Vibrational Spectra of Anhydrous Metal Pyridine Nitrates

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Vibrational spectroscopy has been used to investigate the nature of the metal–ligand environment of $Cu(py)_n(NO_3)_2$ where n = 2, 3, and 4 and $M(py)_3(NO_3)_2$ where M = Co, Ni, and Zn. Extensive use of isotopic substitution and related techniques were made to assign the low frequency i.r. spectra (350—75 cm^{-1}). It has been observed for the $Cu(py)_n(NO_3)_2$ system, that as the covalency of the nitrate bonding increases, the copper–oxygen stretching vibration shifts to higher energy, while the copper–nitrogen stretching vibration moves to lower energy.

SEVERAL i.r. and structural studies of the anhydrous copper nitrate-pyridine (py) series of compounds have been reported.[1-5] The series includes compounds of the stoicheiometry $Cu(py)_n(NO_3)_2$ where $n = 2$, 3, or 4, with the pyridine co-ordinated to the copper atom. Biagetti and co-workers[1] confirmed the existence of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$, but indicated the lack of evidence for the $Cu(py)_3(NO_3)_2$ compound and suggested that it was a 1 : 1 molar mixture of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$. Others[2,3] have reported the far-i.r. spectra of $Cu(py)_4(NO_3)_2$, $Cu(py)_3(NO_3)_2$, and $Cu(py)_2(NO_3)_2$ down to 150 cm^{-1} and some tentative metal–ligand stretching vibration assignments have been suggested.

In addition to $Cu(py)_3(NO_3)_2$, co-ordination compounds of the stoicheiometry $M(py)_3(NO_3)_2$ (where M = Co, Ni, and Zn) have been prepared and characterized.[2,6-8] The low frequency i.r. data for $Zn(py)_3(NO_3)_2$ have been reported[2,6] with the zinc–oxygen and zinc–nitrogen stretching vibrations being tentatively assigned.

For the compounds $Cu(py)_n(NO_3)_2$ (where n = 3 or 4) and $M(py)_3(NO_3)_2$ (where M = Co and Ni) structural information is limited. I.r. data and assignments are incomplete and in some cases conflicting. In an attempt to make more definitive spectral assignments, expand on the existing structural information, and observe the nitrate ligand in various co-ordination environments for a series of related compounds, we have studied the above series by making use of deuterium and metal isotopic substitution, pressure techniques, and, where applicable, Raman spectroscopy. The use of these methods is demonstrated in this paper where the supplementary data expand the diagnostic possibilities in the far-i.r. and thereby provide more definite information on structure and metal–ligand bonding.

EXPERIMENTAL

Materials.—Reagent grade diethyl ether, chloroform, and 2,2-dimethoxypropane were used without further purification. Reagent grade pyridine and methanol were dried.[1,6,7] Cobalt, copper, zinc, and silver nitrates were dried over P_2O_5 *in vacuo* before use. Reagent grade $Co(NO_3)_2,6H_2O$ and $Ni(NO_3)_2,6H_2O$ were used without further purification. $[^2H_5]$Pyridine was obtained in 99% purity from Aldrich Chemical Company, and used without further purification. Metal isotopes were purchased from Oak Ridge National Laboratory. ^{62}Ni was 96·16% pure. Natural nickel metal, containing *ca.* 69% ^{58}Ni isotope was used as the isotopic pair to ^{62}Ni. ^{63}CuO was 99·69% and ^{65}CuO was 99·73% pure.

Dinitratobis(pyridine)copper(II) *and Dinitratotetrakis(pyridine)copper*(II).—$Cu(py)_2(NO_3)_2$ and $Cu(py)_4(NO_3)_2$ were prepared by the method of Biagetti *et al.*[1] The ^{63}Cu and ^{65}Cu isotopic compounds were prepared in milligram quantities from the isotopic copper oxides. The oxides were converted to the metal by standard hydrogen reduction techniques. The products were identified by their i.r. spectra.[1,2]

Dinitratotris(pyridine)copper(II).—$Cu(py)_3(N_3O)_2$ was prepared by repeated recrystallization of stoicheiometric amounts of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ from hot, anhydrous methanol by a method similar to that used by Pfeiffer and Pimmer[9] (Found: C, 42·2; H, 3·55. Calc. for $C_{15}H_{15}CuN_5O_6$: C, 42·4; H, 3·55%). Metal isotopic substitution was not attempted because of the poor yield of pure compound by this method.

