Contribution from the Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, United Kingdom

Spectroscopic Studies of Substituted Imidazole Complexes. IV. Complexes of Cobalt and Nickel with 2-(2′-pyridyl)benzimidazole and 2-(2′-pyridyl)imidazoline

D. M. L. Goodgame and A. A. S. C. Machado

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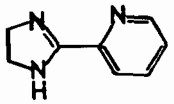
The preparations are reported of a series of complexes of the type ML_3X_2, where M = Co, Ni, or Zn and L = 2-(2′-pyridyl)benzimidazole (PYB) or 2-(2′-pyridyl)imidazoline (PYIM), and of the compounds $M(PYB)_2X_2$ (M = Co, Ni; X = Cl, Br, I, NCS). All the cobalt and nickel complexes show normal, high-spin magnetic properties. Electronic and low-frequency infrared spectra are reported and discussed. For the ML_3X_2 compounds ν(M-N) bands are assigned in the region 200-300 cm^{-1}.

Introduction

We have recently shown[1,2] that the iron(II) complexes FeL_3X_2, L = 2-(2′pyridyl)benzimidazole (PYB, I) and 2-(2′pyridyl)imidazoline (PYIM, II) are members of the interesting class of compounds showing spin-crossover behaviour. During this work we also prepared and studied a range of nickel and cobalt(II) complexes with these ligands to obtain further information about the ligand field properties and for comparison of their low frequency infrared spectra. A few of these compounds had been reported previously[3,4] but physical studies were limited to potentiometric investigations[5] and measurements[4,6] of infrared spectra above 700 cm^{-1}.



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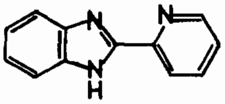

II

Experimental Section

Preparations: *ML_3X_2 (M = Co, Ni, or Zn; X = PYB or PYIM).* These were precipitated by mixing solutions of the corresponding hydrated metal salt and of ligand in 1:3 molar ratios. Where necessary the solutions were concentrated to precipitate the complexes and the solids were recrystallised. Details and analytical results are given in Table I. With 2-(2′-pyridyl)benzimidazole the nickel complexes were lilac and the cobalt(II) compounds were buff-coloured. Most of the nickel compounds with 2-(2′-pyridyl)imidazoline were beige in colour, but $Ni(PYIM)_3(NCS)_2$ was pale blue; the cobalt(II) complexes were again buff-coloured.

Tris[2-(2′-pyridyl)imidazole]nickel(II) Perchlorate Monohydrate. A solution of 1.1 g nickel perchlorate hexahydrate in ethanol (5 ml) was added to one of 2-(2′-pyridyl)imidazoline (1.3 g) also in ethanol (10 ml). The deep blue solution was evaporated almost to dryness, but no solid separated on cooling. Addition of water (10 ml) precipitated the complex, which was recrystallized by dissolving it in 50% aqueous ethanol (15 ml) and concentrating to small volume. The lilac solid was washed with water and dried in vacuo over P_2O_5 for 24 hrs. *Anal.* Calcd for $C_{24}H_{23}Cl_2N_9NiO_9$: C, 40.5; H, 3.3; N, 17.7. Found: C, 40.1; H, 3.3; N, 17.8%.

$M(PYB)_2X_2$ (M = Co or Ni). Pale green nickel complexes [$Ni(PYB)_2(NCS)_2$ was greyish white] and pink or buff cobalt(II) complexes were obtained as for the 3:1 compounds but using a 2:1 mole ratio of ligand and metal salt. $Co(PYB)_2(NCS)_2$ was obtained from an attempt to prepare $Co(PYB)_3(NCS)_2$. Details and analytical results are given in Table I.

Physical Measurements. These were obtained as described previously.[7]

Results

Nickel and cobalt(II) complexes of stoichiometries ML_3X_2 and ML_2X_2 were isolated (Table I) quite easily from acetone or ethanol solutions of the calculated molar proportions of the organic ligand and the requisite metal salt. Several of the compounds were obtained as monohydrates. Attempts to prepare Co-

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(3) B. Chiswell, F. Lions, and B.S. Morris, *Inorg. Chem.*, 3, 110 (1964).
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Table I. Preparative details and analytical results for some complexes of cobalt(II) and nickel with 2-(2'-pyridyl)-benzimidazole (PYB) and -imidazoline (PYIM).

