Coordination Chemistry Reviews, 104 (1990) 251–295
Elsevier Science Publishers B.V., Amsterdam

METAL COMPLEXES OF PYRIDINE: INFRARED AND RAMAN SPECTRA WITH PARTICULAR REFERENCE TO ISOTOPIC LABELLING STUDIES

DAVID A. THORNTON

Department of Chemistry, University of Cape Town, Rondebosch 7700 (Republic of South Africa)

(Received 6 September 1989)

CONTENTS

A. INTRODUCTION

The development of our knowledge concerning the vibrational spectra of metal complexes of pyridine has lagged behind that of other amines such as ammonia and aniline in view of the occurrence of metal–pyridine stretching frequencies below 275 cm^{-1} (usually below 250 cm^{-1}) and by the available instrumentation. The advent of commercial Fourier transform interfero-

0010-8545/90/$15.75

meters led to a dramatic expansion of the literature on the IR spectra of complexes of pyridine and other heterocyclic nitrogenous bases. All the available assignment techniques have been applied to the spectra of these complexes, including empirical methods, normal coordinate analysis, isotopic labelling of both the ligand and the metal ion and the metal ion substitution technique related to crystal field theory.

It is no longer a practicable venture to attempt a review of every publication on the vibrational spectra of complexes of pyridine and substituted pyridines. It is envisaged that the majority of chemists who refer to this review will be seeking realistic assignments or structural or bonding information on pyridine complexes which may have been elicited from their vibrational spectra. Since the most reliable and useful information has undoubtedly been derived from isotopic labelling studies assisted by the effects of substitution of the metal ion, the scope of this review has been confined to those papers in which these aspects assume significance. Hence, although purely empirical studies will not be reviewed per se, the results from such studies will be compared, where possible, with those derived from the application of more sophisticated techniques. Finally, it may be mentioned that complexes of bicyclic and polycyclic heterocyclic bases such as quinoline, substituted quinolines, 2,2′-bipyridine and 1,10-phenanthroline, have been excluded from this review.

B. SPECTRA OF PYRIDINE AND PYRIDINE-d_5

Extensive use of pyridine deuteration has been made for the purpose of assigning internal ligand modes and metal–ligand bands in vibrational studies of metal pyridine complexes. For this reason, some preliminary discussion of the spectra of pyridine and pyridine-d_5 is necessary.

Assignment of the internal ligand modes of pyridine is well established [1–5]. The frequencies for liquid pyridine and pyridine-d_5 are reported in Table 1 where they are compared with the spectra of some pyridine complexes. It has long been recognized that the majority of IR bands which originate in the internal vibrations of pyridine recur on an approximately band-for-band basis in the spectra of pyridine complexes. Hence, so far as the mid-IR region is concerned, once the internal ligand modes of pyridine have been assigned, these assignments may be extended to the complexes, although cross-overs do occasionally occur.

In 1979, Thornton and coworkers [6] examined the ratio (ν^D/ν^H) between the frequencies of corresponding bands in the spectra of normal and deuterated molecules of numerous heterocyclic nitrogenous ligands and their complexes. It was established that, practically without exception, ν^D/ν^H falls within the ranges 0.68–0.85 for C–H vibrations and 0.85–1.00 for ring

TABLE 1

Frequencies of pyridine vibrations, ν^D/ν^H ratios and assignments for pyridine (py) and the complexes $[Zn(py)_2Cl_2]$, $[Co(DH)_2(py)X]$ (DH = dimethylglyoximate anion; X = Cl, Br, I, NCS) and $[Ni(gly)_2(py)_2]$. Frequencies in parentheses are those for the deuterated species

Pyridine frequencies (cm^{-1})	ν^D/ν^H	$[Zn(py)_2Cl_2]$ frequencies (cm^{-1})	ν^D/ν^H	$[Co(DH)_2(py)X]$ mean frequencies (cm^{-1})^{a,b}	ν^D/ν^H	$[Ni(gly)_2(py)_2]$ frequencies (cm^{-1})^b	ν^D/ν^H	Assignments [1–5]	Band number
3083 (2293)	0.74	3109 (2293)	0.74						20b
	0.75	3066 (2273)	0.74			3071 (2294)	0.75		2
3054 (2293)	0.75	3044 (—)				3048 (2274)	0.75	ν(C–H)	13
3036 (2254)	0.74	2925 (—)				2998 (2258)	0.75		20a, 7b
1633 (1585)	0.97	1661 (1653)	0.99						1 + 6b
1599 (1550)	0.97	1656 (1598)	0.96						1 + 6a
1580 (1530)	0.97	1607 (1566)	0.97	1606 ± 6 (1564 ± 3)	0.97	1610 (1557)	0.97		8a
1572 (1542)	0.98	1573 (1539)	0.98			1570 (1536)	0.98		8b
1482 (1340)	0.90	1486 (1320)	0.89	1495 ± 5 (1322 ± 4)	0.88	1481 (1313)	0.89	19a	
1439 (1301)	0.90	1449 (1311)	0.90	1451 ± 4^c (1322 ± 4)	0.91	1447 (1237)	0.85	ν(ring)	19b
		1399 (1374)	0.98						
1375 (1322)	0.96	1379 (1337)	0.97	1370 ± 2^d (1326 ± 5)	0.97				14
1218 (908)	0.74	1245 (992)	0.79	1233 ± 7^e (979 ± 6)	0.79	1238 (886)	0.72		3
(887)	0.73	1216 (890)	0.73	(906 ± 6)	0.73	1213 (852)	0.70		9a
1148 (887)	0.77	1158^g (843)^g	0.73	1164 ± 15 (856 ± 8)	0.76	1158 (844)	0.73	δ(C–H)	15
1068 (833)	0.78	1069 (832)	0.78	1070 ± 4 (837 ± 9)	0.78	1065 (726)	0.68		18b
1029 (1006)	0.98	1045 (1025)	0.98	1040 ± 2 (1013 ± 2)	0.97	1035 (1009)	0.97	ν(ring)	12
992 (962)	0.97	1015 (1013)	0.99	1006 ± 6 (1005 ± 1)	1.00	1009 (975)	0.97		1
886 (690)	0.78	888 (694)	0.78	881 ± 9 (783 ± 6)	0.90^{gh}				10b
749 (567)	0.76	756^g (561)^g	0.74	765 ± 2 (574 ± 4)	0.75	758 (731)	0.96^h	γ(C–H)	11
703 (530)	0.75	696^g (533)^g	0.76	696 ± 6 (536 ± 6)	0.77	705 (600)	0.85		4
605 (582)	0.96	641 (615)	0.96	648 ± 1 (630 ± 4^g)	0.97	625 (542)	0.87	δ(ring)	6a
405 (371)	0.92	423 (384)	0.91	422 ± 2^f (401 ± 5)	0.95	435^{gi} (398)	0.91	γ(ring)	16b

[a] Spectra not determined in 3000–3100 cm^{-1} region. [b] Bands not observed are masked by bands from other coordinated ligands. [c] Coupled with ν(C=N). [d] Coupled with δ(CH_3). [e] Coupled with ν(N–O). [f] Coupled with ν(Co–N). [g] Mean of doublet. [h] Anomalously high value for assignment cited. [i] Coupled with ν($Ni–NH_2$).

modes. The obvious application of this finding is that it enabled distinction to be made between C–H and ring modes in general, thereby assisting in correcting some anomalous assignments which have been proposed on the basis of other techniques. Although the ranges of ν^D/ν^H given above hold for all the ligands and their complexes which were studied, much narrower ranges with improved diagnostic capabilities exist for a specific amine. Thus, based on the assignments of Kline and Turkevich [1], the ranges of ν^D/ν^H for pyridine itself are 0.73–0.78 for C–H modes and 0.90–0.98 for ring modes.

The extent to which the ν^D/ν^H ratio may be used for assisting in the assignment of the internal ligand modes of pyridine complexes is illustrated by the data in Table 1 which includes pyridine complexes of widely differing type exemplified by $[Zn(py)_2Cl_2]$, $[Co(DH)_2(py)X]$ (DH = dimethylglyoximate anion; X = Cl, Br, I, CH_3) and *trans*-$[Ni(gly)_2(py)_2]$ (gly = glycinate anion) [6].

Studies of the IR spectra of pyridine complexes are facilitated by a major simplifying feature, namely, the complete absence of ligand bands with frequencies below 400 cm^{-1}. Thus, the region in which the metal–pyridine modes are observed is free from ligand absorptions, the occurrence of which complicates the assignment problem in the spectra of complexes of many other nitrogenous bases.

C. TETRAHEDRAL COMPLEXES $[Zn(py)_2X_2]$ (X = Cl, Br, I)

These compounds are chosen for initial discussion because they represent the most exhaustively studied complexes of pyridine (especially the chloride). Both IR and Raman spectra have been reported and the techniques of pyridine deuteration, $^{64,68}Zn$ labelling and halide substitution have been applied to the assignment problem [7–11]. The application of metal ion substitution will be discussed in Section D, while the mid-IR region has been discussed in Section B.

The vibrations of lowest frequency in the spectrum of pyridine occur at 605 cm^{-1} (in-plane ring bend, ip δ-ring) and 405 cm^{-1} (out-of-plane ring bend, oop γ-ring). Complexation with zinc chloride shifts these bands to 641 cm^{-1} and 423 cm^{-1} respectively, while deuteration of the complex causes them to move by 26 cm^{-1} and 39 cm^{-1} respectively to lower frequency. Hence, below 400 cm^{-1}, we expect to observe the eight IR-active metal–ligand modes anticipated on the basis of the C_{2v} point-group symmetry of the molecule.

Table 2 summarizes the partial results of the deuteration and metal isotope labelling studies applied to the far-IR and Raman spectra of $[Zn(py)_2Cl_2]$. The bands at 327 and 295 cm^{-1} shift on $^{64,68}Zn$ labelling but not on pyridine deuteration. Substitution of chloride by bromide and iodide

TABLE 2

Comparison of pyridine-d_5 labelling, ^{64,68}Zn labelling and halide substitution on the far-IR and Raman spectra of [Zn(py)$_2$X$_2$] (cm^{-1}) [7,10,11]

IR band frequency (d_5 shift)			X=Cl			Assignment
X=Cl [7,10]	X=Br [11]	X=I [11]	Ir ^{64,68}Zn shift [10]	Raman d_5 shift [10]	Raman ^{64,68}Zn shift [10]	
641 (26,—)	641 (—)	640 (—)	n.r.[a]	n.r.[a]	n.r.[a]	py ip δ-ring
423 (39,—)	424 (40)	425 (39)	n.r.[a]	n.r.[a]	n.r.[a]	py oop γ-ring
327 (0,0.8)	260 (0)	221 (1.5)	4.8	1.0	3.9	ν(Zn–X) B_2
295 (0,0.2)	213 (0)	147 (—)[b]	2.4	0.4	1.3	ν(Zn–X) A_1
219 (4,3.8)	218 (2)	213 (4)	3.6	5.0	4.4	ν(Zn–N) B_1
201 (3,4.1)	182 (3.5)	165 (9)	2.4	4.2	3.2	ν(Zn–N) A_1
200 (—,—)	—	—	—	10	0	δ(X–Zn–N) A_2
154 (—,7)	151 (>4)[b]	154 (>4)[b]	—[c]	6.6	0	δ(N–Zn–N) A_1
140 (5,4.7)	—[b]	—[b]	0.3	—[b]	—[b]	δ(X–Zn–N) B_1, B_2
102 (0,0.7)	—[b]	—[b]	0	—[b]	—[b]	δ(X–Zn–X) A_1

[a] n.r., not reported. [b] Beyond range of measurement. [c] Not determined due to poor band shape.

shifts them progressively towards lower frequency (Fig. 1, Table 3). These bands are clearly the two ν(Zn–Cl) bands expected for C_{2v} symmetry. The bands at 219 and 201 cm^{-1} are shifted by ^{64,68}Zn labelling and by pyridine deuteration but are not significantly affected by halide substitution. These are clearly the two ν(Zn–N) bands expected for C_{2v} symmetry. The bands at

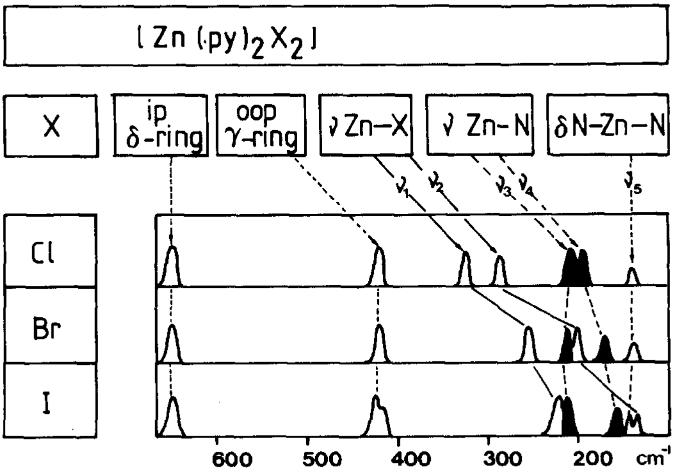


Fig. 1. IR spectra of the complexes [Zn(py)$_2$X$_2$]: solid bands, ν(Zn–N).

TABLE 3

IR frequencies and d-sensitivities (in parentheses) (cm^{-1})[a] for the complexes $[Zn(py)_2X_2]$ (X = Cl, Br, I) [11]

Band	X			Assignment
	Cl	Br	I	
	432 (39)	424 (40)	425 (39)	oop γ-ring
ν_1	331 (0)	260 (0)	222 (1.5)	ν(Zn–X)
ν_2	296 (0)	213 (0)	147 (?)[b]	ν(Zn–X)
ν_3	217 (4)	218 (2)	213 (4)	ν(Zn–N)
ν_4	200 (4)	182 (3.5)	165 (9)	ν(Zn–N)
ν_5	154 (>4)[c]	151 (>4)[c]	154 (>7)[c]	δ(N–Zn–N)

[a] All shifts to lower wavenumber. [b] At limit of measurement. [c] Shifts beyond range of measurement in spectrum of deuterated complex.

200 cm^{-1} (Raman only), 150, 140 and 102 cm^{-1} remain for assignment to the four possible δ(L–M–L) bending modes. These may be distinguished with reasonable certainty as indicated in Table 2 on the basis of their activities and the magnitude of the observed shifts.

D. COMPLEXES $[M(py)_2Cl_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn)

Of these compounds, the spectrum of the tetrahedral zinc(II) complex has been discussed in Section C. Here its spectrum will be mentioned only in relation to the effects of metal ion substitution.

The earliest comprehensive studies of the far-IR spectra of these complexes were those of Clark and Williams [12,13] in 1965 (to 200 cm^{-1}) and Frank and Rogers [14] in 1966 (to 150 cm^{-1}). In neither of these reports were bands below 210 cm^{-1} assigned, nor were any labelling studies carried out. Nevertheless, these classical studies have acquired stature and they are frequently quoted in the literature and in the standard texts on the IR spectra of coordination compounds [15–17].

Three structural species are represented by the range of complexes under discussion. The manganese(II), iron(II), nickel(II) and lilac cobalt(II) compounds have polymeric octahedral coordination with bridging chloride ions. The copper(II) complex is a tetragonal polymer and the zinc(II) and blue cobalt(II) compounds are tetrahedral monomers [18–23]. The spectral band patterns below 400 cm^{-1} are distinctive of the structures. The polymeric complexes of C_i symmetry have all their metal–ligand bands below 295 cm^{-1} (with an extra band for the distorted copper(II) compound) while the tetrahedral compounds exhibit two bands above 295 cm^{-1} and three bands below this frequency.