Dinitratotris(pyridine)cobalt(II).—$Co(py)_3(NO_3)_2$ was prepared according to the method described by Biagetti and Haendler[7] (Found: C, 42·7; H, 3·6; N, 17·25. Calc. for $C_{15}H_{15}CoN_5O_6$: C, 42·85; H, 3·6; N, 16·65%). The $[^2H_5]$pyridine analogue was prepared in milligram quantities by substituting $[^2H_5]$pyridine for pyridine in the above procedure.

Dinitratotris(pyridine)nickel(II).—$Ni(py)_3(NO_3)_2$ was prepared by dehydration of the hexa-aquonickel(II) nitrate with 2,2-dimethoxypropane followed by the addition of an excess of pyridine.[7] The purity of the product was confirmed by the mid-i.r., u.v., and visible spectra and by the microanalyses (Found: C, 43·15; H, 3·65; N, 17·3. Calc. for $C_{15}H_{15}N_5NiO_6$: C, 42·9; H, 3·6; N, 16·65%).

The procedure was repeated on a milligram scale using $[^2H_5]$pyridine to prepare $Ni(py\text{-}d)_3(NO_3)_2$. Metal isotopic substitution was accomplished by conversion of commercially available ^{62}Ni to $^{62}Ni(NO_3)_2,6H_2O$ and subsequent repetition of the above procedure. The conversion of ^{62}Ni to the hexa-aquo nitrate was achieved by dissolving the metal in concentrated nitric acid, heating to near dryness on a water-bath, followed by repeated recrystallization from water.

Dinitratotris(pyridine)zinc(II).—$Zn(py)_3(NO_3)_2$ was prepared from zinc metal by the method of Ouellette and

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[1] R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 379, and references therein.

[2] C. W. Frank and L. B. Rogers, *Inorg. Chem.*, 1966, **5**, 615.

[3] R. H. Nuttall and D. W. Taylor, *Chem. Comm.*, 1968, 1471.

[4] N. Logan and W. Simpson, *Spectrochim. Acta*, 1965, **21**, 857.

[5] A. F. Cameron, K. P. Forrest, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 210; *J. Chem. Soc.* (*A*), 1971, 2492.

[6] T. J. Ouellette and H. M. Haendler, *Inorg. Chem.*, 1969, **8**, 1777.

[7] R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 383.

[8] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840.

[9] P. Pfeiffer and V. Pimmer, *Z. anorg. Chem.*, 1906, **48**, 98.

Haendler.[6] The [$^2H_5$]pyridine analogue was similarly prepared (Found: C, 42·1; H, 3·55; N, 16·5. Calc. for $C_{15}H_{15}N_5O_6Zn$: C, 42·3; H, 3·55; N, 16·8%). All microanalyses were preformed by Micro-Tech Labs., Skokie, Illinois, and the Argonne Analytical Division.

Spectral Measurements.—I.r. spectra from 4000 to 200 cm^{-1} were recorded in both Nujol and halogenocarbon mulls on CsI windows using a Beckman IR12 spectrophotometer calibrated with polystyrene. Low-frequency spectra were run in Nujol mulls on polyethylene windows with a Perkin-Elmer 301 Spectrophotometer (666—70 cm^{-1}) and a Perkin-Elmer FIS3 Spectrophotometer (400—70 cm^{-1}). The former was calibrated with mercury emission lines while the latter was calibrated by using water vapour and $Na_3[Co(NO_2)_6]$. The low-frequency i.r. spectra of several natural compounds were observed under high-external pressure up to 30 kbar, using a diamond anvil cell. Procedures and instrumentation for such measurements have been described previously.[10]

Laser Raman spectroscopy was attempted for all compounds. The Argon ion (4879·9 Å) and Helium–Neon (6328·1 Å) laser lines were used as the energy sources. The power of the argon line was reduced from *ca.* 700 to *ca.* 35 mW; the helium–neon line being used at a maximum of 30 mW. A low temperature Raman cell was used to run some samples at liquid-nitrogen temperatures.

