato) complexes by means of CD_2 labelling of the glycolato ligand on the Co(II) complex [1]. The remaining bands are related to O—H vibrations as well as hydrogen bonding in the compounds as shown by shifts to lower energy upon α—OD substitution.

The intense bands appearing in the 1600 cm^{-1} region, which, in all cases overlap with bands associated to pyridine ring vibrations are assigned to the C=O asymmetric vibration. In the Ni(II) compound, the band appearing at 1388 cm^{-1} in the [$NiG_2(py)_2$] and [$NiG_2(py\text{-}d_5)_2$] compounds shifts to 1089 cm^{-1} in both the [$Ni(G\text{-}d)_2(py)_2$] and [$Ni(G\text{-}d)_2\ (py\text{-}d_5)_2$] compounds and has thus been assigned as an OH in plane deformation.

The weak intensity bands appearing in the 1220–1230 cm^{-1} region have been assigned to CH_2 deformations as they remain unchanged in the spectra of all the different compounds prepared. These values are consistent to those reported in the [MG_2] compounds prepared by Nakamoto [1] and in transition metal compounds with glycine and other α-aminoacids [18–22]. The bands appearing in the 1070 cm^{-1} region have been assigned to νC—OH and appear very close to the values reported for the [MG_2] compounds, except for the Cu(II) compound, for which there is a shift of 10 cm^{-1} to higher energy. This increase in energy must arise from tetragonal distortion weakening the Cu—OH bond and thus, an increase in the C—OH bond strength is observed. It is this band that indicates *cis* configuration in the Ni(II) complex and this band has also been observed to split in the *cis*-[$Zn(H_2O)_2G_2$] compound [23] obtained by Fischinger, *et al.* [7], but not studied by IR. The intense band appearing in the 900–840 cm^{-1} region has been assigned to the out-of-plane OH deformation as it shifts some 240 cm^{-1} to lower energy on α—OD substitution in both the Ni(II) and Cu(II) compounds. The —CO_2 deformations have been assigned following the assignments given by Nakamoto [1] for the [MG_2] compounds and those given by Percy *et al.*, for glycine compounds [19–21]. Assignments for the Ni(II) py adduct with gycolato are consistent with assignments given for the *cis,cis*-bis(glycinato)*cis*-bis(imidazole)nickel(II) compound by multiple isotopic labelling [18] as far as the glycinato and glycolato units are concerned.

The far infrared spectra of the complexes (Fig. 4) exhibit the in-plane, δ(py ring), and out-of-plane, γ(py ring), deformations of the pyridine ligand, both of which shift to lower energy on py-d_5 substitution (bands ν_{31} and ν_{36}, respectively). A weak intensity band at 453 cm^{-1} observed in the spectrum of the [$NiG_2(py)_2$] complex is unaffected by py-d_5 substitution. This band is not observed in the spectrum of the [$Ni(G\text{-}d)_2(py)_2$] compound as it occurs in the same region as the out-of-plane py-d_5 deformation, however, it shifts 14 cm^{-1} to lower energy upon α—OD labelling as is observed in the