Five studies have referred to the effects of deuteration of the pyridine ring on the far-IR bands of the complexes [7,11,18,24]. The assignments resulting from this work and from earlier studies are given in Table 4. The ensuing discussion is based on the work of Rüede and Thornton [18]. The spectra over the range 650–150 cm^{-1} are depicted in Fig. 2. The two bands near 640 and 440 cm^{-1} are the ip δ-ring and oop γ-ring bands of the pyridine ring. These were found to shift approximately 40 cm^{-1} towards lower frequency on deuteration of the complex. The following bands are numbered ν_1, ν_2, ν_3, ν_4 and ν_5 in order of decreasing frequency. The data in Table 4 indicate that, in general, ν_1 and ν_2 are little affected by deuteration whereas ν_3 (where present) and ν_4 are substantially shifted. An exception is the zero shift observed for ν_4 in $[\mathrm{Mn(py)_2Cl_2}]$ [19]. The shift of ν_5 is variable. On this basis, ν_1 and ν_2 were assigned to ν(M–Cl) and ν_3 and ν_4 to ν(M–N).

Symmetry considerations require one ν(M–L) and two ν(M–X) IR-active

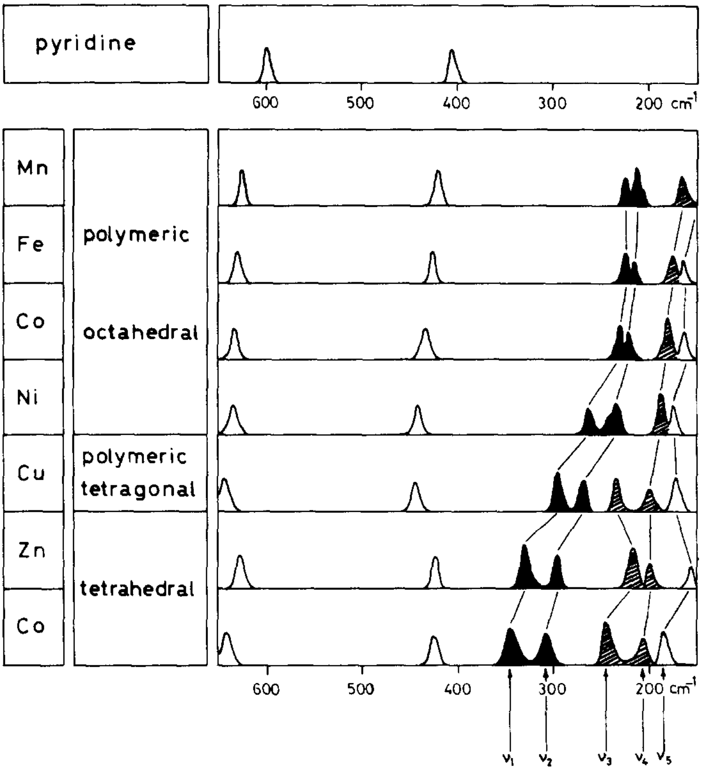


Fig. 2. IR spectra of the complexes $[\mathrm{M(py)_2Cl_2}]$ (650–150 cm^{-1}): shaded bands, ν(M–N); solid bands, ν(M–Cl).

TABLE 4

Frequencies (cm^{-1}) and assignments of IR bands for complexes $[M(py)_2Cl_2]$[a]

Band	Ref.	Mn pol. oct.		Fe pol. oct		Co pol. oct	
ν_1	18	226 (1)	ν(M–Cl)	226	ν(M–Cl)	230 (0)	ν(M–Cl)
	13	233	ν(M–Cl)	227	n.a.	233	n.a.
	14	231	ν(M–Cl)		n.s.	234	ν(M–Cl)
	19, 24	230 (−1)	ν(M–N)	227	ν(M–N)	235	ν(M–N)
	20		n.s.		n.s.		n.s.
	11		n.s.		n.s.		n.s.
	21	222	ν(M–N)	222	ν(M–N)	235	ν(M–N)
	22		n.s.		n.s.		n.s.
	23		n.s.		n.s.		n.s.
ν_2	18	212 (1)^c	ν(M–Cl)	217	ν(M–Cl)	222 (2)	ν(M–Cl)
	13	212	ν(M–N)	219	n.a.	224	n.a.
	14	213	ν(M–N)		n.s.	227	ν(M–N)
	19, 24	214 (3)^f	ν(M–N)	220	ν(M–N)	227	ν(M–N)
	20		n.s.		n.s.		n.s.
	11		n.s.		n.s.		n.s.
	21		n.r.		n.r.		n.r.
	22		n.s.		n.s.		n.s.
	23		n.s.		n.s.		n.s.
ν_3	18						
	13						
	14						
	19, 24						
	20						
	11						
	21						
	22						
	23						
ν_4	18	167 (4)	ν(M–N)	176	ν(M–N)	182 (5)	ν(M–N)
	13		b.r.		b.r.		b.r.
	14	174	n.a.		n.s.	176	n.a.
	19, 24	175 (0)	ν(M–Cl)	182	ν(M–Cl)	188	ν(M–Cl)
	20		n.s.		n.s.		n.s.
	11		n.s.		n.s.		n.s.
	21		b.r.		b.r.		b.r.
	22		n.s.		n.s.		n.s.
	23		n.s.		n.s.		n.s.
ν_5	18		b.r.	165	δ(L–M–L)	163 (0)	δ(L–M–L)
	13		b.r.		b.r.		b.r.
	14		b.r.		b.r.		b.r.
	19, 24		b.r.		n.s.		n.r.
	20	160 (1)	ν(M–Cl)	162	ν(M–Cl)	167	ν(M–Cl)
	11		n.s.		n.s.		n.s.
	21		n.s.		n.s.		n.s.
	22		b.r.		b.r.		b.r.
	23		n.s.		n.s.		n.s.
			n.s.		n.s.		n.s.

[a] Figures in parentheses following the frequencies are the shifts (nearest integral value in cm^{-1}) studied; n.a., band not assigned; n.r., frequency not reported; b.r., beyond range of measurement; (coupled with ν(M–N)?). [c] Shoulder at 205 (0) cm^{-1}. [d] Shoulder at 241 (1) cm^{-1}. [e] Doublet. [f] Raman

Ni pol. oct.		Cu pol. tetrag.		Zn tetrahedral		Co tetrahedral	
264 (3)^b	ν(M–Cl)	294 (1)	ν(M–Cl)	331 (0)	ν(M–Cl)	346 (0)	ν(M–Cl)
263	n.a.	294	ν(M–Cl)	329	ν(M–Cl)	344	ν(M–Cl)
264	ν(M–Cl)	294	ν(M–Cl)	331	ν(M–Cl)		n.s.
262	ν(M–N)	287	ν(M–Cl)		n.s.		n.s.
	n.s.	293	ν(M–Cl)		n.s.		n.s.
	n.s.		n.s.	329 (1)	ν(M–Cl)		n.s.
258	ν(M–N)	287	ν(M–Cl)	329	ν(M–Cl)	339	ν(M–Cl)
	n.s.		n.s.	326	ν(M–Cl)		n.s.
	n.s.		n.s.	330	ν(M–Cl)		n.s.
236 (2)^d	ν(M–Cl)	269 (2)	ν(M–Cl)	296 (0)	ν(M–Cl)	307 (0)	ν(M–Cl)
239	n.a.	268	ν(M–N)	296	ν(M–Cl)	304	ν(M–Cl)
244^e	ν(M–N)	269	ν(M–N)	298	ν(M–Cl)		n.s.
237	ν(M–N)	266	ν(M–N)		n.s.		n.s.
	n.s.	268	ν(M–N)		n.s.		n.s.
	n.s.		n.s.	296 (0)	ν(M–Cl)		n.s.
235	n.a.		n.s.	291	ν(M–Cl)	299	ν(M–Cl)
	n.s.		n.s.	293	ν(M–Cl)		n.s.
	n.s.		n.s.	297	ν(M–Cl)		n.s.
		232 (10)	ν(M–N)	217 (4)	ν(M–N)	248 (2)	ν(M–N)
		235	ν(M–Cl)	220	ν(M–N)	252	ν(M–N)
		237	ν(M–Cl)	222	ν(M–N)		n.s.
		228	ν(M–Cl)		n.s.		n.s.
		235	ν(M–Cl)		n.s.		n.s.
			n.s.	222 (4)	ν(M–N)		n.s.
			n.r.		n.r.	243	ν(M–N)
			n.s.	218	ν(M–N)		n.s.
			n.s.		n.r.		n.s.
190 (7)	ν(M–N)	201 (10)	ν(M–N)	200 (4)	ν(M–N)	208 (4)	ν(M–N)
	b.r.		n.r.		n.r.		n.r.
194	n.a.	204	n.a.	205	n.a.		n.s.
193	n.s.	200	δ(N–M–L)		n.s.		n.s.
	n.s.	203	n.a.		n.s.		n.s.
	n.s.		n.s.	204 (4)	ν(M–N)		n.s.
	b.r.		n.r.		n.r.		n.r.
	n.s.		n.s.	200	δ(Cl–M–L)		n.s.
	n.s.		n.s.		n.r.		n.s.
178 (4)	δ(L–M–L)	176 (1)	δ(L–M–L)^g	154 (>4)	δ(L–M–L)	188 (4)	δ(L–M–L)
	b.r.		b.r.		b.r.		b.r.
	b.r.		b.r.		b.r.		b.r.
181	n.a.	178	n.a.		n.r.		n.r.
182	ν(M–Cl)	177	δ(Cl–M–Cl)		n.s.		n.s.
	n.s.	178	n.a.		n.s.		n.s.
	n.s.		n.s.	154 (7)	δ(N–M–N)		n.s.
	b.r.		b.r.		b.r.		b.r.
	n.s.		n.s.	154	δ(N–M–L)		n.s.
	n.s.		n.s.		b.r.		n.s.

towards lower frequency induced by deuteration of the pyridine ring: n.s., complex not
pol. oct., polymeric octahedral; pol. tetrag., polymeric tetragonal. [b] Anomalously large shift
band at 207 (1) cm^{-1} [24]. [g] Alternative assignment: ν(Cu–Cl) (see text).

modes for polymeric octahedral complexes $[ML_2X_2]_n$ of C_i symmetry. If ν_5 is assigned to a bending mode (as had been previously suggested [25,26] for the copper and zinc complexes) the deuteration study revealed the required number of each vibration, i.e. ν_1 and ν_2 are ν(M–Cl) and ν_4 is ν(M–N). In these complexes, ν_3 is absent. Similarly, for tetrahedral complexes $[ML_2X_2]$, C_{2v} symmetry requires two IR-active ν(M–X) and two IR-active ν(M–N) modes and the deuteration study revealed two of each. In the tetragonal copper(II) complex, the existence [21] of two Cu–Cl bonds with different bond lengths (2.28 and 3.05Å) should cause splitting of ν(Cu–Cl). It is possible that the lower frequency component lay beyond the range of measurement or that the band at 176 cm^{-1}, which is very little affected by deuteration, may alternatively be assigned to ν(Cu–Cl) rather than to δ(L–Cu–L).

The manner in which the metal–ligand stretching frequencies shift on varying the coordinated metal ion assists in verifying the assignments proposed on the basis of the deuteration method. It is now well established [27] that the ν(M–L) values for a series of octahedral complexes containing successive metal(II) ions of the first transition period follow the Irving–Williams [28] stability sequence (assuming the copper complex to be tetragonally distorted). In the series of pyridine complexes under discussion, the zinc(II) compound is tetrahedral so that the bonding capacity of the metal ion is distributed over four bonds rather than six, and the ν(Zn–L) values will be higher than would be the case for octahedral zinc(II). The fact that $\nu(\text{Zn–N}) \approx \nu(\text{Cu–N})$ and $\nu(\text{Zn–Cl}) > \nu(\text{Cu–Cl})$ in the pyridine complex is therefore understandable in view of the lower coordination number of zinc(II). In all other respects, the Irving–Williams sequence was observed for both the ν(M–N) and ν(M–Cl) bands, providing support for the proposed assignments.

A comparison of the frequencies of the zinc(II) complex and blue cobalt(II) complexes is of interest. Both complexes are tetrahedral, but whereas the cobalt(II) complex is strongly stabilized by the crystal field, the zinc(II) complex is not. In this event, it is expected that $\nu(\text{Co–L}) \gg \nu(\text{Zn–L})$. The data in Table 4 show that both the ν(M–N) and ν(M–Cl) values are much greater for the cobalt(II) than for the zinc(II) complex.

There is some measure of disagreement between the earlier assignments and those proposed by Rüede and Thornton [18] on the basis of isotopic labelling. Principally, the labelling study resulted in a band between 167 and 208 cm^{-1} (ν_4) being assigned to ν(M–N). This band was either not observed or not assigned in most earlier studies. For this reason, earlier reports failed to yield the number of ν(M–N) and ν(M–Cl) bands expected from symmetry requirements based on the known structures of the complexes. Of those bands which had previously been assigned, the principal amendment proposed on the basis of deuteration concerns ν_2. Formerly assigned to ν(M–N), this band was found to exhibit very little shift on deuteration of the pyridine ring. In the copper(II) complex, the earlier assignment of ν_3 to ν(M–Cl) is clearly in error as it is strongly shifted by deuteration of the pyridine ring ($\Delta\nu = 10$ cm^{-1}).

The assignments in respect of the zinc(II) complex exhibit the greatest measure of agreement. This spectrum is also the most widely studied and is the only one subjected to a labelling study [10] in which isotopic labelling of both the zinc(II) ion and deuteration of the pyridine ring enabled the ν(Zn–N) and ν(Zn–Cl) bands to be distinguished. The results of the two studies are in perfect agreement.

E. COMPLEXES [M(py)$_2$(NCS)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn) AND [M(py)$_4$(NCS)$_2$] (M = Mn, Fe, Co, Ni)

Prior to 1977, no isotopic labelling studies of pyridine complexes of transition metal isothiocyanates had been made although spectra–structure correlations had been employed to assign ν(M–NCS) and, in a few cases, ν(M–py) [14,19]. In 1977, Engelter and Thornton [26] reported a systematic labelling study of all the preparatively accessible complexes [ML_2X_2] and [ML_4X_2] (L = py; X = NCS) of first transition series metal(II) ions. Both ^{15}NCS labelling and pyridine deuteration were employed over the range 500–140 cm^{-1}. The complexes of type [ML_2X_2] have the same structures as the corresponding halides, i.e. polymeric octahedral for M = Mn, Co and Ni, polymeric tetragonal for M = Cu and tetrahedral for M = Zn [26,30,31]. The [ML_4X_2] complexes are all trans octahedral monomers [26,32]. Figure 3 depicts the spectra, with [Mn(py)$_2$Cl$_2$] included for comparison. The isothiocyanate spectra are, of course, more complex than those of the halides because of the occurrence of δ(NCS) modes. Table 5 records the data from all three IR studies.