X-Ray Measurements.—Powder diffraction patterns of all compounds were recorded by a Cu-K_α radiation source.

RESULTS AND DISCUSSION

Mid-i.r. Region.—Results obtained in this region (4000—400 cm^{-1}) for the complexes studied in the paper are listed in Table 1. The results indicate that both pyridine and nitrate complexation have occurred.[11,12]

TABLE 1

Diagnostic nitrate and pyridine ligand bands in the mid-i.r. region (cm^{-1})

Monodentate [a,b] nitrate assignments	$Cu(py)_4(NO_3)_2$	Bidentate [b] nitrate assignments	$Cu(py)_3(NO_3)_2$	$Cu(py)_2(NO_3)_2$	$Co(py)_3(NO_3)_2$	$Ni(py)_3(NO_3)_2$	$Zn(py)_3(NO_3)_2$
ν_4 (b_1)	1408vs	ν_1 (a_1)	1458vs	1474vs	1482vs	1502s	1456vs
ν_1 (a_1)	1306vs	ν_4 (b_1)	1291vs	1282vs	1294vs	1312vs	1300vs
$\Delta\nu$ ($\nu_4 - \nu_1$)	102	$\Delta\nu$ ($\nu_1 - \nu_4$)	167	192	188	190	156
ν_2 (a_1)	1026s	ν_2 (a_1)	1034s	1024s	1033s	1036s	1031s
ν_6 (b_2)	820m	ν_6 (b_2)	819m	814m	815m	818m 811m	818m
ν_3 (a_1)	730 (calc)	ν_3 (a_1)			735 (calc)		727 (calc)
ν_5 (b_1)	718 (calc)	ν_5 (b_1)			698 (calc)		704 (calc)
$\nu_2 + \nu_3$	1756w	$\nu_2 + \nu_3$	1754w 1731w 1725w	1776w 1747w 1722sh 1717w	1768w	1762w 1745w 1711w	1758w
$\nu_2 + \nu_5$	1744w	$\nu_2 + \nu_5$			1731w		1736w
$\Delta\nu'[(\nu_2 + \nu_3) - (\nu_2 + \nu_5)]$	12	$\Delta\nu'[(\nu_2 + \nu_3) - (\nu_2 + \nu_5)]$			37		22
π_{op} pyridine [c]	641m	π_{op} pyridine	643m	645m	632m	636m	637m
π_{ip} pyridine [c]	429m	π_{ip} pyridine	435m	440m	429m	435m	422m

[a] vs, Very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; op, out-of-plane; ip, in-plane. [b] Assignments of ν_1, ν_2, ν_3 . . . are made according to conversions established by Addison *et al.*, refs. 18 and 19. [c] Occasional splitting occurs in these pyridine bands which are probably due to crystal environment effects. Where such splitting occurs the average value is given.

TABLE 2

Far-i.r. spectra of $Cu(py)_n(NO_3)_2$ (where n = 4, 3, or 2) from 350 to 80 cm^{-1}

	$Cu(py)_4(NO_3)_2$			$Cu(py)_3(NO_3)_2$		$Cu(py)_2(NO_3)_2$		
Assignments [a,b]	^{63}Cu	$\Delta\nu$ [c]	$\Delta\nu$ [d]	Natural abundance	$\Delta\nu$ [d]	^{63}Cu	$\Delta\nu$ [c]	$\Delta\nu$ [d]
ν_{Cu-O}	266vs	3	3	268vs	1·0	322vs	3	0
						282s	3	0
ν_{Cu-N}	250m	2	8	223m	10	205w	1	5
δ_{N-Cu-N}	200w	1	10			173sh	0	*ca.* 5
δ_{O-Cu-N}	192w	1	7	211sh		220w sh	2	2
	130m b	1	*ca.* 5	156w	*ca.* 2	133m	1	1
						ca. 115w	0	2
						ca. 82w	0	1

[a] vs, Very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; op, out-of-plane; ip, in-plane. [b] ν, Stretching vibration; δ, bending vibration. [c] $\Delta\nu = \nu(^{63}Cu) - \nu(^{65}Cu)$. [d] $\Delta\nu = \nu(Cu,py) - \nu(Cu,py\text{-}d)$.