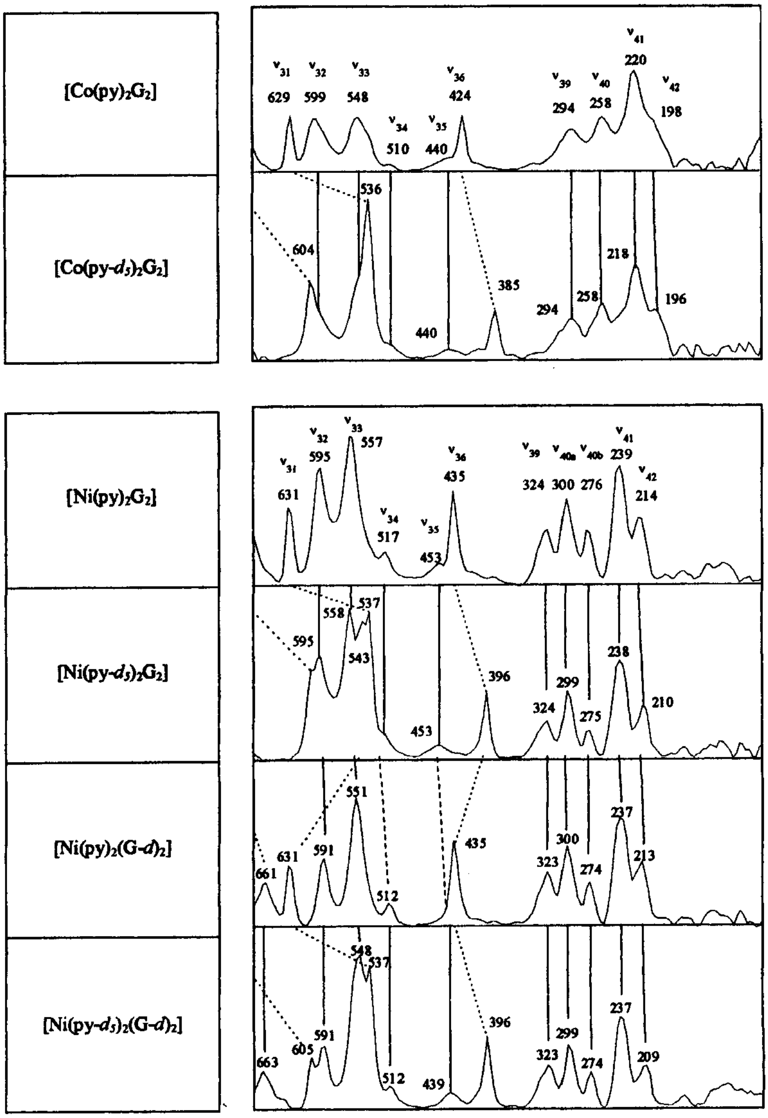

FIGURE 4 Far infrared spectra of the [$MG_2(py)_2$] compounds, M = Co, Ni, Cu and Zn and ligand labelled compounds.

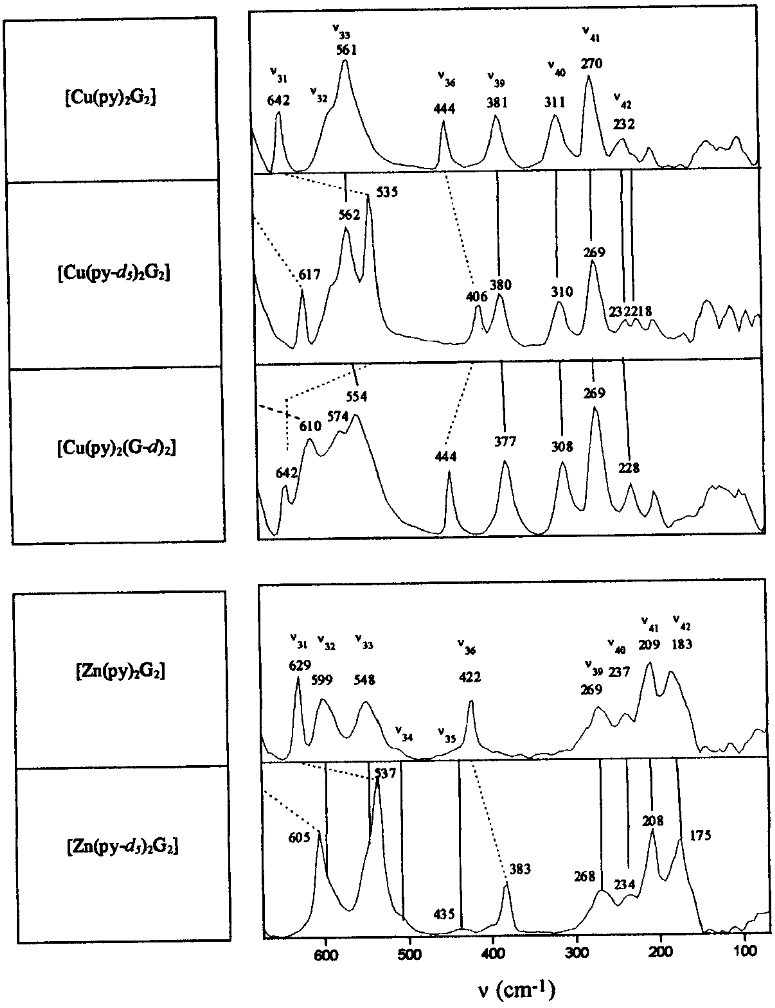

FIGURE 4 (Continued).