The principal problem with interpreting the IR spectra of these complexes is the proximity of the ν(M–NCS) and ν(M–py) bands which enhances the prospects for vibrational coupling between these modes. Thus ν_4 was in general found to be sensitive to both ^{15}NCS labelling and pyridine deuteration and was therefore assigned to a coupled vibration, ν(M–NCS) + ν(M–py). However, vibrationally pure ν(M–NCS) bands were observed within the range 330–250 cm^{-1} and pure ν(M–py) bands were found between 230 and 160 cm^{-1}. The measure of agreement between the three studies is very good. If one considers ν_4 to be principally ν(M–NCS) rather than ν(M–py), the C_i symmetry requirements for the polymeric octahedral complexes (one ν(M–py) and two ν(M–NCS) bands) are satisfied. In the spectrum of the tetrahedral zinc complex, an additional ν(M–py) band was

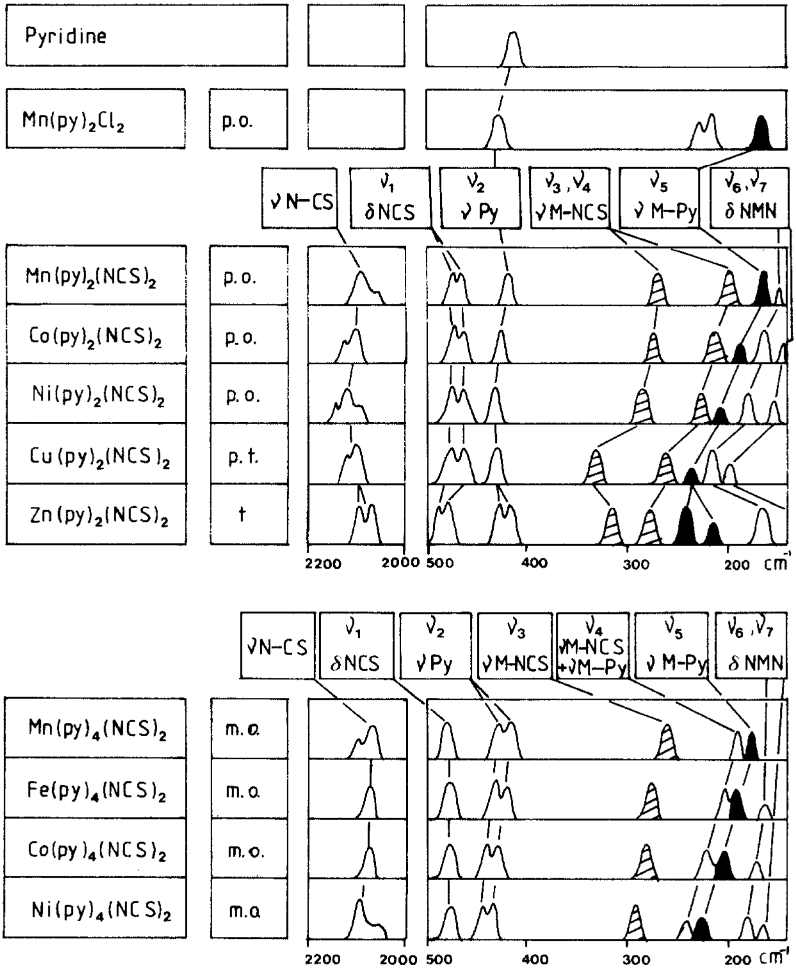


Fig. 3. IR spectra of the complexes $[M(py)_n(NCS)_2]$ ($n = 2$ or 4). Spectra of pyridine and $[Mn(py)_2Cl_2]$ are included for comparison. Abbreviations: m.o., monomeric octahedral; p.o., polymeric octahedral; p.t., polymeric tetragonal; t., tetrahedral.

observed, as predicted for C_{2v} symmetry. In the octahedral monomers of formula *trans*-$[ML_4X_2]$, one ν(M–py) and one ν(M–NCS) band is expected for their D_{4h} symmetry and one of each was observed, but there is an additional coupled band near 300 cm^{-1} (ν_4). Two of the four bending modes were observed within the range studied.

Throughout all the complexes recorded in Table 5, the δ(NCS) bands were readily identified (ν_1). With the single exception of $[Ni(py)_2(NCS)_2]$, these bands were found to be significantly sensitive towards ^{15}NCS labelling only. Conversely, the vibrationally pure ν(M–py) bands (ν_5) were found to

TABLE 5

Frequencies, isotopic shifts (cm^{-1}) and band assignments for complexes $[\mathrm{M(py)}_n\mathrm{(NCS)_2}]^{a}$ ($n=2$ or 4)

Band	Ref.	$[\mathrm{Mn(py)_2(NCS)_2}]$		$[\mathrm{Co(py)_2(NCS)_2}]$		$[\mathrm{Ni(py)_2(NCS)_2}]$		$[\mathrm{Cu(py)_2(NCS)_2}]$		$[\mathrm{Zn(py)_2(NCS)_2}]$	
	26	2094^{b} (28, 1)	ν(N–CS)	2102^{b} (27, 0)	ν(N–CS)	2114^{b} (29, 0)	ν(N–CS)	2098^{b} (30, 1)	ν(N–CS)	2109 (29, 0)	ν(N–CS)
										2081 (29, 0)	ν(N–CS)
	29	2095	ν(N–CS)	2099	ν(N–CS)	2100	ν(N–CS)	2085	ν(N–CS)	2100	ν(N–CS)
										2075	ν(N–CS)
ν_1	26	476 (3, 1)	δ(NCS)	475 (3, 0)	δ(NCS)	477 (0.1)	δ(NCS)	478 (4, 0)	δ(NCS)	486 (3, 0)	δ(NCS)
		470 (4, 0)	δ(NCS)	470 (t.b.)	δ(NCS)	469 (4, 0)	δ(NCS)	469 (3, 0)	δ(NCS)	481 (3, 0)	δ(NCS)
	29	475	δ(NCS)	472	δ(NCS)	474	δ(NCS)	477	δ(NCS)	484	δ(NCS)
		468	δ(NCS)	468	δ(NCS)	466	δ(NCS)	468	δ(NCS)	478	δ(NCS)
	14	475	δ(NCS)	473	δ(NCS)	477	δ(NCS)	478	δ(NCS)	486	δ(NCS)
		468	δ(NCS)			469	δ(NCS)	468	δ(NCS)		
ν_2	26	418 (0, 40)	ν(py)	426 (0, 40)	ν(py)	433 (0, 40)	ν(py)	434 (0, 40)	ν(py)	426 (0, 39)	ν(py)
										414 (0, 39)	ν(py)
	29	417	ν(py)	422	ν(py)	429	ν(py)	431	ν(py)	n.r.	
	14	417	ν(py)	425	ν(py)	432	ν(py)	435	ν(py)	427	ν(py)
										414	ν(py)
ν_3	26	258 (1, 0)	ν(M–NCS)	270 (0, 0)	ν(M–NCS)	285 (2, 0)	ν(M–NCS)	324 (1, 3)	ν(M–NCS)	315 (1, 1)	ν(M–NCS)
	29	254	ν(M–NCS)	268	ν(M–NCS)	280	ν(M–NCS)	319	ν(M–NCS)	312	ν(M–NCS)
	14	256	ν(M–NCS)	270	ν(M–NCS)	283	ν(M–NCS)	324	ν(M–NCS)	313	ν(M–NCS)
ν_4	26	196 (0, 2)	ν(M–NCS)^{c}	208 (2, 2)	ν(M–NCS)^{c}	226 (2, 4)	ν(M–NCS)^{c}	257 (1, 0)	ν(M–NCS)	270 (0, 2)	ν(M–NCS)
	29	b.r.		213	ν(M–py)	229	ν(M–py)	256	ν(M–py)	268	ν(M–py)
	14	201	ν(M–py)	211	ν(M–py)	230	ν(M–py)	256	ν(M–py)	268	ν(M–py)
ν_5	26	164 (1, 4)	ν(M–py)	185 (1, 3)	ν(M–py)	206 (1, 9)	ν(M–py)	225 (0, 5)	ν(M–py)	232 (0, 4)	ν(M–py)
										207 (0, 5)	ν(M–py)
	29	b.r.		b.r.		b.r.		n.r.		215	ν(M–py)
	14	168	n.a.	n.r.		n.r.		218	n.a.	231	n.a.

TABLE 5 (continued)

Band	Ref.	[Mn(py)$_2$(NCS)$_2$]		[Co(py)$_2$(NCS)$_2$]		[Ni(py)$_2$(NCS)$_2$]		[Cu(py)$_2$(NCS)$_2$]		[Zn(py)$_2$(NCS)$_2$]	
ν_6	26	153 (t.b.)	δ(NMN)	162 (1, 3)	δ(NMN)	179 (0, 3)	δ(NMN)	212 (1, 5)	δ(MNM)	162 (4, 5)	δ(MNM)
	29	b.r.		b.r.		b.r.		214	ν(M–py)	b.r.	
	14	155	n.a.	165	n.a.	n.r.		218	n.a.	166	n.a.
ν_7	26	b.r.		145 (0, 3)	δ(MNM)	155 (1, 4)	δ(MNM)	193 (0, 8)	δ(MNM)	b.r.	
	29	b.r.		b.r.		b.r.		b.r.		b.r.	
	14	b.r.		b.r.		158	n.a.	197	n.a.	b.r.	
Band	**Ref.**	**[Mn(py)$_4$(NCS)$_2$]**		**[Fe(py)$_4$(NCS)$_2$]**		**[Co(py)$_4$(NCS)$_2$]**		**[Ni(py)$_4$(NCS)$_2$]**			
	26	2062^b (27, 1)	ν(N–CS)	2066 (29, 0)	ν(N–CS)	2074^b (27, 1)	ν(N–CS)	2084^b (27, 0)	ν(N–CS)		
	29	2066	ν(N–CS)	2070^g	ν(N–CS)	2072	ν(N–CS)	2079	ν(N–CS)		
ν_1	26	481 (3, 0)	δ(NCS)	483 (3, 0)	δ(NCS)	483 (3, 0)	δ(NCS)	483 (3, 0)	δ(NCS)		
	29	482	δ(NCS)	482^{dg}	δ(NCS)	481^d	δ(NCS)	483^d	δ(NCS)		
	14	482	δ(NCS)	—^{h}		483	δ(NCS)	482	δ(NCS)		
ν_2	26	422 (0, 40)	ν(py)	428 (0, 38)	ν(py)	431 (0, 40)	ν(py)	437 (0, 38)	ν(py)		
		414 (0, 40)	ν(py)	420 (0, 38)	ν(py)	423 (0, 39)	ν(py)	430 (0, 38)	ν(py)		
	29	420	ν(py)	424^g	ν(py)	426	ν(py)	434	ν(py)		
		414		420^g	ν(py)	420	ν(py)	429	ν(py)		
	14	422	ν(py)	—^{h}		433	ν(py)	438	ν(py)		
		415^e	ν(py)			423^e	ν(py)	432^e	ν(py)		
ν_3	26	256 (0, 0)	ν(M–NCS)	271 (1, 0)	ν(M–NCS)	272 (0, 0)	ν(M–NCS)	287 (0, 0)	ν(M–NCS)		
	29	254	ν(M–NCS)	266^g	ν(M–NCS)	268	ν(M–NCS)	280	ν(M–NCS)		
	14	259	ν(M–NCS)	—^{h}		272	ν(M–NCS)	287	ν(M–NCS)		
ν_4	26	188 (0, 0)	ν(M–py)^f	201 (0, 3)	ν(M–py) + ν(M–NCS)	212 (2, 0)	ν(M–py) + ν(M–NCS)	230 (0, 2)	ν(M–py) + ν(M–NCS)		
	29	b.r.		203^g	ν(M–py)	215	ν(M–py)	233	ν(M–py)		
	14	195	ν(M–py)	—^{h}		212	ν(M–py)	232	ν(M–py)		

ν_5	26	174 (1, 3)	ν(M–py)	193 (0, 4)	ν(M–py)	202 (2, 4)	ν(M–py)	220 (0, 4)	ν(M–py)
	29	b.r.		b.r.		205	ν(M–py)	n.r.	
	14	172	n.a.	—[h]		204	n.a.	n.r.	
ν_6	26	b.r.		163 (0, 2)	δ(NMN)	165 (t.b.)	δ(NMN)	172 (1, 3)	δ(NMN)
	29	b.r.		b.r.		b.r.		b.r.	
	14	b.r.		—[h]		170	n.a.	174	n.a.
ν_7	26	b.r.		b.r.		b.r.		160 (1, 7)	δ(NMN)
	29	b.r.		b.r.		b.r.		b.r.	
	14	b.r.		—[h]		b.r.		164	n.a.

---

[a] Abbreviations: b.r., beyond range of measurement; n.a., not assigned; n.r., not reported; t.b., too broad for determination of shift. Figures in parentheses following the frequencies are the shifts (nearest integral values in cm^{-1}) towards lower frequency induced by ^{15}NCS labelling (first figure) and pyridine deuteration (second figure). Shifts of less than 1 cm^{-1} are not regarded as significant and are reported as zero shifts. [b] Sharp shoulders on ν(N–CS) bands are ignored (see Fig. 3). [c] Some *d* sensitivity in these bands indicates coupling with ν(M–py). [d] Shoulders reported to precede these bands by about 2 cm^{-1} were not observed in ref. 26. [e] Additional bands reported near 400 cm^{-1} (not observed in ref. 26 nor cited in ref. 29). [f] Coupled with ν(M–NCS). [g] Compound incorrectly formulated as cis isomer. [h] Compound not studied.

be significantly sensitive towards pyridine deuteration only. The oop γ-ring mode of pyridine is readily detected by the very large shift (about 40 cm^{-1}) which it undergoes on pyridine deuteration. The M–S bonds in the polymeric NCS-bridged complexes are about 2.8 Å long [31] and this probably places ν(M–S) beyond the range of measurement.

F. COMPLEXES *cis*- AND *trans*-$[Pt(py)_2X_2]$ (X = Cl, Br, I, SCN)

The first isotopic labelling studies on the far-IR spectra of these complexes were made by Thornton and coworkers in 1978 [33]. Despite the existence of several earlier reports on their IR spectra [13,31,32,34,36] some ambiguities concerning the metal–ligand band assignments required to be resolved. Some workers had proposed that bands with frequencies as high as 500 cm^{-1} be assigned to ν(Pt–N) while others favoured a frequency nearer 250 cm^{-1} [16] but had failed [32,35] to observe the second ν(Pt–N) band required by the C_{2v} symmetry of the cis isomers. On the other hand, too many bands were observed in the spectra of the trans isomers on the basis of their D_{2h} symmetry [34,35].

The spectra are depicted in Fig. 4 and the frequency data are reported in Table 6. As in the previous sections, the data from six earlier studies [13,31,32,34–36] are compared with those resulting from the labelling work [33].

(i) cis- *and* trans-*$[Pt(py)_2X_2]$ (X = Cl, Br, I)*

In view of their square planar coordination [37], the selection rules for C_{2v} (cis) and D_{2h} (trans) symmetries are expected to apply, namely, two ν(Pt–N) and two ν(Pt–X) bands for the cis isomer and one of each for the trans complex. Four bending modes are anticipated for each isomer; however, not all of these were observed since the range was restricted to a low frequency limit of 140 cm^{-1}.

Reference to Fig. 4 shows that the first band (trans complexes) or band pair (cis complexes) below 500 cm^{-1} in the spectra of the chlorides exhibits a large shift on both ^{15}N labelling ($\Delta\nu \approx 8$ cm^{-1}) and pyridine deuteration ($\Delta\nu \approx 40$ cm^{-1}). These large shifts rule out earlier suggestions that these bands be assigned to ν(Pt–N) [16]. Clearly they originate in the oop γ-ring vibration of the pyridine ring. However, since the band is split in the spectrum of the cis isomer, some coupling with ν(Pt–N) evidently occurs.

Fig. 4 (opposite). IR spectra of the complexes *cis*- and *trans*-$[Pt(py)_2X_2]$ (X = Cl, Br, I, SCN), and of some ^{15}N and deuterated derivatives. An asterisk indicates that these ν(Pt–N) bands mask the δ(N–Pt–N) and δ(N–Pt–X) bands.