Low Frequency Infrared Region.—1. $Cu(py)_n(NO_3)_2$ *Complexes.* The far-i.r. absorptions (350—80 cm^{-1}) observed for copper–pyridine nitrate complexes are listed in Table 2 and spectra are presented in Figure 1. Metal isotopic shifts and deuteriopyridine shifts have been observed for $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$. Metal-isotope compounds were not prepared for $Cu(py)_3(NO_3)_2$ due to the poor yields of the pure product. Only partial data for $Cu(py\text{-}d)_3(NO_3)_2$ are listed (Table 2)

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[10] J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 269; L. J. Basile, C. Postmus, and J. R. Ferraro, *Spec. Letters*, 1968, 189.

[11] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79, and references therein.

[12] C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 71; C. C. Addison, N. Logan, S. C. Wallwork, and D. C. Garner, *Quart. Rev.*, 1971, **25**, 316, and references therein.

since this spectrum was somewhat obscured by the decomposition product, $Cu(py\text{-}d)_2(NO_3)_2$.

As previously reported,[1] thermal decomposition of $Cu(py)_4(NO_3)_2$ at temperatures above 75° in a stream of dry nitrogen appears to proceed by the loss of two molecules of pyridine to give only $Cu(py)_2(NO_3)_2$ with no trace of the intermediate compound. Pure crystals of $Cu(py)_3(NO_3)_2$ were obtained by the recrystallization of 1 : 1 molar mixture of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ from methanol solution. Individual *X*-ray powder patterns for all three compounds and individual far-i.r. spectra verify the formation of a new compound. The 1 : 1 molar mixture of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ heated in a sealed glass tube at 90—100° for several days gave a substantial amount of $Cu(py)_3(NO_3)_2$ in the presence of the starting materials, but complete conversion did not occur. $Cu(py)_4(NO_3)_2$ placed in a vacuum desiccator over P_2O_5 slowly lost pyridine to give a *ca.* 1 : 1 molar ratio of $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ after two days and had converted completely to $Cu(py)_2(NO_3)_2$ after 6—8 days. A sequence of far-i.r. measurements (Figure 2) made it possible to observe the slow conversion of $Cu(py)_4(NO_3)_2$ to $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ followed by the rapid loss of one molecule of pyridine from $Cu(py)_3(NO_3)_2$ to give stable $Cu(py)_2(NO_3)_2$. Pure crystals of $Cu(py)_3(NO_3)_2$ prepared from the 1 : 1 molar mixture of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ can be kept in a sealed bottle at least several weeks with no observable disproportionation or change. However, heating and exposure to P_2O_5 or to a nitrogen stream all promote the loss of one mole of pyridine to form $Cu(py)_2(NO_3)_2$.

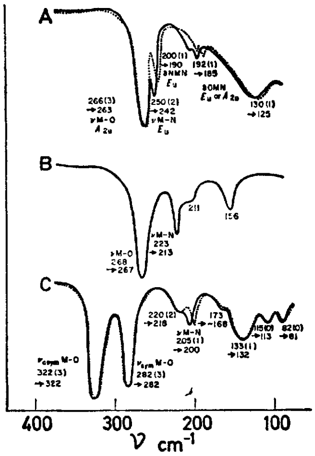

FIGURE 1 Far i.r. spectra of $Cu(py)_n(NO_3)_2$ (n = 4, 3, or 2) from 375 to 80 cm^{-1}; A, ——, $^{63}Cu(py)_4(NO_3)_2$; · · · ·, $Cu(py\text{-}d)_4(NO_3)_2$; B, $Cu(py)_3(NO_3)_2$ natural abundance; C, ——, $^{63}Cu(py)_2(NO_3)_2$; · · · ·, $Cu(py\text{-}d)_2(NO_3)_2$; the number in parentheses is the metal-isotope shift; the number following the arrow in the absorption for the deuteriopyridine compound