[Ni(G-d)$_2$(py-d_5)$_2$] spectrum, which is the largest shift observed in the far infrared region induced by deuteration of the α—OH group. This is almost in direct agreement with the 0.98 $\nu_{\mathrm{Ni-OD}}/\nu_{\mathrm{Ni-OH}}$ ratio expected if the OH group is considered as a point mass vibrating against the metal atom in the harmonic oscillator approximation. It has thus been assigned as a νM—OH vibration. Despite its sensitivity to α—OD labelling, it is not one of the bands most sensitive to metal ion substitution (Fig. 5) although this does not rule out its assignment as a M—OH band as will be discussed later.

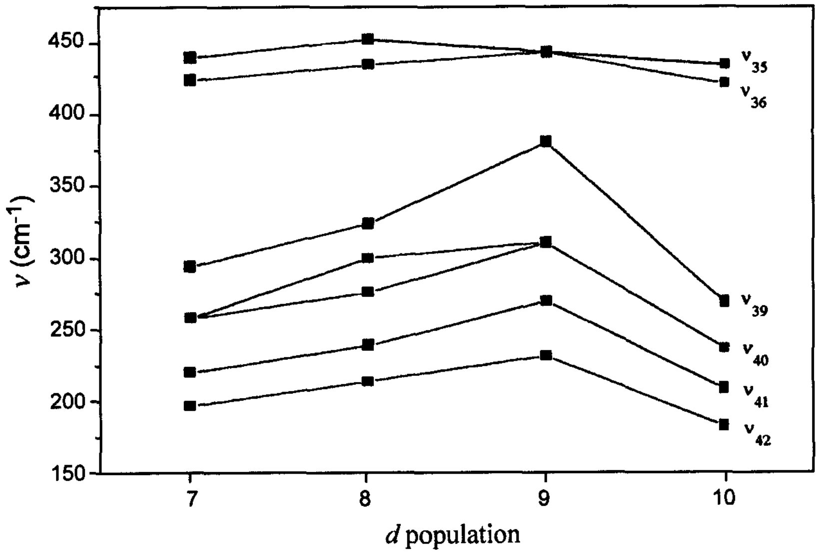

FIGURE 5 Vibration frequencies in the far infrared and their relation to CFSE.

The Cu(II) complex does not exhibit this band, although it appears in a similar region in all the [MG_2] complexes [1] and shifts less upon α—OD substitution in the [Co(G-d)$_2$] complex studied by Nakamoto. Similar observations have been made on the [Ni(G-d)$_2$] and [Cu(G-d)$_2$] compounds [23]. Tetragonal distortion plays a significant part in the Cu(II) pyridine complex so this band may well shift to lower energy and is perhaps obscured by the higher intensity bands appearing at lower energy. For the Ni(II) complex, both M—OH bonds are *trans* to the M—N bonds and this may account for weakening of the Ni—OH bonds and thus a smaller effect on metal ion substitution. It is interesting to note that coupled ν M—NH_2 bands have been observed in this same region in bis(aminoacidato) complexes [18–21].

The bands that are most sensitive to metal ion substitution occur in the 230–380 cm^{-1} region (Fig. 5). However, the bands appearing in this region show little sensitivity to α—OD labelling, which may be explained on the basis of coupling of the M—O and M—OH bonds. They have been assigned as the principal M—O bands occurring in these compounds due to their metal ion substitution shifts [9–11]. The bands in this region appear to be sensitive to the geometry of the complexes, as three Ni—O bands are observed in this region while only two M—O bands for M = Co, Cu, and Zn are observed. Considering the local symmetry of the complexes, the Co(II), Cu(II) and Zn(II) complexes have D_{2h} symmetry and three M—L stretching bands are expected, one each for the M—OH, M—O and M—N vibrations. The Ni(II) compound has C_{2v} symmetry and six M—L bands are expected to appear in the far infrared region, two for each of the different M—L bonds present. Although there are more bands in the spectrum of the $[NiG_2(py)_2]$ complex, there also appears to be some strong coupling in this region with low frequency bands associated to the glycolato ligand (band ν_{41}) as there are at least two bands present in this region in the spectrum of the protonated glycolato ligand. M—N vibrations appear in the 240–210 region and are coupled to other M—O vibrations.