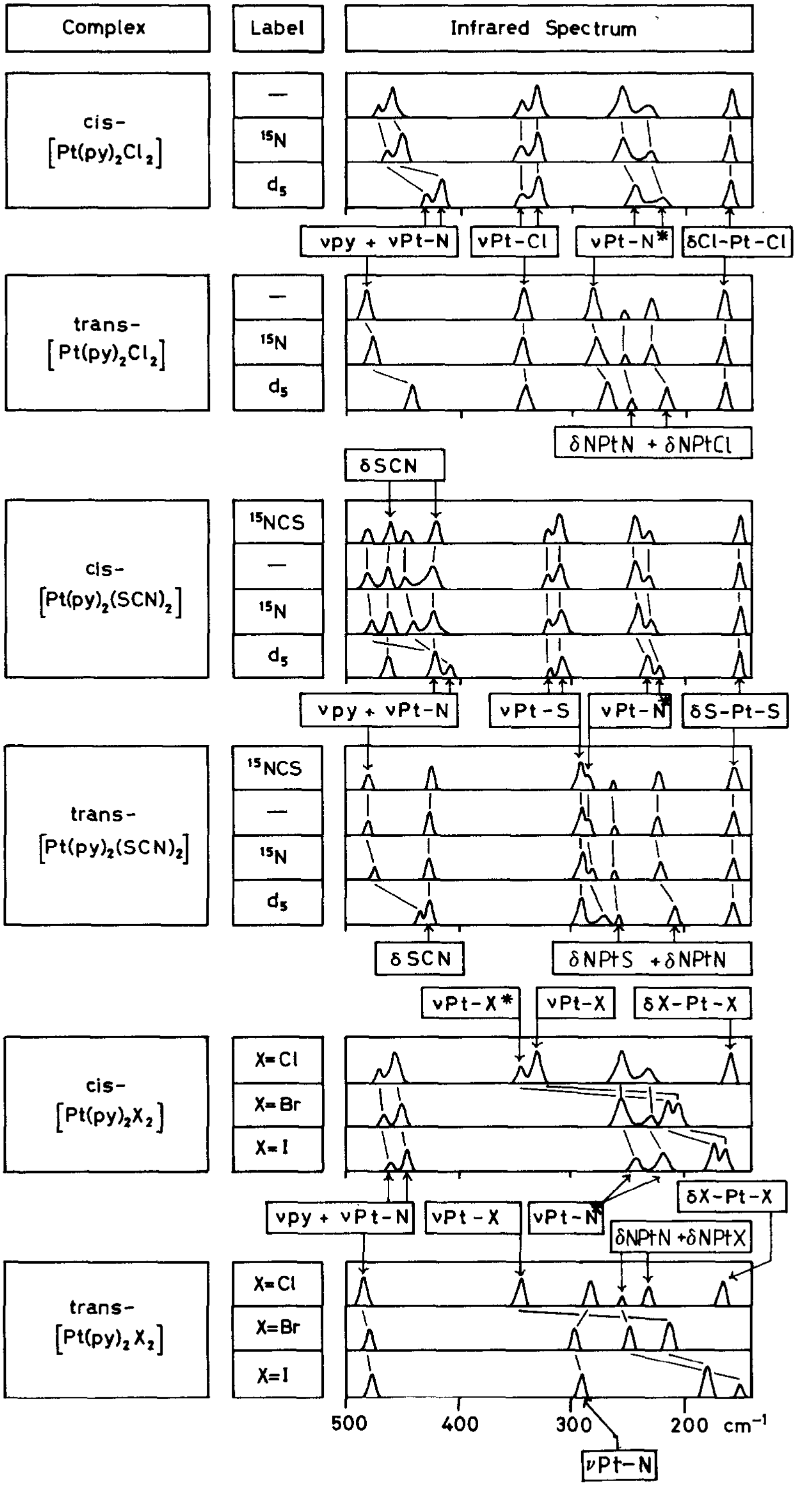

Complex
Label
Infrared Spectrum
cis-[Pt(py)$_2$Cl$_2$]
—
^{15}N
d$_5$
νpy + νPt-N
νPt-Cl
νPt-N*
δCl-Pt-Cl
trans-[Pt(py)$_2$Cl$_2$]
—
^{15}N
d$_5$
δNPtN + δNPtCl
δSCN
cis-[Pt(py)$_2$(SCN)$_2$]
^{15}NCS
—
^{15}N
d$_5$
νpy + νPt-N
νPt-S
νPt-N*
δS-Pt-S
trans-[Pt(py)$_2$(SCN)$_2$]
^{15}NCS
—
^{15}N
d$_5$
δSCN
δNPtS + δNPtN
νPt-X*
νPt-X
δX-Pt-X
cis-[Pt(py)$_2$X$_2$]
X=Cl
X=Br
X=I
νpy + νPt-N
νPt-X
νPt-N*
δX-Pt-X
δNPtN + δNPtX
trans-[Pt(py)$_2$X$_2$]
X=Cl
X=Br
X=I
500
400
300
200 cm^{-1}
νPt-N

TABLE 6

Frequencies (cm^{-1}), isotopic shifts (cm^{-1}) and assignments for complexes [Pt(py)$_2$X$_2$] (X = Cl, Br, I, SCN) [33]

Frequency	Shift ($\Delta\nu$)			Assignment	Previously reported frequencies and assignments[a]
	^{15}N	d_5	^{15}NCS		
cis-*[Pt(py)$_2$Cl$_2$]*					
471	8	42		ν(py) + ν(Pt–N)	467 ν(Pt–N) [31], 466 n.a. [32], 467 ν(py) [35]
457	7	42		ν(py) + ν(Pt–N)	454 ν(Pt–N) [31], 456 n.a. [34], 454 n.a. [32], 456 n.a. [35], 455 n.a. [36]
345	0	0		ν(Pt–X)	344 ν(Pt–X) [31], 343 ν(Pt–X) [34], 342 ν(Pt–X) [32], 343 ν(Pt–X) [35], 342 ν(Pt–X) [36]
331	0	1		ν(Pt–X)	330 ν(Pt–X) [31], 328 ν(Pt–X) [34], 328 ν(Pt–X) [32], 329 ν(Pt–X) [35], 330 ν(Pt–X) [36]
256	2	12		ν(Pt–N)[b]	260 n.a. [34], 260 n.a. [32], 260 ν(Pt–N) [35]
232	2	12		ν(Pt–N)[c]	233 n.a. [34], 235 n.a. [35]
160	0	0		δ(X–Pt–X)	163 ν(Pt–X) [35]
cis-*[Pt(py)$_2$Br$_2$]*					
467		42		ν(py) + ν(Pt–N)	464 ν(py) [35]
452		41		ν(py) + ν(Pt–N)	452 n.a. [34], 448 ν(py) [13], 451 n.a. [35]
259		9		ν(Pt–N)[b]	254 n.a. [34], 260 ν(Pt–N) [13], 262 ν(Pt–N) [35]
230		9		ν(Pt–N)[c]	234 n.a. [34], 234 ν(Pt–N) [13], 235 ν(Pt–X) [35]
216		7		ν(Pt–X)[c]	219 ν(Pt–X) [34], 216 n.a. [35]
208		0		ν(Pt–X)	211 ν(Pt–X) [34], 209 ν(Pt–X) [13]
cis-*[Pt(py)$_2$I$_2$]*					
460				ν(py) + νPt–N	460 ν(py) [35]
446				ν(py) + νPt–N	447 n.a. [35]
244				ν(Pt–N)[b]	246 ν(Pt–N) [35]
220				ν(Pt–N)[c]	
175				ν(Pt–X)	178 ν(Pt–X) [35]
165				ν(Pt–X)	167 ν(Pt–X) [35]

cis-$[Pt(py)_2(SCN)_2]$					
480	4	59	0	ν(py) + ν(Pt–N)	
462	0	0	2	δ(SCN)	
447	6	39	0	ν(py) + ν(Pt–N)	
423	0	2	3	δ(SCN)	
321	0	2	1	ν(Pt–S)	
311	0	1	0	ν(Pt–S)	
244	2	11	0	ν(Pt–N)[d]	
231	1	9	0	ν(Pt–N)[e]	
151	0	0	0	δ(S–Pt–S)	
trans-$[Pt(py)_2Cl_2]$					
482	8	41		ν(py) + ν(Pt–N)	480 ν(Pt–N) [31], 479 ν(py) [13], 478 n.a. [32], 481 ν(py) [35]
344	0	3		ν(Pt–X)	343 ν(Pt–X) [31], 343 ν(Pt–X) [34], 341 ν(Pt–X) [13], 342 ν(Pt–X) [32], 342 ν(Pt–X) [35]
285	3	14		ν(Pt–N)	283 n.a. [34], 282 ν(Pt–N) [13], 279 ν(Pt–N) [32], 284 ν(Pt–N) [35]
254	1	7		δ(N–Pt–N)	256 n.a. [34], 242 n.a. [13], 256 n.a. [35]
230	1	14		δ(N–Pt–X)	232 n.a. [34], 233 n.a. [13], 235 n.a. [35]
165	0	0		δ(X–Pt–X)	167 δ(Pt–X) [35]
trans-$[Pt(py)_2Br_2]$					
479		41		ν(py) + ν(Pt–N)	476 ν(py) [13], 478 ν(py) [35]
296		12		ν(Pt–N)	298 n.a. [34], 297 ν(Pt–N) [13], 300 ν(Pt–N) [35]
247		9		ν(Pt–X)[b]	251 ν(Pt–X) [34], 249 ν(Pt–X) [13], 252 ν(Pt–X) [35]
212		9		δ(N–Pt–X)	216 n.a. [34], 214 n.a. [13], 215 n.a. [35]
trans-$[Pt(py)_2I_2]$					
476				ν(py) + ν(Pt–N)	475 ν(py) [35]
290				ν(Pt–N)	293 ν(Pt–N) [35]
179				ν(Pt–X)	183 ν(Pt–X) [35]
149				δ(N–Pt–X)	150 n.a. [35]

TABLE 6 (continued)

Frequency	Shift ($\Delta\nu$)			Assignment
	^{15}N	d_5	^{15}NCS	
trans-*[Pt(py)$_2$(SCN)$_2$]*				
480	5	46	0	ν(py) + ν(Pt–N)
427	0	0	2	δ(SCN)
292	0	0	0	ν(Pt–S)
288 sh	3	15	0	ν(Pt–N)
263	0	4	0	δ(N–Pt–S)
224	2	14	0	δ(N–Pt–N)
158	1	0	2	δ(S–Pt–S)

[a] n.a., not assigned. [b] These bands probably mask δ(N–Pt–N) bands (see text). [c] These bands probably mask δ(N–Pt–X) bands (see text). [d] This band probably masks a δ(N–Pt–S) band (see text). [e] This band probably masks a δ(N–Pt–N) band (see text).

The ν(Pt–Cl) bands occur near 340 cm^{-1} (split in the spectra of the cis complexes). They are identified by an absence of sensitivity towards ^{15}N labelling and pyridine deuteration but are obviously shifted by halide substitution.

The ν(Pt–N) bands were found within the range 300–230 cm^{-1} where they were identified by their sensitivities towards ^{15}N labelling and pyridine deuteration but not towards halide substitution. The shifts on deuteration are of the order expected for a Pt–C_5H_5N "diatomic" oscillator, i.e. about 12 cm^{-1}. For the cis isomer, two ν(Pt–N) bands were observed, as expected for C_{2v} symmetry. The selection rules for the D_{2h} symmetry of the trans isomer require one ν(Pt–N) band but paradoxically three were observed. The band of highest frequency, at 285 cm^{-1}, exhibits the greatest ^{15}N and *d* sensitivities and was therefore readily assigned to ν(Pt–N). The origin of the other bands is of interest since they are unexpected and have been reported but not assigned by others [13,34,35]. They are certainly not due to contamination of the sample by the cis isomer since no other cis bands recurred in the trans spectrum. Nor (as pointed out by a referee of this review) can they be ascribed to vibrationally coupled $\nu(\text{Pt–N}) + \nu(\text{Pt–Cl})$ modes as had been proposed by Thornton and coworkers [33] since vibrational coupling cannot increase the number of normal modes. Any satisfactory explanation of their existence would have to take into account their sensitivities towards deuteration of the pyridine ring and substitution of X. Perhaps they may be bending modes such as δ(N–Pt–X). Their occurrence at 254 and 230 cm^{-1} in the trans chloro complex would imply that they are masked in the spectrum of the cis complex by the bands at 256 and 232 cm^{-1} which have been assigned to ν(Pt–N). The reviewer suggests that extension of the spectra to frequencies below 140 cm^{-1} and determination of the Raman spectra may shed some light on the origin of these additional bands.

Substitution of Br and I for Cl caused the band(s) near 340 cm^{-1} (ν(Pt–Cl)) to move to the 210 cm^{-1} and 170 cm^{-1} regions respectively. The ratios $\nu(\text{Pt–Br})/\nu(\text{Pt–Cl}) \approx 0.63$ and $\nu(\text{Pt–I})/\nu(\text{Pt–Cl}) \approx 0.50$ are similar to those observed [38] for the square planar anions $[PtX_4]^{2-}$ (X = Cl, Br, I). An interesting feature of the labelling work is the finding that one of the ν(Pt–Br) bands in the spectra of the bromo complexes is significantly more sensitive towards deuteration than ν(Pt–Cl) in the spectra of the chloro complexes, suggesting strong coupling between ν(Pt–Br) and ν(Pt–N), as expected from the increase in covalency of the Pt–X bonds in the order Cl < Br.

(ii) cis- *and* trans-*$[Pt(py)_2(SCN)_2]$*

Square planar coordination, with terminal S-bonded thiocyanate groups, has been established [39] for the trans isomer. Pt–S bonding is supported by the IR spectra [33] which exhibit relatively high ν(C≡N) frequencies near 2120 cm^{-1} with a ^{15}NCS sensitivity of 28 cm^{-1}.

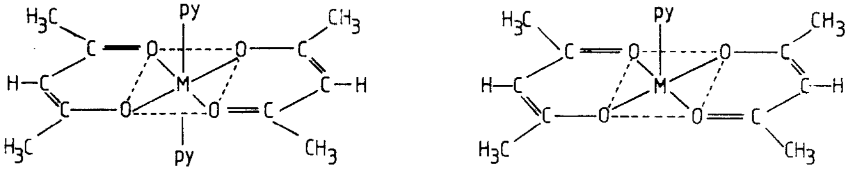
In the 500–400 cm^{-1} region, there are four bands in the spectrum of the cis isomer and two in that of the trans isomer. The assignments for the cis isomer are clearly made by the isotopic labelling technique. Thus the first and the third bands are sensitive only towards pyridine deuteration, i.e., they are the oop γ-ring pyridine mode (coupled with ν(Pt–N)); the second and fourth bands, being sensitive only towards ^{15}NCS labelling, were assigned to the δ(SCN) mode.

In the 350–270 cm^{-1} region, there are two moderate to strong bands for the cis isomer and a strong band with a shoulder for the trans isomer. The two cis bands and the strong trans band are unaffected by ^{15}N or ^{15}NCS labelling or by pyridine deuteration, suggesting they be assigned to ν(Pt–S). The shoulder on the ν(Pt–S) band in the spectrum of the trans complex was found to shift on ^{15}N labelling and on pyridine deuteration but not on ^{15}NCS labelling, indicating that it is ν(Pt–N). It is in the same region as ν(Pt–N) is the spectrum of *trans*-$[Pt(py)_2Cl_2]$. The two ν(Pt–N) bands of the cis isomer were observed between 270 and 200 cm^{-1} where they are unaffected by ^{15}NCS labelling but are sensitive towards ^{15}N labelling and deuteration of the pyridine ring.

The *trans*-$[Pt(py)_2(SCN)_2]$ spectrum resembles that of the analogous chloride in that, after accounting for the single ν(Pt–N) band expected for D_{2h} symmetry, there remain two further bands at 263 and 224 cm^{-1}. For reasons similar to those given for the extra bands in the spectrum of *trans*-$[Pt(py)_2Cl_2]$, it is suggested that these may originate in δ(N–Pt–S) and δ(N–Pt–N) vibrations. The single remaining bands in the spectra of the cis and trans complexes are practically unaffected by any form of labelling and were therefore assigned to δ(S–Pt–S).