As seen in Table 2 and Figure 1 five i.r.-active bands are observed in the region 350—80 cm^{-1} for $Cu(py)_4(NO_3)_2$. All the bands show shifts of 1—3 cm^{-1} with metal isotope substitution. The strongest band at 266 cm^{-1} shows negligible sensitivity to deuteriopyridine substitution and can therefore be assigned to the Cu–O stretching. The 250 cm^{-1} band shows a large deuteriation shift indicating a Cu–N stretching mode. The three remaining weaker bands can be attributed to skeletal bending modes. The 200 cm^{-1} absorption shows a very significant deuteriation shift of 10 cm^{-1} indicating that this mode involves a large displacement of the pyridine molecules. Therefore, an assignment of the δ(NCuN) is reasonable. The remaining two bands are probably due to the δ(OCuN) modes.

The far-i.r. spectrum of $Cu(py)_3(NO_3)_2$ (Table 2, Figure 1) reveals four bands below 350 cm^{-1}. The strong band at 268 cm^{-1} can be assigned to the copper–oxygen stretching vibration. The band at 223 cm^{-1} can be assigned to the Cu–N stretching mode since it gives a large shift by the deuteriation of pyridine. Tentative assignments for bending vibrations are given in Table 2.

For $Cu(py)_2(NO_3)_2$ eight absorption bands from 350 to 80 cm^{-1} are observed which may originate from skeletal vibrations. The two highest and strongest bands at 322 and 282 cm^{-1} show metal-isotope sensitivity by giving shifts of *ca.* 3 cm^{-1} on the ^{63}Cu–^{65}Cu substitution. Since no significant deuteriopyridine shifts are observed for these bands, they can be assigned to the Cu–O stretching modes. Under pressures up to 8 kbar, the 322 cm^{-1} band shows little change while the 282 cm^{-1} band decreases notably in size as the pressure is increased. It has been demonstrated that pressure sensitivity is greater for the symmetric vibration than for the antisymmetric.[13] On the basis of this information, we can assign the 322 cm^{-1} absorption to an

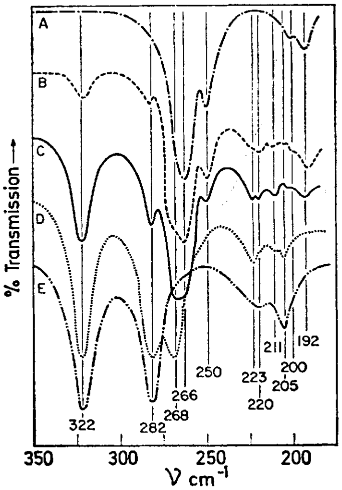

FIGURE 2 Transition of $Cu(py)_4(NO_3)_2$ to $(Cupy)_2(NO_3)_2$ *via* $Cu(py)_3(NO_3)_2$ (350—175 cm^{-1}). A, Freshly prepared $Cu(py)_4(NO_3)_2$ under dry nitrogen; B, $Cu(py)_4(NO_3)_2$ after 4 h *in vacuo*, traces of $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ are apparent; C, $Cu(py)_4(NO_3)_2$ after 24 h *in vacuo* over P_2O_5; substantial conversion to $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ is evident; D, $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ only after 60 h *in vacuo* over P_2O_5, no evidence of the starting material, $Cu(py)_4(NO_3)_2$, is apparent; E, after 6 days *in vacuo* over P_2O_5, total conversion to $Cu(py)_2(NO_3)_2$

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[13] C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, 1967, **6**, 2194.

asymmetric Cu–O stretching whereas the absorption at 282 cm^{-1} probably originates from a symmetric Cu–O stretching vibration. The band at 205 cm^{-1} must be assigned to the Cu–N stretching vibration which exhibits metal-isotope sensitivity and significant deuteriation sensitivity. Although complete assignments are questionable without detailed factor group analysis, some further tentative assignments are suggested in Table 2. Nuttall and Taylor[3] previously assigned the Cu–O stretching bands at 288 and 328 cm^{-1} whereas Rogers and Frank[2] tentatively assigned the Cu–O stretching to the 324 cm^{-1} band and the 281 cm^{-1} band to the Cu–N stretching. Our results agree with Nuttall and Taylor.[3]