Calculated Frequencies

In Table IV, distances and angles from Gaussian's geometrical optimization are listed together with the experimental results of x-ray diffraction. The experimental and theoretical results are in good agreement. The largest difference is in the Ni—OH bond distance (2.0997 and 2.23 Å, experimental and theoretical values, respectively) and for the N—Ni—N

TABLE IV Selected bond lengths (Å) and angles (°) experimental and calculated for bis(glycolato)bis(pyridine) complexes with Ni(II). Energy minimum value: −2599.236619 a.u.

Bonds	$NiG_2(py)_2$ (*Experimental*)	$NiG_2(py)_2$ (*Calculated*)
Ni—O[a]	2.0279(16)	1.97
Ni—OH[a]	2.0924(16)	2.07
Ni—O[b]	2.0301(16)	2.06
Ni—OH[b]	2.0997(18)	2.23
Ni—N	2.0897(19)	1.95
Ni—N	2.092(2)	1.98
Angle		
O(2)—Ni(1)—O(12)	167.78(6)	167.3
O(2)—Ni(1)—N(21)	92.77(7)	93.2
O(12)—Ni(1)—N(21)	95.39(8)	90.8
O(12)—Ni(1)—N(31)	92.79(8)	93.2
O(2)—Ni(1)—N(31)	96.11(8)	97.6
N(21)—Ni(1)—N(31)	91.19(8)	107.3
O(2)—Ni(1)—O(1)	78.39(6)	79.4
O(12)—Ni(1)—O(1)	93.39(7)	93.8
N(21)—Ni(1)—O(1)	171.16(7)	168.3
N(31)—Ni(1)—O(1)	89.46(8)	82.3
O(2)—Ni(1)—O(11)	91.45(7)	93.8
O(12)—Ni(1)—O(11)	79.53(7)	79.4
N(21)—Ni(1)—O(11)	89.79(7)	82.3
N(31)—Ni(1)—O(11)	172.32(7)	160.4
O(1)—Ni(1)—O(11)	90.74(7)	80.6

TABLE V Selected experimental and calculated infrared assignments (4000–70 cm^{-1}) for *cis*-[$NiG_2(py)_2$]

[$NiG_2(py)_2$]	*Assignment*	*Calculated*
3107, 3070	νC—H(py)	3142–3111
2949, 2922	νC—H(G)	3059, 2939
1586	νC=O	1651, 1591
1569–1445	ν ring (py)	1539–1409
1388, 1304	δC—OH + CH_2 wag	1407–1305
1217, 1151	δC—H(py)	1195, 1193
1040, 1012	ν ring (py)	1021, 1013
986, 925	νC—C(G) + CH_2 scissor	966, 947, 899, 830
595, 557	CO_2 wag + ring def. (MG)	639, 576
453	νM—OH	478
414, 387	ring def. (MG)	380, 346
324	νM—OH + νM—O	321
239	νM—O + def. G	289
214, 184	νM—N + δO—M—OH	260, 233

angle (91.19 and 107.3°, experimental and theoretical values, respectively). The theoretical structure has a slight distortion in comparison with the experimental values.

In Table V we compare some selected frequencies of the calculated infrared spectrum with those obtained experimentally. In the calculations, a value of 0.95 was used for the scale factor. Considering the high degree of coupling in vibrations associated with the coordination framework, there is a good agreement between theory and experiment. The small differences may be attributed to solid state effects in the experimental determination, while calculated geometries and frequencies are for the gas phase.

As pointed out before, the title compound forms hydrogen bonds involving the OH of the glycolate moiety and water molecules in the crystal lattice. In the calculations the molecule is in gas phase and no hydrogen bonds are considered. For this reason, the frequencies involving the OH groups (not shown in the table) are not in good agreement with the experimental values. Despite this, there is good agreement between the theoretical and experimental results.

The calculations on the [$NiG_2(py)_2$] complex help confirm the experimental assignment done on the experimental infrared spectra.

Supplementary Material

Crystallographic data for the reported x-ray structure were deposited to the CSD with number CCDC-142221. Structure factors are available on request from the correspondence author.

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