G. PYRIDINE ADDUCTS OF METAL ACETYLACETONATES, $[M(acac)_2(py)_n]$ (M = Co, Ni, Zn)

In 1970, Nakamoto et al. [40] examined the spectra of *trans*-$[Ni(acac)_2(py)_2]$ (Fig. 5) and the labelled compounds in which the nickel atom of



M = Co,Ni

M = Zn

Fig. 5. Structures of *trans*-$[M(acac)_2(py)_2]$ and $[Zn(acac)_2(py)]$.

natural isotopic abundance was replaced by the stable ^{58}Ni and ^{62}Ni isotopes. In the 800–150 cm^{-1} region, only two bands (at 276 and 253 cm^{-1}) were found to exhibit isotopic shifts exceeding 1 cm^{-1}. These bands were assigned to ν(Ni–O) and ν(Ni–N) respectively. The study was extended by Engelter and Thornton in 1977 [41] to include the effects of deuteration of the pyridine ring and substitution of the metal ion on the spectra.

Figure 6 depicts the far-IR spectra of the complexes shown in Fig. 5. The relevant data are assembled in Table 7. The spectra of pyridine and pyridine-d_5 are also shown for comparison. From the ligand spectrum it is seen that the ip δ-ring and oop γ-ring bands of pyridine at 604 (ν_1) and

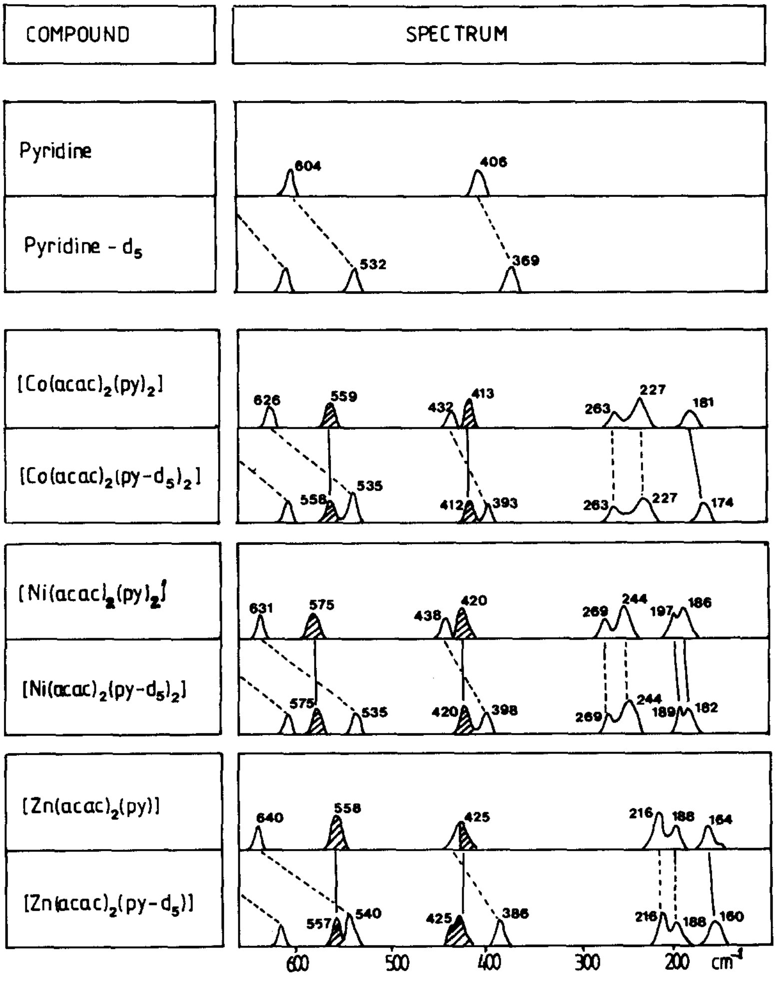


Fig. 6. IR spectra (650–150 cm^{-1}) of pyridine and pyridine-d_5 adducts of cobalt(II), nickel(II) and zinc(II) bis(acetylacetonates).

TABLE 7

Frequencies (cm^{-1}) of far-IR bands in [Ni(acac)$_2$(py)$_2$] and their ^{i}M, *d* and M sensitivities

Band	Frequency	^{i}M sensitivitiy[a] [40]	*d* sensitivity [41]	M sensitivity[c]		Assignment	
				Co	Zn	By ^{i}M technique [40]	By py-d_5 technique [41]
ν_1	631	0.5	96	5	−9	π(CH$_3$CCO)	ν(py)[d]
ν_2	575	0.8	0	16	17	ν(Ni–O) + ring[e]	Coupled ν(Ni–O)
ν_3	438	0.8	40	6	13	ν(Ni–O) + ν(C–CH$_3$)	ν(py)[f]
ν_4	420	0.4	0	7	−5	Ring[g]	Coupled ν(Ni–O)
ν_5	269	5.4	0	6	53	ν(Ni–O)	ν(Ni–O)
ν_6	244	3.8	0	17	56	ν(Ni–N)	ν(Ni–O)
ν_7^{a}	197[h]	n.o.[i]	8	11[j]	28[j]	n.o.[i]	ν(Ni–N)
ν_7^{b}	186	n.r.[k]	4			Ring	

[a] ^{i}M sensitivity = {frequency for [^{58}Ni(acac)$_2$(py)$_2$]} − {frequency for [^{62}Ni(acac)$_2$(py)$_2$]} [40].

[b] *d* Sensitivity = {frequency for [Ni(acac)$_2$(py)$_2$]} − {frequency for [Ni(acac)$_2$(py-d_5)$_2$} [41].

[c] M sensitivity (Co) = {frequency for [Ni(acac)$_2$(py)$_2$]} − {frequency for [Co(acac)$_2$(py)$_2$]} [41].
M sensitivity (Zn) = {frequency for [Ni(acac)$_2$(py)$_2$]} − {frequency for [Zn(acac)$_2$(py)]} [41].

[d] A_1 mode, δ-ring [42]. [e] Independently assigned to ν(Ni–O) [43]. [f] B_2 mode, γ-ring [42]. [g] Independently assigned to ν(Ni–O) [43]. [h] Shoulder. [i] n.o., shoulder not observed [40]. [j] ν(Ni–N) taken as mean of 197 and 186 cm^{-1} bands. [k] n.r., shift not reported [40].

406 cm^{-1} (ν_3) are shifted by 72 cm^{-1} and 37 cm^{-1}, respectively, towards lower frequency on deuteration. In the complexes these bands occur near 630 and 430 cm^{-1} where they are similarly shifted by deuteration. These shifts are in contrast with the unshifted bands (ν_2) near 560 cm^{-1} which clearly qualify for assignment to ν(M–O). The same argument applies to ν_4, ν_5 and ν_6, which were also assigned to ν(M–O). The occurrence of four (or even more) ν(M–O) bands in metal acetylacetonate spectra is well established [44]. It is generally considered that those of higher frequency are coupled ν(M–O) modes while those near 250 cm^{-1} are the vibrationally pure ν(M–O) bands.

The bands within the range 200–160 cm^{-1} (ν_7) were assigned to ν(M–N) on the basis of their sensitivities towards pyridine deuteration ($\Delta\nu$ between 4 and 8 cm^{-1}). It is noteworthy that both ν(M–O) and ν(M–N) shift in the sequence cobalt < nickel > zinc which is also the sequence of crystal field stabilization energies (CFSE's) and this observation assisted in confirming the proposed assignments [27].

Agreement between the metal isotope [40] and pyridine deuteration [41] assignments is poor. The former technique established that only ν_5 and ν_6 were significantly sensitive towards metal isotope labelling and these bands were assigned to ν(Ni–O) and ν(Ni–N) respectively. The shoulder at 197 cm^{-1} (ν_{7a}) was not observed in the metal isotope labelling study and ν_{7b} was assigned to a ring mode although its shift could not be determined. Furthermore, the ip δ-ring pyridine mode at 631 cm^{-1} (ν_1) was assigned to a π(CH_3CCO) vibration. It shifts 96 cm^{-1} on pyridine deuteration! Agreement between the two techniques is therefore confined to ν_2 and ν_5.

The effect of introducing electron-withdrawing and electron-releasing substituents into the heterocyclic ring on the ν(Ni–O) and ν(Ni–N) bands of the pyridine adducts has also been determined [41]. The results assisted in confirming the assignments given above on the basis of the deuteration study. These substituent effects did not involve isotopic labelling work and the reader is referred elsewhere for a review of this area [44].

H. OCTAHEDRAL TIN(IV) COMPLEXES [SnL_2X_4] (L = PYRIDINE OR A SUBSTITUTED PYRIDINE; X = Cl, Br)

In 1973, Ohkaku and Nakamoto [45] examined the IR and Raman spectra of several complexes of general formula [SnL_2X_4] where L is a series of ligands including pyridine, δ-picoline and 4-*t*-butylpyridine. Vibrational assignments were based on shifts in far-IR bands which occurred on deuteration of pyridine and the isotopic substitution of [$^{116}Sn(py)_2X_4$] by [$^{124}Sn(py)_2X_4$].

Using vibrational spectroscopy, Beattie et al. [46] concluded that $[Sn(py)_2Cl_4]$ has the trans configuration. Later, Clark and Wilkins [47] assigned the cis configuration to both $[Sn(py)_2Cl_4]$ and $[Sn(py)_2Br_4]$ (which were shown to be isomorphous) since the IR spectrum of the bromide comprised three bands in the ν(Sn–Br) spectral region. However, Beattie et al. [48] concluded from an X-ray diffraction study that the complexes were isomorphous and had the trans configuration, while Tanaka et al. [49, 50] claimed that the IR spectrum showed them to be cis although they were unable to distinguish between ν(Sn–N) and ν(Sn–X).

This highly confusing situation was resolved by the isotopic labelling study of Ohkaku and Nakamoto [45]. Table 8 shows the observed and calculated frequencies for these compounds. Thus $[Sn(py)_2Cl_4]$ exhibits six IR and five Raman bands in the low frequency region. Upon ^{116,124}Sn substitution, two IR bands at 323.0 and 227.5 cm^{-1} showed large isotopic shifts relative to others. This is in perfect agreement with the predictions for the trans configuration. This conclusion was confirmed by the Raman spectra; no tin isotope effect was observed for all Raman-active fundamentals since the central metal ion does not move in the *g*-type vibrations. Two IR bands at 323.0 and 227.5 cm^{-1} which are metal isotope sensitive, may be assigned to the ν(Sn–Cl) (E_u) and ν(Sn–N) (A_{2u}) modes respectively, since the former band is insensitive to pyridine deuteration while the latter band was observed to shift by 3.0 cm^{-1} to lower frequency. Similar findings were made for the complex $[Sn(py)_2Br_4]$.

I. COMPLEXES $[Au(py)X_3]$ (X = Cl, Br)

The square planar complex $[Au(py)Cl_3]$ and its pyridine-d_5 analogue were studied by Clark and coworkers [51] in 1968. The strong band at 362 cm^{-1} moves only 3 cm^{-1} to lower frequency on pyridine deuteration but substitution of Br$^-$ for Cl$^-$ caused it to shift to 260 cm^{-1}; hence it was assigned to ν(Au–X). An additional ν(Au–X) band was observed at 333 cm^{-1} (X = Cl) and 225 cm^{-1} (X = Br). The ν(Au–N) band was tentatively assigned to the range 306–234 cm^{-1} for a series of substituted pyridine complexes $[Au(R–py)X_3]$ which spanned a wide range of R. The assignment is supported by the order of R sensitivity of the frequency of ν(Au–N) which is 4-CN < H < 3-CH_3 < 4-CH_3 < 2-CH_3 < 3,5-di-CH_3 < 2,6-di-CH_3 < 2,4-di-CH_3, i.e. in the order of pK_a values. ν(Au–Br) was assigned to bands within the range 202–175 cm^{-1}. An attempt was also made to assign the δ(X–Pt–X) bands.

Empirical assignments have been made for several series of complexes of formula $[MLX_3]^-$ where L is py or a substituted pyridine [52].

TABLE 8

Isotopic shift data (cm^{-1}) for [Sn(py)$_2$Cl$_4$] [45]

Symmetry species	Calculated			Observed			Assignment
	$\nu(^{116}Sn)$	$\Delta\nu(^{116,124}Sn)$	$\Delta\nu(py\text{-}d_5)$	$\nu(^{116}Sn)$	$\Delta\nu(^{116,124}Sn)$	$\Delta\nu(py\text{-}d_5)$	
E_u	324.8	3.0	0.0	323.0[a]	5.0	0.0	ν(Sn–Cl)
A_{1g}	307.1	0.0	0.4	(307.1)[b]	0.3		ν(Sn–Cl)
B_{1g}	254.2	0.0	0.0	(244.8)[b]			ν(Sn–Cl)
A_{2u}	234.6	3.8	3.4	227.5	4.0	3.0	ν(Sn–N)
B_{2g}	186.2	0.0	0.0	(173.5)[b]			δ(Cl–Sn–Cl)
E_g	172.6	0.0	1.8	(157.3)[b,c]			δ(Cl–Sn–Cl)
E_u	167.6	2.2	0.5	187.0	1.2		δ(Cl–Sn–Cl)
A_{1g}	158.8	0.0	4.6	(157.3)[b,c]			ν(Sn–N)
B_{2u}	139.4	0.0	0.0	(inactive)			δ(N–Sn–Cl)
E_u	116.3	0.1	1.8	170.0	1.0	4.0	δ(Cl–Sn–Cl)
A_{2u}	119.2	0.9	0.5	145.0	0.5	1.0	π(Sn–Cl$_4$)
				90	0	0	Lattice

[a] This band is sometimes accompanied by a shoulder at about 305 cm^{-1}. The appearance of this shoulder may indicate splitting of the E_u mode due to lowering of the D_{4h} symmetry in the solid state. [b] Frequency of [Sn(py)$_2$Cl$_4$] containing Sn in natural abundance. [c] Overlapped band.

J. COMPLEXES *cis*- AND *trans*-$[M(py)_3Cl_3]$ (M = Cr, Rh, Ir, In)

Compounds of this formula result from reaction of py with halides of the transition metal(III) ions. The rhodium(III) and iridium(III) chloro complexes have been isolated as cis and trans isomeric pairs and their IR spectra have been reported [13] but no isotopic labelling studies have been made. Some relevant data are recorded in Table 9. It is interesting to note that the increased CFSE on passing from the second to the third transition series leads to an increase in ν(M–N) as has been established for metal tropolonate complexes [54]. Isotopic labelling studies on these complexes would be of interest.

K. COMPLEXES *trans*-$[ML_4X_2]$ (L = py OR A SUBSTITUTED PYRIDINE; X = Cl, Br, I)

Complexes of this formula with L = py, X = NCS have been discussed in Section E. Complexes of formula $[M(py)_4X_2]$ embrace examples with the symmetries C_{3v} and T_d where X is a weakly coordinating ligand such as ClO_4^- or BF_4^-; or D_{4h} if they are trans octahedral monomers. The C_{3v} and T_d complexes in which the anion may or may not be coordinated will not be discussed here since no labelling studies have been reported [55]. Most of the literature on the vibrational spectra of these complexes refers to the octahedral complexes, *trans*-$[M(py)_4X_2]$ [13,14,21,24,56–59]. The most important of these studies are the papers by Nakamoto and coworkers [56], Goldstein and Unsworth [58] and Lever and Ramaswamy [59], all of which involved isotopic labelling.

In 1973, Nakamoto and coworkers [56] carried out a multiple isotopic labelling study of the octahedral complexes *trans*-$[NiL_4Cl_2]$ (L = py, γ-

TABLE 9

Assignment of ν(M–N) and ν(M–Cl) (cm^{-1}) for some complexes of formulae *cis*- and *trans*-$[M(py)_3Cl_3]$

Complex	ν(M–N)	ν(M–Cl)
$[Cr(py)_3Cl_3]^a$	221	364, 341, 307
cis-$[Rh(py)_3Cl_3]^a$	266, 245	341, 325
trans-$[Rh(py)_3Cl_3]^a$	265, 245, 230	355, 332, 295
cis-$[Ir(py)_3Cl_3]^a$	270, 266	325, 317, 303
trans-$[Ir(py)_3Cl_3]^a$	272, 264, 255	329, 318, 307
cis-$[In(py)_3Cl_3]^b$	195, 184^c 200, 189^{bd}	276, 242

[a] Data from ref. 13. [b] Data from ref. 53. [c] In CH_3CN. [d] Raman frequencies in CH_3CN.

picoline) in which deuteration of pyridine, ^{58,62}Ni labelling and ^{37}Cl labelling were employed. Attention was confined to the far-IR spectra. The frequencies and observed shifts are shown in Table 10. According to the isotopic labelling data, one ν(Ni–N) mode was observed for the complex with X = Br, but two ν(Ni–N) bands were observed for those with X = Cl and I, contrary to the D_{4h} symmetry requirements.