TABLE 3

Far-i.r. spectra of $M(py)_3(NO_3)_2$ (where M = Co, Ni, or Zn) from 350 to 75 cm^{-1}

Assignments [a,b]	$Co(py)_3(NO_3)_2$		$Ni(py)_3(NO_3)_2$			$Zn(py)_3(NO_3)_2$
	Co	$\Delta\nu$ [d]	Ni	$\Delta\nu$ [c]	$\Delta\nu$ [d]	Zn
ν_{M-O}	238s	1	294s	4	2	204vs,vb
			246s	3	2	
ν_{M-N}	260sh	?	260sh	?	?	*ca.* 238vb,sh
δ_{NMN}	199w	4	191w	1	10	
	139w	1	101w	0	0	151w
	92m	0				*ca.* 128vw
						ca. 110vw
						86w

[a] vs, Very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; op, out-of-plane; ip, in-plane. [b] ν, stretching vibration; δ, bending vibration. [c] $\Delta\nu = [\nu(Ni) - \nu(^{62}Ni)]$. [d] $\Delta\nu = [\nu(M,py) - (M,py\text{-}d)]$.

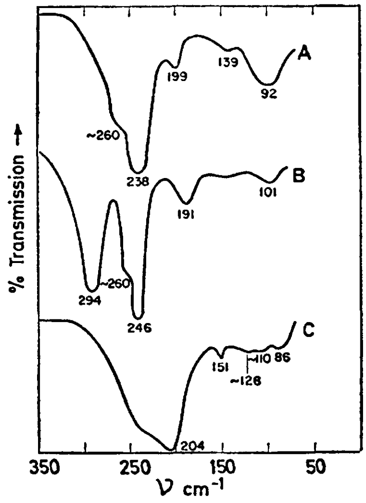

FIGURE 3 I.r. spectra of $M(py)_3(NO_3)_2$ (M = Co, Ni, or Zn) from 350 to 75 cm^{-1}; A, $Co(py)_3(NO_3)_2$; B, $Ni(py)_3(NO_3)_2$; C, $Zn(py)_3(NO_3)_2$

2. $M(py)_3(NO_3)_2$ *Complexes*. The low frequency spectra (375—75 cm^{-1}) for $M(py)_3(NO_3)_2$ (where M = Co, Ni, or Zn) are listed in Table 3 and Figure 3. Deuteriopyridine shifts are included as well as metal-isotopic data for nickel. The cobalt and zinc compounds all give surprisingly simple spectra with rather broad bands. In the case of the zinc compound, although other authors[2,6] report two strong broad bands in the region f 200 and 210 cm^{-1}, we have not been able to resolve these bands using similar instruments. Because of the broadness and marked asymmetry of this band, it is reasonable to conclude as reported by Frank and Rogers[2] and Ouellette and Haendler,[6] that the band is composed of several overlapping vibrations. Ouellette *et al.*[6] have assigned the Zn–O and Zn–N stretching vibrations at 220 cm^{-1} and 204 cm^{-1} respectively; Frank and Rogers[2] at 210 and 200 cm^{-1}.

$Co(py)_3(NO_3)_2$ has five absorption bands from 350 to 75 cm^{-1}. The strongest band at 238 cm^{-1} shifts only by 1 cm^{-1} on substitution of deuteriated pyridine, indicating negligible participation of pyridine in this vibration. This absorption can best be assigned to the Co–O stretching mode, ν(Co–O). The weak band at 199 cm^{-1} gives a large shift of 4 cm^{-1} on deuteriation. Therefore, the 199 cm^{-1} band may be due to either the Co–N stretching or to the N–Co–N bending mode. Unfortunately, the shoulder band at 260 cm^{-1} of $Co(py)_3(NO_3)_2$ overlaps with the strong band at 238 cm^{-1} such that the exact location and subsequent isotropic shift are difficult to determine precisely. It is possible that this shoulder band at *ca.* 260 cm^{-1} is the Co–N stretching vibration in which case the 199 cm^{-1} band would be assigned to the N–Co–N bending mode.