Included in Table 10 are the empirically based assignments of Clark and Williams [13] and those of Goldstein and Unsworth [58], based on pyridine deuteration. Except for the 249 cm^{-1} band of the chloro complex, the agreement between the various studies is good. However, the work of

TABLE 10

Isotopic labelling data (cm^{-1}) [56] and assignments for the complexes *trans*-[Ni(py)$_4$X$_2$] (X = Cl, Br, I)

$\nu(^{58}$Ni)	$\Delta\nu(^{62}$Ni)	$\Delta\nu$(py-d_5)	$\Delta\nu(^{37}$Cl)	Assignment [56]	Other assignments
trans-*[Ni(py)$_4$Cl$_2$]*					
249.0	4.2	≈7	0.7	ν(Ni–N) (E_u)	ν(Ni–N) [14,58] ν(Ni–Cl) [13]
238.8	5.4	4.5	0.2	ν(Ni–N) (A_{2u})	ν(Ni–N) [13,14,58]
207.0	1.8	2.5	2.3	ν(Ni–Cl)	ν(Ni–Cl) [58]
—[a]				δ(N–Ni–N)	
194 sh	—[b]	≈6	—[b]		
176.1	0.0	8.7	0.7	δ(N–Ni–Cl)	
154.8	0.1	2.5	2.0	δ(Cl–Ni–Cl)	δ(N–Ni–Cl) [58]
trans-*[Ni(py)$_4$Br$_2$]*					
238.0	5.0	5.5		ν(Ni–N)(E_u,A_{2u})	ν(Ni–N) [13,58]
200.5	0.9	7.5		δ(N–Ni–N)	
185	—[b]	≈5			
151 sh	—[b]	≈7		δ(N–Ni–Br)	
140.5	≈1	3.0		ν(Ni–Br)	ν(Ni–Br) [58]
120.2	≈0	3.4		δ(Br–Ni–Br)	δ(N–Ni–Br) [58]
trans-*[Ni(py)$_4$I$_2$]*					
241.0	4.5	8.0		ν(Ni–N) (A_{2u})	ν(Ni–N) [13,21,58]
229.0	3.0	5.3		ν(Ni–N) (E_u)	
189.3	—[b]	9.5		δ(N–Ni–N)	
172.5	—[b]	≈10			
140.3	—[b]	≈12		δ(N–Ni–I)	
104.5	>1	2.0		ν(Ni–I)	ν(Ni–I) [58]
(104.5)	(>1)	(2.0)		δ(I–Ni–I)	

[a] Masked by neighbouring band. [b] Shift not determined because of poor band shape.

Nakamoto and coworkers [56] indicates that an appreciable amount of vibrational coupling between ν(Ni–N) and ν(Ni–X) occurs since the ν(Ni–X) bands are all to some extent sensitive to pyridine deuteration. This finding emphasizes the desirability of incorporating more than one type of isotopic labelling in solving the assignment problem. The assignments resulting from the multiple isotopic labelling study of the $[Ni(py)_4X_2]$ complexes were used for empirically assigning the metal–ligand modes in the complexes $[Ni(\gamma\text{-pic})_4X_2]$. The data, together with those reported in the same year by Lever and Ramaswamy [59] for $[Ni(\beta\text{-pic})_4X_2]$ (which were based on ^{62}Ni labelling) are shown in Table 11.

In the course of their investigation of the *trans*-$[Ni(\beta\text{-pic})_4X_2]$ complexes and those of compounds $[CuL_4X_2]$ (L-α-pic, β-pic; X = Cl, Br) Lever and Ramaswamy [59] found that low temperatures induced high frequency shifts in the IR bands and that the effect is much more significant on metal–ligand bands than on internal ligand modes. The shifts were rationalized in terms of the reduction in unit cell volume which accompanies cooling. The distortion which occurs will have its greatest effect on the metal–ligand bonds. Some results which were obtained for the copper complexes are shown in Table 12. Data for the nickel complexes $[Ni(\beta\text{-pic})_4X_2]$ are included in Table 11.

L. COMPLEXES $[Cu(py)_n(NO_3)_2]$ ($n = 2, 3, 4$) AND $[M(py)_3(NO_3)_2]$ (M = Co, Ni, Zn)

The trio of structurally distinct complexes derived from the reaction of copper(II) nitrate with pyridine results partly from the monodentate/bidentate nature of the NO_3^- ligand and partly from whether it is terminal or bridging. The spectra of these complexes have been reported down to 150 cm^{-1} [14,60] and 75 cm^{-1} [61]. The far-IR spectra from the latter paper yield the data shown in Table 13.

The distinction between ν(Cu–O) and ν(Cu–N) is quite reasonably made on the basis of the shift data (except for the shift of 3 cm^{-1} on pyridine deuteration of the 266 cm^{-1} band of $[Cu(py)_4(NO_3)_2]$ which possibly indicates some vibrational coupling between ν(Cu–N) and ν(Cu–O) in this complex). The spectrum of $[Cu(py)_4(NO_3)_2]$ is consistent with a trans tetragonal structure, the axial positions being occupied by two monodentate nitrate groups. This proposal is based partly on the frequency difference of 102 cm^{-1} between the ν_1 and ν_4 nitrate modes [62]. The D_{4h} symmetry of the trans octahedral complex requires five IR-active modes: one each of ν(Cu–O), ν(Cu–N) and δ(N–Cu–N) and two δ(N–Cu–O) modes. These are observed and assigned as indicated in Table 13.

The spectra of $[Cu(py)_3(NO_3)_2]$ and $[Cu(py)_2(NO_3)_2]$ are indicative of bidentate nitrate coordination since the differences between the ν_1 and ν_4

TABLE 11

Reported frequencies (cm^{-1}) and assignments for the complexes $[\mathrm{Ni}(\beta\text{-pic})_4\mathrm{X}_2]$ and $[\mathrm{Ni}(\gamma\text{-pic})_4\mathrm{X}_2]$

$\mathrm{Ni}(\beta\text{-pic})_4\mathrm{X}_2$[a]			$\mathrm{Ni}(\gamma\text{-pic})_4\mathrm{X}_2$[b]			Assignment
X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	
			266	265	267	
251.5	230	249	222	222	221	ν(Ni–N)
(2.5, +9)	(5.5, +11)	(—, +7)	(222)	205	198	
243.5 (5.5, +7)			183	128	95	ν(Ni–X)
			175	178		δ(N–Ni–N)
			168	166	156	δ(N–Ni–X)
			147	115	95	δ(X–Ni–X)
Other assignments						
	241^{d}	225, 210^{c} 263, 234^{d}		267, 228^{d}	234^{d}	ν(Ni–N)

[a] Figures in parentheses are the shift to lower frequency on ^{62}Ni labelling relative to the atom with natural abundance and the shift to higher frequency on reducing the temperature of the sample in liquid N_2. Data from ref. 59. [b] Data from ref. 56. [c] Data from ref. 13. [d] Data from ref. 21.

TABLE 12

Cu–N and Cu–X stretching frequencies (cm^{-1}) of complexes [CuL_4X_2] (L = α- or β-picoline) [59]

Complex[a]	ν(Cu–N)	ν(Cu–X)
Cu(α-pic)$_4$Cl$_2$	254 (3)[b]	305 (0)[b]
l.t.	257 (+3)[c], 229	305 (0)[c]
Cu(α-pic)$_4$Br$_2$	268.5 (2), 261 (2)[b]	233 (3)[b]
l.t.	276 (+6), 262 (+1)[c]	236 (+3)[c]
Cu(β-pic)$_4$Cl$_2$	267 (1.5), 236 (1.5)[b]	294 (1.5)[b]
l.t.	273 (+5)[c], 237 (+4)[c]	297 (+3)[c], 301
Cu(β-pic)$_4$Br$_2$	270.5 (2.5)[b]	240 (2.5)[b]
l.t.	275 (+4)[c]	248 (+7)[c]

[a] l.t., low temperature. [b] Low frequency shift on ^{65}Cu substitution in parentheses. [c] High frequency shift (positive) on reducing temperature in liquid N_2.

nitrate frequencies are 167 and 193 cm^{-1} respectively [62]. The increase in ν(Cu–O) from four to three to two coordinated pyridines, is consistent with a change from monodentate terminal to bidentate terminal to bidentate bridging nitrate groups. As the ν(Cu–O) values increase, so the ν(Cu–N) values decrease. This was explained [61] by assuming that the covalency of the Cu–nitrate bonding increases at the expense of the Cu–pyridine bonding. The spectra of the complexes [$M(py)_3(NO_3)_2$] (M = Co, Ni, Zn) were also determined and their assignments were based on the effects of pyridine deuteration.

M. COMPLEXES [$Mo(CO)_5L$] (L = PYRIDINE OR A SUBSTITUTED PYRIDINE)

Studies of transition metal carbonyl complexes generally give very little attention to the far-IR spectra. For this reason, the work of Desseyn et al. [63] on the spectra of the molybdenum(0) complex [$Mo(CO)_5(py)$] and its d_5 analogue is of considerable interest since it represents the only known example of a pyridine-substituted metal carbonyl which has been investigated by the isotopic labelling technique and which incorporates both the IR and Raman spectra over the full spectral range. The ν(C≡O), δ(Mo–C≡O), ν(Mo–C) and ν(Mo–N) fundamentals were assigned on the basis of C_{4v} symmetry and a complete vibrational analysis was given for the pyridine and pyridine-d_5 complexes.

N. CORRELATION OF SHIFTS OF INTERNAL PYRIDINE MODES ON METAL ION COORDINATION WITH THE M–N BOND STRENGTH

It is well known that metal ion coordination causes shifts (usually increases) in the frequencies of the internal pyridine ligand modes (i.e. ring

TABLE 13

Frequency and shift data (cm^{-1}) from the far-IR spectra of the complexes [Cu(py)$_n$(NO$_3$)$_2$] [61]

[Cu(py)$_4$(NO$_3$)$_2$]			[Cu(py)$_3$(NO$_3$)$_2$]		[Cu(py)$_2$(NO$_3$)$_2$]			Assignment
$\nu(^{63}\mathrm{Cu})$[a]	$\Delta\nu(^{65}\mathrm{Cu})$[b]	$\Delta\nu(\mathrm{py}\text{-}d_5)$[c]	ν^{NA}[d]	$\Delta\nu(\mathrm{py}\text{-}d_5)$[c]	$\nu(^{63}\mathrm{Cu})$[a]	$\Delta\nu(^{65}\mathrm{Cu})$[b]	$\Delta\nu(\mathrm{py}\text{-}d_5)$[c]	
266	3	3	268	1	322	3	0	ν(Cu–O)
					282	3	0	
250	2	8	223	10	205	1	5	ν(Cu–N)
200	1	10			173 sh	0	≈5	δ(N–Cu–N)
192	1	7	211 sh		220 sh	2	2	δ(O–Cu–N)
130	1	≈5	156	≈2	133	1	1	
					115	0	1	
					82	0	1	

[a] Frequency of ^{63}Cu-labelled complex. [b] Low frequency shift on substitution of ^{63}Cu by ^{65}Cu. [c] Low frequency shift on pyridine deuteration. [d] Frequency from spectrum of complex with copper of natural isotopic abundance.

and C–H modes). In an interesting series of papers, Akyüz and coworkers [42,64,65] have investigated the magnitude of these shifts in relation to the metal–N bond strengths as determined for instance, by the magnitude of the metal–N stretching frequencies. The work has been of a very careful nature in that reliance has not been placed on observation of the shift in a single vibrational band but rather in the sum of the shifts in a number of such bands which are common to the IR and Raman spectra of the series of complexes under consideration.

A comparison of the sum of the shifts of 13 ligand IR modes ($\Sigma\Delta\nu$) and the ν(M–N) values for a series of pyridine and 4-methylpyridine (γ-picoline) complexes of formulae [ML_2X_2] and [ML_4X_2] (M = first transition series divalent metal ion; L = py or γ-pic; X = Cl, Br) are shown in Table 14. It is observed that the sequence of values of $\Sigma\Delta\nu$ matches the sequence of ν(M–N) values* except for the abnormally high value of $\Sigma\Delta\nu$ for the complex [$Zn(\gamma\text{-pic})_2Br_2$] and the values of $\Sigma\Delta\nu$ are smaller for the tetrakis(pyridine) complexes than the bis(pyridine) complexes. However, the most interesting observation made by Akyüz and coworkers [65] lay in the comparison between the $\Sigma\Delta\nu$ values of the pyridine and γ-picoline complexes. The fact that they were much higher in the latter was attributed to

TABLE 14

Comparison of summated IR shift values ($\Sigma\Delta\nu$) and ν(M–N) values (cm^{-1}) of py and γ-pic complexes of formulae [ML_2X_2] and *trans*-[ML_4X_2] [65]

M	X = Cl				X = Br			
	L = py		L = γ-pic		L = py		L = γ-pic	
	$\Sigma\Delta\nu$	ν(M–N)	$\Sigma\Delta\nu$	ν(M–N)	$\Sigma\Delta\nu$	ν(M–N)	$\Sigma\Delta\nu$	ν(M–N)
[ML_2X_2] complexes								
Mn	60	222	89	228	70	200	88	233
Co	78	250	103	246	68	250	92	246
Cu	94	267	114	281	111	269	98	255
Zn	84	220		238	78	220	112	238
[ML_4X_2] complexes								
Fe	24		64	208				
Co	44	227	68	209	39	215	69	210
Ni	53	241	77	223	49	237	78	220

---

* Although some of the ν(M–N) assignments are not in agreement with those proposed in Sections C and K, their sequence is the same, so that the conclusions drawn from the sequence remain valid.

the strong electron-releasing effect of the γ-methyl groups which would prevent metal$\rightarrow$ligand π-bonding. Further investigation of these effects would be of great interest.

O. IR AND RAMAN SPECTRA OF THE COMPLEXES *trans*-[Pt(CH_2=CH_2)(py)X_2] (X = Cl, Br)

The vibrational spectra of Zeise's salt, K[Pt(CH_2=CH_2)Cl_3], and its derivatives *trans*-[Pt(C_2H_4)(L)X_2] where L represents various oxygen and nitrogen donor ligands, have elicited much interest [66–75] although, before 1983, isotopic (C_2D_4) labelling had only been applied to the IR spectra of Zeise's salt itself. In view of the doubt which attended certain of the metal–ligand assignments in these complexes, Thornton and coworkers [74] examined the IR and Raman specra of a series of the complexes *trans*-[Pt(C_2H_4)(L)X_2] including those with L = pyridine. The compounds were isotopically labelled by deuteration of the coordinated ethylene (C_2D_4) and pyridine (py-d_5) molecules. The vibrational data for the chloro complex are recorded in Table 15, from which it is clear that distinction between the ethylene and internal pyridine modes is readily achieved by the double isotopic labelling technique. The ν(C–C) modes of the coordinated ethylenes near 1250 cm^{-1} are very weak in the IR but, as expected, very intense in the Raman spectra. This feature is important because of the earlier arguments concerning the position of this band which had placed it near 1500 cm^{-1} [69]. The 1250 cm^{-1} region seems much more appropriate to a C–C stretching mode which has lost much of its double-bond character. The more specific assignments for the internal py modes (i.e. distinction between ring and C–H bands) were made on the basis of the ν^D/ν^H ratio as has been discussed in Section B.