The far-i.r. spectrum of $Ni(py)_3(NO_3)_2$ (350—75 cm^{-1}) is different from the other $M(py)_3(NO_3)_2$ compounds in that it contains two strong bands (294 and 246 cm^{-1}). We assign both of these bands to the Ni–O stretching vibration based on the observation that both of these bands show significant metal-isotope sensitivity (4 and 3 cm^{-1} respectively), but small deuteriopyridine shifts (2 cm^{-1} on $[^2H_5]$pyridine substitution) (Table 3). As in $Co(py)_3(NO_3)_2$, the 260 cm^{-1} shoulder band overlaps with the strong neighbouring band, obscuring its exact position and isotopic sensitivity. Like the cobalt analogue, this band at 260 cm^{-1} may be due to the Co–N stretching. Then the weak band at 191 cm^{-1} which displays metal sensitivity (2 cm^{-1} shift on metal isotope substitution) and very large pyridine sensitivity (10 cm^{-1} shift on deuteriopyridine substitution) can be reasonably assigned to the N–Ni–N bending mode.

Raman Spectra.—Attempts have been made to measure the Raman spectra of all compounds by choosing the exciting line which is not absorbed by the compound. The solid copper compounds showed marked decomposition after short exposures to laser radiation with reduced power (35 mW) even at liquid nitrogen temperatures. Solution laser Raman spectra of $Cu(py)_2(NO_3)_2$ and $Cu(py)_4(NO_3)_2$ were attempted using CH_2Cl_2 and CH_3CN as solvents. Solvent bands from both methylene chloride and acetonitrile in the region 1350—1450 cm^{-1} tend to obscure the position of the highest nitrate stretching frequency. However, for saturated methylene chloride solutions of $Cu(py)_2(NO_3)_2$, the nitrate stretching band appeared as a shoulder on the 1423 cm^{-1} solvent band of methylene chloride. Polarization studies indicated that the 1022 cm^{-1} was strongly polarized, the 1263 cm^{-1} band was depolarized, and the 1470 cm^{-1} was apparently polarized.

The latter band, a shoulder on the 1423 cm^{-1} solvent band which is distinct for perpendicularly polarized light, seems to disappear for parallel polarized light. This sequence of polarization of the highest three nitrate stretching frequencies is consistent with that expected for bidentate bonding of nitrates.[12,14]

$Ni(py)_3(NO_3)_2$ exhibited visible decomposition accompanied by a colour change from light blue to brown. No decomposition was apparent for powdered $Co(py)_3(NO_3)_2$ even after extended exposure to laser radiation. However, no Raman spectrum was detectable. Only crystalline $Zn(py)_3(NO_3)_2$, a colourless compound, gave a good Raman spectrum without decomposition; the Raman nitrate bands occur at 1462m (ν_{NO}), *ca.* 1295w (ν_{asym} NO_2), 1028vs (ν_{sym} NO_2), 729w (δ_{sym} NO_2), and 704w cm^{-1} (δ_{asym} NO_2), in reasonable agreement with the i.r. nitrate absorptions (Table 1). However, the 818 cm^{-1} NO_2 deformation was too weak to be detected in the Raman. The characteristic intensity pattern observed for the first three nitrate fundamentals of $Zn(py)_3(NO_3)_2$ (*i.e.*, m, w, vs) is consistent with that observed for symmetrically bidentate nitrate ligands.[12,15]