The far-IR spectra are depicted in Fig. 7 and the frequencies are shown in Table 16. The ν(Pt–C_2) modes were assigned to the bands of highest frequency within the range 600–50 cm^{-1} which exhibited significant shifts

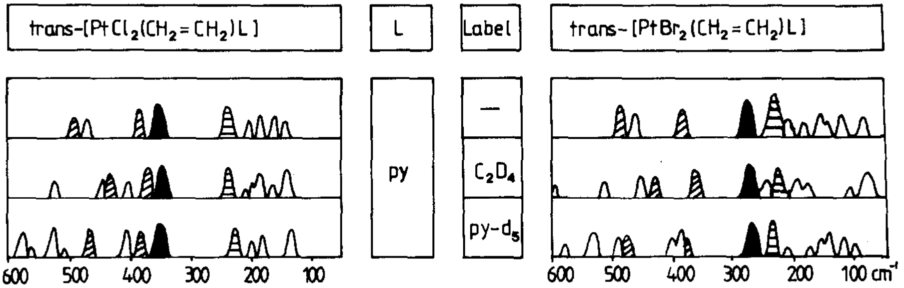


Fig. 7. Far-IR spectra of the complexes *trans*-[Pt(C_2H_4)(py)X_2]: bands with diagonal bars, ν(Pt–C_2); bands with horizontal bars, ν(Pt–N); solid bands, ν(Pt–X) [74].

TABLE 15

Internal ligand frequencies (cm^{-1}) and assignments for the complexes *trans*-[Pt(CH_2–CH_2)(py)Cl_2]

Unlabelled[a]	C_2D_4 labelled[a]	py-d_5 labelled[a]	Assignment[b]	
3098 (3098)	2368 (2368)	3092	ν(C–H) (ethylene)	
3078 (3076)	2334 (2331)	3078 (3083)		
3066 (3064)	2287 (2294)	3062 (3067)		
2980 (2977)	2214 (2224)	2980 (2973)		
	(3081)	2370	ν(C–H) (py)	
	(3067)	2342		
3030 (3046)	3040 (3046)	2310 (2316)		
		2294 (2297)		
		2268 (2289)		
1610 (1606)	1602 (1608)	1569 (1569)	ν(ring)	(8a)
(1570)	(1571)	1534 (1528)		(8b)
1473 (1528)	1472	1321		(19a)
1438	1434	1239		(19b)
1418	962 (964)	1429 (1426)	CH_2 scissor	
1395	1393 (1374)	1381	ν(ring)	(14)
1343	1342	1324		
1257 (1258)	962 (964)	1260 (1260)	ν(C–C) (ethylene)	
1245	1243	980 (985)	δ(C–H) (py)	(3)
1214 (1211)	1210 (1215)	889 (896)		(9a)
1153 (1156)	1151 (1159)	845 (842)		(15)
1075 (1070)	1065 (1074)	831	δ(C–H) (py)	(18b)
1068 (1050)	1065 (1054)	835		
1038 (1032)	716	1040	CH_2 wag	
1026	1019	1025	δ(ring)	(12)
1017 (1018)	1006 (1020)	1025		(1)
979	978	980 (985)		
944	943			
873	872 (822)	703 (705)	γ(C–H) (py)	(10b)
764	760 (772)	571		(11)
705 (702)	512 (514)	703 (680)	CH_2 rock	
692 (655)	688	528	γ(C–H) (py)	(4)
652 (646)	650 (650)	635 (623)	δ(ring)	(6a)
445	443 (432)	406	γ(ring)	(16b)

[a] Values in parentheses are the Raman frequencies. [b] Values in parentheses are the band numbers in the notation of Kline and Turkevich [1].

on ethylene-d_4 labelling but which were substantially less sensitive to deuteration of py. Conversely, those bands which shift most on deuteration of py were assigned to ν(Pt–N). Bands which are relatively insensitive to deuteration of both py and ethylene but which shift on substitution of the halides were assigned to ν(Pt–X). In this way, clear distinction between the three types of metal–ligand stretching frequency was possible.

TABLE 16

Metal–ligand frequencies and isotopically induced shifts (cm^{-1}) in the IR and Raman spectra of the complexes *trans*-$[Pt(CH_2{=}CH_2)(py)X_2]$ (X = Cl, Br) [74]

X	$\nu(Pt{-}C_2)$	$\Delta\nu$		$\nu(Pt{-}N)$	$\Delta\nu$		$\nu(Pt{-}X)$	$\Delta\nu$		$\delta(L{-}Pt{-}L)$	$\Delta\nu$	
		C_2D_4	py-d_5		C_2D_4	py-d_5		C_2D_4	py-d_5		C_2D_4	py-d_5
X = Cl												
IR	474	40	5	239	3	14	345	0	4	196	10	0
	381	12	5							171	0	0
										151	1	18
										133	1	0
Raman	472	40	0	227		17	336	0	0	207	11	5
	378	17	0				331	0	0	160	0	10
X = Br												
IR	468	38	0	260	3	30	260	3	3	217	1	5
	374	17	0							177	5	0
										149		0
										120	2	0
										92	2	0

Three previous studies of the spectra of the complexes with L = py, X = Cl had been made [68,71,73]. All three sets of data are internally consistent and were supported by the isotopic labelling study. The $\nu(\mathrm{Pt{-}C_2})$ bands of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$ have been assigned to the bands at 491 and 403 $\mathrm{cm^{-1}}$. The data in Table 16 show that both frequencies are lowered on replacing $\mathrm{Cl^-}$ by py ($\Delta\nu = 17\ \mathrm{cm^{-1}}$ and $22\ \mathrm{cm^{-1}}$ respectively). In Zeise's salt, the ligand trans to the olefin is chloride which is capable of forming only weak π bonds. The py molecule, on the other hand, is capable of forming strong π bonds with platinum(II) with consequent weakening of the Pt–olefin bonding [34].

P. 2-AMINOMETHYLPYRIDINE COMPLEXES OF MANGANESE, IRON, COBALT, NICKEL, COPPER, ZINC AND PLATINUM

2-Aminomethylpyridine (amp) is a structural intermediate between 2,2′-bipyridine and ethylenediamine. It belongs in this review because it is a (chelating) 2-substituted pyridine. Furthermore, it forms structurally interesting tris-, bis- and mono(amp) coordination compounds with rather complex IR spectra which were first comprehensively studied by Thornton and coworkers in 1977, employing ND_2 labelling of the amino groups [75].

The structural versatility of amp is indicated by the far-IR spectra depicted in Fig. 8 which are separated into groups of complexes with common stoichiometry. Figure 8 also includes the spectrum of amp itself which is observed to have four bands over the range 700–140 $\mathrm{cm^{-1}}$. Three (or occasionally all four) of these bands recur in the spectra of the complexes. The remaining bands are attributable to the metal–ligand stretching and bending modes.

The complexes of highest symmetry (C_3) are the tris(amp) complexes *fac*-$[M(amp)_3](ClO_4)_2$. The assignments for these and the bis and mono(amp) complexes were made on the following basis. The ND_2- and metal-sensitive band pair near 650 and 590 $\mathrm{cm^{-1}}$ which flank the ligand band near 625 $\mathrm{cm^{-1}}$ were assigned to the NH_2 rocking mode. In some of the complexes they are both on the low frequency side of the 625 $\mathrm{cm^{-1}}$ ligand band. A band which lies between the two ligand peaks of lowest frequency and another band with a frequency of about 380 $\mathrm{cm^{-1}}$ were assigned to $\nu(\mathrm{M{-}NH_2})$ since they are also ND_2 and metal sensitive. Some complexes exhibit only one $\nu(\mathrm{M{-}NH_2})$ band.

The first two bands below 300 $\mathrm{cm^{-1}}$ were assigned to ν(M–py) on the grounds of their insensitivity towards ND_2 labelling and the fact that they were metal sensitive in the sequence of crystal field stabilization energies of the complexes. Metal–halide stretches, ν(M–X), which were present only in the spectra of the complexes of formula $[M(amp)_2X_2]$ (M = Ni, Zn) and

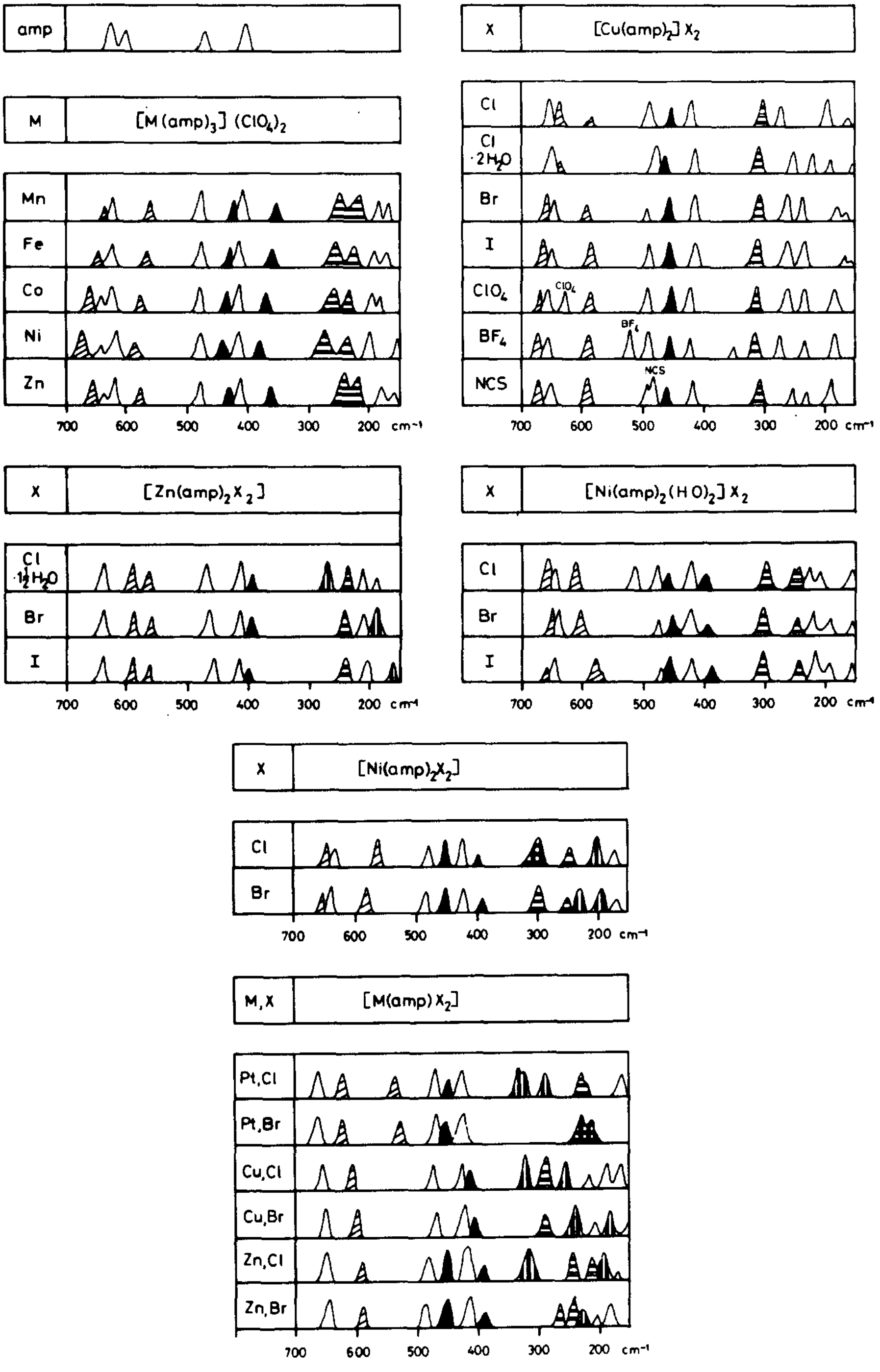


Fig. 8. IR spectra of 2-aminomethylpyridine (amp) complexes: shaded bands, NH_2 rock; solid bands, $\nu(M-NH_2)$; bands with horizontal bars, $\nu(M-py)$; bands with vertical bars, $\nu(M-X)$.

$[M(amp)X_2]$ (M = Cu, Zn, Pt), were identified by their X sensitivities and absence of ND_2 sensitivity. No ν(M–X) bands were observed in the complexes $[Cu(amp)_2]X_2$ or $[Ni(amp)_2(H_2O)_2]X_2$; hence they are formulated as shown. The basic structures and the number and frequency ranges of the metal–ligand stretching modes are summarized in Table 17.

Q. COBALOXIMES WITH AXIALLY COORDINATED PYRIDINE

Apart from a single labelling study [76] involving deuteration of the methyl group of $[Co(DH)_2(py)(CH_3)]$ (DH = dimethylglyoximate anion) all band assignments in cobaloxime complexes had been empirically based [77–83] preceding the multiple isotopic labelling study of $[Co(DH)_2(py)X]$ (Fig. 9; X = Cl, Br, I, CH_3) by Rutherford and Thornton in 1979 [84]. In the latter work, the assignments over the range 1650–150 cm^{-1} were based on ^{15}N labelling of the dimethylglyoximate anion and the pyridine nitrogen atom as well as pyridine deuteration and the effects of varying the trans axial ligand X. This technique had the advantages of enabling clear distinction to be made between the internal ligand modes of the dimethylglyoximate anion and the pyridine ring and of distinguishing between the two types of Co–N stretching bands, designated ν(Co–N)(DH) and ν(Co–N)(py). Furthermore, variation of X and the absence of isotopic shifts of the ν(Co–X) modes enabled firm assignments to be provided for the ν(Co–X) bands.

Figure 10 illustrates the spectra of the unlabelled and labelled derivatives of the complex with X = Cl and also the spectra of the complexes with various other groups X related to the spectra of pyridine and dimethyglyoxime. The internal pyridine modes can readily be identified in the spectra of the complexes since they are shifted very little by coordination but many of the dimethylglyoximate bands are significantly shifted by coordination and ^{15}N labelling of the anionic ligand is essential in order to identify the bands in the coordinated DH^- species.

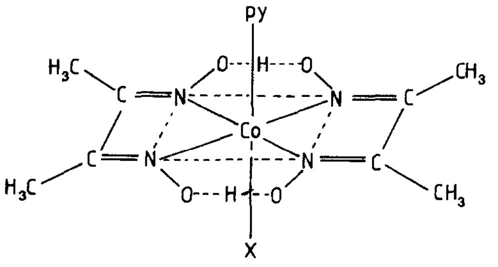


Fig. 9. Structure of cobaloxime complexes, $[Co(DH)_2(py)X]$.