Structural Inferences.—1. $Cu(py)_n(NO_3)_2$ *Complexes*. All the vibrational spectral data available for $Cu(py)_4(NO_3)_2$ are consistent with a *trans*-tetragonal structure in which copper is six-co-ordinate with four pyridine ligands in the equatorial plane and two monodentate nitrate groups along the axis perpendicular to the plane. The splitting ($\Delta\nu = \nu_4 - \nu_1$, Table 1) of the symmetric and asymmetric NO_2 stretchings by 102 cm^{-1} is in the range previously noted for monodentate bonding.[7,12,16–19] Similarly the splitting (12 cm^{-1}) of the combination bands in the 1680—1800 cm^{-1} region has been cited as a criterion for monodentate bonding.[16] If a *trans*-configuration having D_{4h} symmetry is assumed, five i.r.-active skeletal vibrations are predicted by group theory in the far-i.r. region. These are $\nu_{CuN}(e_u)$, $\nu_{CuO}(a_{2u})$, $\delta_{NCuN}(e_u)$, and $2\delta_{OCuN}(e_u + a_{2u})$. As would be expected, all observed vibrations show metal-isotope sensitivity, the stretching mode being more sensitive than the bending mode. Furthermore, all except the Cu–O stretching mode are sensitive to pyridine deuteriation with the $\nu_{CuN}(e_u)$ and $\delta_{NCuN}(e_u)$ demonstrating the largest deuteriopyridine shifts.

The spectral results for $Cu(py)_3(NO_3)_2$ and $Cu(py)_2(NO_3)_2$ are indicative of bidentate co-ordination of the nitrate to the copper, since the ($\Delta\nu = \nu_4 - \nu_1$, Table 1) separations are 167 and 192 cm^{-1} respectively. The far-i.r. assignments based on isotopic shifts agree with this. Further, the three nitrate stretching frequencies in the Raman scattering experiment for $Cu(py)_2(NO_3)_2$ showed the polarizability sequence consistent with bidentate bonding. These data are consistent with the *X*-ray structure previously determined for $Cu(py)_2(NO_3)_2$.[5]

Based on the i.r. evidence above, we conclude that the covalent character of the Cu–O band increases as one moves from $Cu(py)_4(NO_3)_2$ to $Cu(py)_3(NO_3)_2$ to $Cu(py)_2(NO_3)_2$. This increase in covalency is indicated by a gradual increase in the $\Delta\nu(NO_2)$ splitting in the sodium chloride region where Δ = 102, 167, and 192 cm^{-1} respectively. Also, a comparable shift to higher energy of the Cu–O stretching frequencies occurs in the far-i.r. where the Cu–O stretching vibration occurs at 266 cm^{-1} for $Cu(py)_4(NO_3)_2$, at 268 cm^{-1} for $Cu(py)_3(NO_3)_2$, and at an average value of *ca.* 300 cm^{-1} for $Cu(py)_2(NO_3)_2$. This is accompanied by a change in the nitrate co-ordination from monodentate to bidentate to bridging-bidentate. It is interesting to note a concomitant decrease in the vibrational energy of the copper–pyridine bonds, with absorptions at 250, 223, and 205 cm^{-1} respectively, as the covalency of the nitrate increases in the co-ordination sphere. This can be explained by assuming that as the covalency of the copper–nitrate bond increases, greater electron density is accepted from oxygen in preference to the pyridine nitrogen donor such that the metal–oxygen bond strength increases and the metal–nitrogen bond strength decreases in the above series. It is possible that the frequency found for the Cu–O stretching modes in $Cu(py)_4(NO_3)_2$ are a reflection of Jahn–Teller effects occurring in the molecule.

2. $M(py)_3(NO_3)_2$ *Complexes*. The mid-i.r. region suggests that $M(py)_3(NO_3)_2$ (M = Co, Ni, or Zn) contains bidentate nitrate ligands and co-ordinated pyridine ligands. *X*-Ray powder patterns suggest that $Cu(py)_3(NO_3)_2$, $Co(py)_3(NO_3)_2$, and $Zn(py)_3(NO_3)_2$ are isomorphous. The crystal structure of the zinc compound has been determined previously;[20] it exists in monomeric units where three pyridine and two non-symmetric bidentate nitrates are arranged around the metal such that steric interactions are minimized.

The *X*-ray powder pattern of $Ni(py)_3(NO_3)_2$ indicates that it does not have the same structure as the other $M(py)_3(NO_3)_2$ compounds. Previous studies[8] suggest the presence of both monodentate and bidentate nitrate. Although mid-i.r. bands suggest the presence of strong bidentate bonding, bands consistent with monodentate bonding have not been observed. A complete *X*-ray analysis of this compound would be very useful.

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