TABLE 17

Formulae, structures and metal–ligand frequency ranges (cm^{-1}) for amp complexes [75]

Formula	Structure	$\nu(\mathrm{M{-}NH_2})$	$\nu(\mathrm{M{-}py})$	$\nu(\mathrm{M{-}Cl})$	$\nu(\mathrm{M{-}Br})$	$\nu(\mathrm{M{-}I})$
fac-$[\mathrm{M(amp)}_3](\mathrm{ClO}_4)_2$	Cis, cis octahedral	445–426	274–249			
		381–359	237–216			
trans-$[\mathrm{Zn(amp)}_2\mathrm{X}_2]$	Trans octahedral	398	240–239	273	188	160
trans-$[\mathrm{Cu(amp)}_2]\mathrm{X}_2$	Trans square planar	466–455	319–309			
cis-$[\mathrm{Ni(amp)}_2(\mathrm{H}_2\mathrm{O})_2]\mathrm{X}_2$	Cis octahedral	457–449	302–299			
		397–384	247–245			
cis-$[\mathrm{Ni(amp)}_2\mathrm{X}_2]$	Cis octahedral	452–450	299–291	291	235	
		397–394	252–248	205	194	
(*cis*)-$[\mathrm{Pt(amp)X}_2]$	(Cis) square planar	531–527	227	330	227	
		449	210	294	210	
$[\mathrm{Cu(amp)X}_2]$	Distorted octahedral with bridging and terminal X	411–405	292–287	318	245	
				254	182	
$[\mathrm{Zn(amp)X}_2]$	Tetrahedral	452–449	266–247	196	?	
		392–386	239–210			

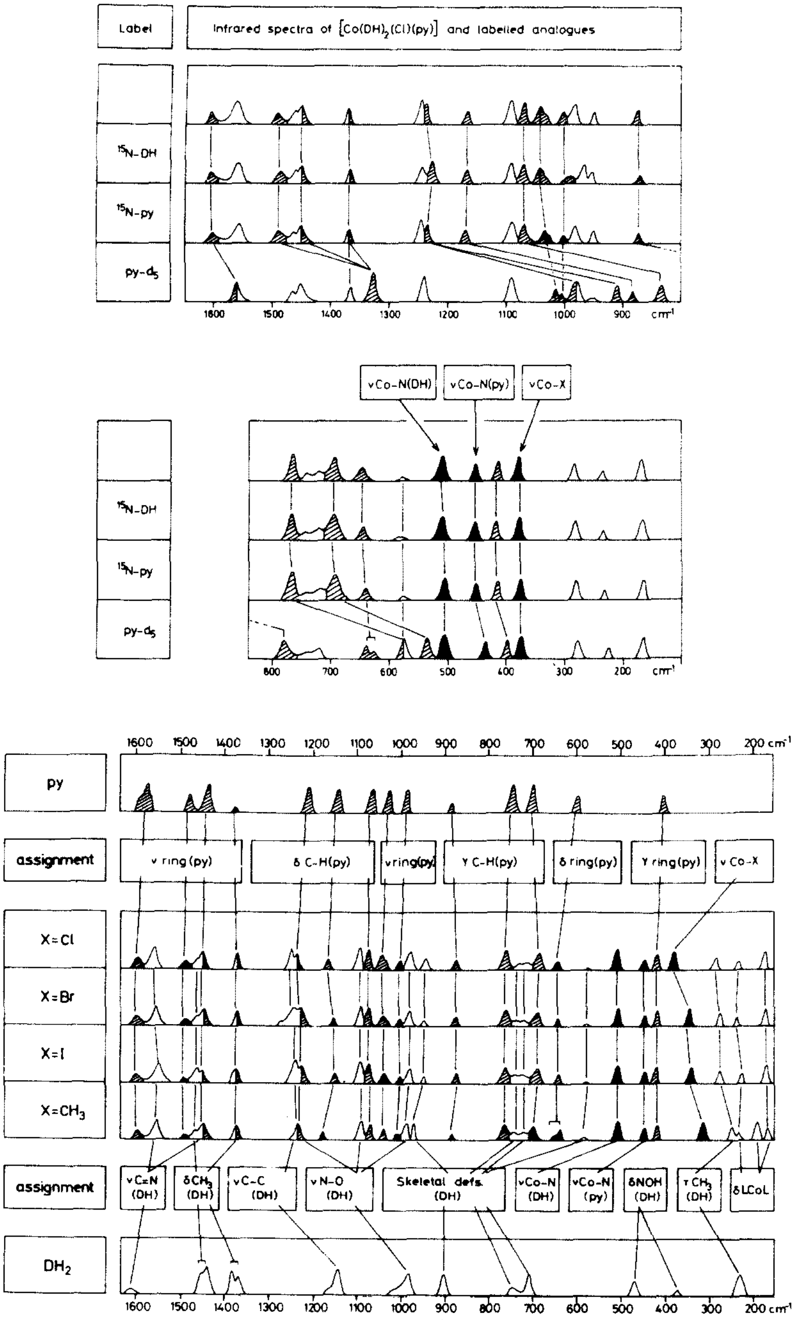


Fig. 10. Effects of isotopic labelling on the IR spectra of cobaloxime complexes, $[Co(DH)_2(py)X]$.

The strong band near 510 cm^{-1} is firmly assigned to ν(Co–N)(DH) by virtue of its sensitivity towards ^{15}N(DH) labelling but not towards deuteration or ^{15}N labelling of pyridine. Furthermore, it was virtually unaffected by varying X. The band near 450 cm^{-1} was assigned to ν(Co–N)(py) because of its sensitivity towards deuteration and ^{15}N labelling of pyridine but not towards ^{15}N(DH) labelling. It is also unaffected by X. The ν(Co–X) band is firmly assigned to the range 400–300 cm^{-1} where it is sensitive to X but unaffected by any type of isotopic labelling.

Rutherford and Thornton [85] extended the labelling study to the linkage isomers [Co(DH)$_2$(py)(NCS)] and [Co(DH)$_2$(py)(SCN)] by ^{15}N labelling of the py and NCS species as well as by deuterating the pyridine ring. In this way, the following assignments were made: isothiocyanate isomer; ν(Co–N)(DH) 513 cm^{-1}; ν(Co–N)(py) 464, 450 cm^{-1}; ν(Co–NCS) 377 cm^{-1}; thiocyanate isomer: ν(Co–N)(DH) 513 cm^{-1}; ν(Co–N)(py) 464 cm^{-1}; ν(Co–SCN) 356 cm^{-1}.

ACKNOWLEDGEMENTS

I wish to thank the pubishers for permission to reproduce figures and tables as follows: Elsevier Publishing Co. for Fig. 2 (from ref 18); Fig. 3 and Table 5 (from ref. 26); Fig. 4 and Table 6 (from ref. 33); Fig. 6 (from ref. 41); Fig. 7 and Table 15 (from ref. 74) and Fig. 8 (from ref. 75); Pergamon Press for Fig. 10 (from ref. 84) and Marcel Dekker Inc. for Table 1 (from ref. 6). I should also like to thank Mesdames M.A.P. Joska and G.A. Rootman for secretarial assistance and Mrs. E. Foulds and Dr. P.S. Hall for drawing the figures.

REFERENCES

1 C.H. Kline and J. Turkevich, J. Chem. Phys., 12 (1944) 300.
2 L. Corrsin, B.J. Fax and R.C. Lord, J. Chem. Phys., 21 (1952) 1170.
3 J.K. Wilmshurst and H.J. Bernstein, Can. J. Chem., 18 (1957) 1183.
4 D.A. Long, F.S. Murfin and E.L. Thomas, Trans. Faraday Soc., 59 (1963) 12.
5 D.B. Cunliffe-Jones, Spectrochim. Acta, 21 (1965) 747.
6 G.A. Foulds, J.B. Hodgson, A.T. Hutton, M.L. Niven, G.C. Percy, P.E. Rutherford and D.A. Thornton, Spectrosc. Lett., 12 (1979). 25.
7 A.T. Hutton and D.A. Thornton, Spectrochim. Acta, Part A, 34 (1978) 645.
8 P.T.T. Wong, Can. J. Chem., 52 (1974) 2005.
9 J. Bradbury, K.P. Forest, R.H. Nuttall and D.W.A. Sharp, Spectrochim. Acta, Part A, 23 (1967) 2701.
10 Y. Saito, M. Cordes and K. Nakamoto, Spectrochim. Acta, Part A, 28 (1972) 1459.
11 A.T. Hutton and D.A. Thornton, Spectrosc. Lett., 10 (1977) 57.
12 R.J.H. Clark and C.S. Williams, Chem. Ind. (London), (1964) 1317.
13 R.J.H. Clark and C.S. Williams, Inorg, Chem., 4 (1965) 350.

14 C.W. Frank and L.B. Rogers, Inorg. Chem., 5 (1966) 615.

15 D.M. Adams, Metal–Ligand and Related Vibrations, Arnold, London, 1967, p. 277.

16 J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York, 1971, p. 161.

17 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Ed., Wiley, New York, 1986, p. 206.

18 J.E. Rüede and D.A. Thornton, J. Mol. Struct., 34 (1976) 75.

19 M. Goldstein, E.F. Mooney, A. Anderson and H.A. Gebbie, Spectrochim. Acta, 21 (1965) 105.

20 P.T.T. Wong and D.G. Brewer, Can. J. Chem., 46 (1968) 139.

21 J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, J. Inorg. Nucl. Chem., 27 (1965) 1305; J. Chem. Soc. A, (1966) 1031.

22 C. Postmus, J.R. Ferraro and W. Wozniak, Inorg. Chem., 6 (1967) 2030.

23 G.E. Coates and D. Ridley, J. Chem. Soc., (1964) 166.

24 M. Goldstein and W.D. Unsworth, Inorg. Chim. Acta, 4 (1970) 342; Spectrochim. Acta, Part A, 28 (1972) 1107.

25 J.M. Haigh, R.D. Hancock, L.G. Hulett and D.A. Thornton, J. Mol. Struct., 4 (1969) 369.

26 C. Engelter and D.A. Thornton, J. Mol. Struct., 42 (1977) 51.

27 D.A. Thornton, Coord. Chem. Rev., 55 (1984) 113.

28 H. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.

29 R.J.H. Clark and C.S. Williams, Spectrochim. Acta, 22 (1966) 1081.

30 M.A. Porai-Koshits and A.S. Antsyshkina, Sov. Phys. Crystallogr., 3 (1958) 694.

31 A.D. Allen and T. Theophanides, Can, J. Chem., 42 (1964) 1551.

32 F. Herbelin, J.D. Herbelin, J.P. Mathieu and H. Poulet, Spectrochim. Acta, 22 (1966) 1515.

33 C. Engelter, A.T. Hutton and D.A. Thornton, J. Mol. Struct., 44 (1978) 23.

34 D.M. Adams, J. Chatt, J. Gerratt and A.D. Westland, J. Chem. Soc., (1964) 734.

35 J.R. Durig, B.R. Mitchell, D.W. Sink, J.N. Willis and A.S. Wilson, Spectrochim. Acta, Part A, 23 (1967) 1121.

36 A.H. Norbury and I.P. Sinha, J. Inorg, Nucl. Chem., 35 (1973) 1211.

37 P. Colamarino and P.L. Orioli, J. Chem. Soc., Dalton Trans., (1975) 1656.

38 J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York, 1971, p. 181.

39 M.R. Caira and L.R. Nassimbeni, Acta Crystallogr., Sect. B, 31 (1975) 581.

40 K. Nakamoto, C. Udovich and J. Takemoto, J. Am. Chem. Soc., 92 (1970) 3973.

41 C. Engelter and D.A. Thornton, J. Mol. Struct., 39 (1977) 25.

42 S. Akyüz, A.B. Dempster, R.L. Morehouse and S. Suzuki, J. Mol. Struct., 17 (1973) 105.

43 J.M. Haigh, N.P. Slabbert and D.A. Thornton, J. Mol. Struct., 7 (1971) 199.

44 D.A. Thornton, Coord. Chem. Rev., 104 (1990) 173.

45 N. Ohkaku and K. Nakamoto, Inorg. Chem., 12 (1973) 2440.

46 I.R. Beattie, G.P. McQuillan, L. Rule and M. Webster, J. Chem. Soc., (1963) 1514.

47 J.P. Clark and C.J. Wilkins, J. Chem. Soc. A, (1966) 871.

48 I.R. Beattie, M. Milne, W. Webster, H.F. Blayden, P.J. Jones, R.C.G. Killean and J.L. Lawrence, J. Chem. Soc. A, (1969) 482.

49 I. Tanaka, Organomet. Chem. Rev., Sect. A, 5 (1970) 1.

50 I. Tanaka, Y. Matsumura, R. Okawara, Y. Musya and S. Kinumaki, Bull. Chem. Soc. Jpn., 41 (1968) 1497.

51 L. Cattalani, R.J.H. Clark, A. Orio and C.K. Poon, Inorg. Chim. Acta, 2 (1968) 62.

52 D.H. Brown, K.P. Forest, R.H. Nuttall and D.W.A. Sharp, J. Chem. Soc. A, (1968) 2146.

53 R.A. Walton, J. Chem. Soc. A, (1969) 61.

54 L.G. Hulett and D.A. Thornton, Spectrochim. Acta, Part A, 29 (1973) 757.

55 D.H. Brown, R.H. Nuttall, J. McAvoy and D.W.A. Sharp, J. Chem. Soc., (1966) 892.
56 Y. Saito, C.W. Schläpfer, M. Cordes and K. Nakamoto, Appl. Spectrosc., 27 (1973) 213.
57 N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, J. Inorg. Nucl. Chem., 18 (1961) 79.
58 M. Goldstein and W.D. Unsworth, Spectrochim. Acta, Part A, 28 (1972) 1297.
59 A.B.P. Lever and B.S. Ramaswamy, Can. J. Chem., 51 (1973) 1582.
60 R.H. Nuttall and D.W. Taylor, Chem. Commun., (1968) 1471.
61 M. Choca, J.R. Ferraro and K. Nakamoto, J. Chem. Soc., Dalton Trans., (1972) 2297.
62 C.C. Addison and N. Logan, Adv. Inorg. Chem. Radiochem., 6 (1964) 71.
63 H.O. Desseyn, B.J. van der Veken, J.R. Moss, B.J. Smith, P. Verhoeven and D.A. Thornton, Spectrochim. Acta, Part A, 40 (1984) 467.
64 S. Akyüz, J.E.D. Davies, A.B. Dempster and K.T. Holmes, J. Chem. Soc., Dalton Trans., (1976) 1746.
65 S. Akyüz, J.E.D. Davies and K.T. Holmes, J. Mol. Struct., 42 (1977) 59.
66 S.I. Shupack and M. Orchin, J. Am. Chem. Soc., 85 (1963) 902.
67 S.I. Shupack and M. Orchin, Inorg. Chem., 3 (1964) 374.
68 H.P. Fritz and D. Sellmann, J. Organomet. Chem., 6 (1966) 558.
69 M. Orchin and P.J. Schmidt, Coord. Chem. Rev., 3 (1968) 345; Inorg. Chim. Acta Rev., 1 (1968) 123.
70 J. Hiraishi, Spectrochim. Acta, Part A, 25 (1969) 749.
71 T. Iwayanagi and Y. Saito, Inorg. Nucl. Chem. Lett., 11 (1975) 459.
72 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 14 (1975) 25.
73 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 16 (1976) 191.
74 T.P.E. Auf der Heyde, G.A. Foulds, D.A. Thornton, H.O. Desseyn and B.J. van der Veken, J. Mol. Struct., 98 (1983) 11.
75 M.L. Niven, G.C. Percy and D.A. Thornton, J. Mol. Struct., 68 (1980) 73.
76 O.S. Roshchupkina, I.P. Rudakova, T.A. Pospelova, A.M. Yurkevich and Yu G. Borod'ko, J. Gen. Chem. USSR, 40 (1970) 432.
77 A. Bigotto, G. Costa, V. Galasso and G. de Alti, Spectrochim. Acta, Part A, 26 (1970) 1939.
78 N. Yamazaki and Y. Hohokabe, Bull. Chem. Soc. Jpn., 44 (1971) 63.
79 D.G. Batyr, M.P. Starysh, V.N. Shafranskii and Yu Ya Kharitonov, Russ. J. Inorg. Chem., 17 (1972) 1728.
80 M.P. Starysh, V.N. Shafranskii, D.G. Batyr and Yu Ya Kharitonov, Russ. J. Inorg. Chem., 19 (1974) 508.
81 B.A. Bovykin and E.N. Yurchenko, Russ. J. Inorg. Chem., 20 (1975) 1574.
82 V.N. Shafranskii, D.D. Buburuz and T.N. Solkan, Russ. J. Inorg. Chem., 19 (1974) 1111.
83 A.A. Popova, V.N. Shafranskii and Yu Ya Kharitonov, Russ. J. Inorg. Chem., 20 (1975) 1002.
84 P.E. Rutherford and D.A. Thornton, Spectrochim. Acta, Part A, 35 (1979) 711.
85 P.E. Rutherford and D.A. Thornton, Spectrosc. Lett., 13 (1980) 427.