Complex	Solvent	Yield %		Analysis [a], %	
			C	H	N
$Ni(PYB)_3(BF_4)_2$	EtOH	91	52.8 (52.85)	3.5 (3.3)	15.6 (15.4)
$Ni(PYB)_3(ClO_4)_2 . H_2O$	EtOH	73	50.1 (50.1)	3.4 (3.4)	14.5 (14.6)
$Ni(PYB)_3I_2$	EtOH	45	47.8 (48.1)	3.2 (3.0)	14.0 (14.0)
$Ni(PYB)_3Br_2$	EtOH	62	53.8 (53.8)	3.45 (3.4)	15.7 (15.7)
$Ni(PYB)_3Cl_2$	EtOH [b]	53	59.2 (60.4)	3.85 (3.8)	17.5 (17.6)
$Ni(PYB)_3(NCS)_2$	EtOH	91	58.4 (59.1)	4.3 (3.6)	19.8 (20.2)
$Co(PYB)_3(BF_4)_2 . H_2O$	EtOH	64	51.7 (51.6)	3.6 (3.5)	15.8 (15.0)
$Co(PYB)_3(ClO_4)_2 . H_2O$	EtOH	85	49.9 (50.2)	3.5 (3.4)	14.7 (14.6)
$Co(PYB)_3I_2$	Me_2CO/DMP [c,d]	70	48.3 (48.1)	3.3 (3.0)	14.1 (14.05)
$Co(PYB)_3Br_2$	Me_2CO/DMP [c]	62	53.5 (53.7)	3.5 (3.4)	15.9 (15.7)
$Co(PYB)_3Cl_2$	EtOH [e]	47	59.0 (60.4)	4.0 (3.8)	17.7 (17.6)
$Zn(PYB)_3(BF_4)_2 . H_2O$	EtOH [b]	68	51.8 (51.3)	3.7 (3.5)	14.6 (14.9)
$Zn(PYB)_3(ClO_4)_2$	n-BuOH	82	50.7 (50.9)	3.8 (3.2)	14.5 (14.8)
$Ni(PYIM)_3(BF_4)_2$	EtOH	52	42.7 (42.8)	4.0 (4.0)	18.65 (18.7)
$Ni(PYIM)_3(ClO_4)_2$	EtOH	43	41.2 (41.4)	3.8 (3.9)	18.0 (18.0)
$Ni(PYIM)_3I_2$	Me_2CO/DMP [f]	59	37.7 (38.2)	3.5 (3.6)	16.6 (16.7)
$Ni(PYIM)_3Br_2$	EtOH/DMP [f]	67	42.65 (43.7)	4.1 (4.1)	18.9 (19.1)
$Ni(PYIM)_3Cl_2$	EtOH/DMP [g]	35	49.5 (50.4)	4.9 (4.75)	21.6 (22.0)
$Ni(PYIM)_3(NCS)_2$	Me_2CO/DMP	32	50.5 (50.7)	4.3 (4.4)	24.0 (25.0)
$Co(PYIM)_3(BF_4)_2$	i-PrOH	59	43.3 (42.9)	4.5 (4.0)	18.7 (18.7)
$Co(PYIM)_3(ClO_4)_2$	i-PrOH [b]	72	41.3 (41.4)	4.0 (3.9)	17.8 (18.0)
$Co(PYIM)_3I_2$	EtOH	66	39.2 (38.4)	4.2 (3.6)	17.2 (16.7)
$Ni(PYB)_2Cl_2$ [e,h]	EtOH/DMP [d]	62	53.5 (52.6)	3.8 (3.7)	15.6 (15.0)
$Ni(PYB)_2Br_2$	Me_2CO/DMP [d]	50	47.25 (47.4)	3.3 (3.0)	13.6 (13.8)
$Ni(PYB)_2I_2$	Me_2CO/DMP [d]	33	41.9 (40.9)	3.0 (2.6)	11.5 (12.0)
$Ni(PYB)_2(NCS)_2$	EtOH	71	54.3 (55.1)	3.7 (3.2)	19.9 (19.8)
$Co(PYB)_2Cl_2$ [e,i]	EtOH [d]	52	53.4 (53.5)	3.7 (3.7)	15.2 (15.6)
$Co(PYB)_2Br_2$	EtOH [b]	65	47.2 (47.4)	3.25 (3.0)	13.7 (13.8)
$Co(PYB)_2I_2$	EtOH [b]	20	41.2 (41.0)	2.8 (2.6)	12.0 (11.95)
$Co(PYB)_2(NCS)_2$	EtOH	83	55.1 (55.2)	3.5 (3.2)	21.1 (19.9)

[a] Calcd. values in brackets. [b] Recryst. from EtOH. [c] DMP = 2,2-dimethoxypropane. [d] Recryst. from MeOH/EtOH. [e] Dried at 120°C in vacuum for 24 hours. [f] An oil formed initially, which solidified on heating and stirring. [g] Recryst. from n-BuOH/DMP. [h] Analytical figures are for monohydrate. Wt. loss on drying: found, 3.0%; Calcd. 3.3%. [i] Analytical figures are for monohydrate. Wt. loss on drying: found, 4.1%; Calcd. 3.3%.

$(PYB)_3(NCS)_2$ gave only the analogous 2:1 complex, although a 3:1 compound was obtained with nickel thiocyanate.

Electronic Spectra and Magnetic Properties. Although the conditions required for a change from high- to low-spin for cobalt(II) are met with ligand fields only slightly greater than for corresponding types of iron(II) complex, none of the CoL_3X_2 compounds studied here shows spin-crossover behaviour. Their room temperature magnetic moments (Table II) are nearly all in the range 4.9 ± 0.15 B.M., as frequently found[8] for high-spin six-coordinate cobalt(II). The moments of the various salts of the $Co(PYB)_3^{2+}$ cation change very little with the counter anion, but there is a marked anion depndence of the moment of the $Co(PYIM)_3^{2+}$ ion, and for two compounds, $Co(PYIM)_3X_2$ (X = BF_4 and I) the room temperature moments are quite low for six-coordinate cobalt(II). Despite its low room-temperature moment (4.47 B.M.), $Co(PYIM)_3(BF_4)_2$ was found to obey the Curie-Weiss law over the range 100-301 K with a relatively small Weiss constant (22°) (Table III). There is therefore no clear evidence that the relatively low moments observed for this compound, and, to a smaller extent, for the iodo-analogue, arise from spin-crossover behaviour. Indeed, the behaviour observed is similar to that found[8] for $Cophen_3(ClO_4)_2$, which has a moment of 4.66 B.M. at room temperature, decreasing to 4.25 B.M. at 78 K. The lower moments of the $Co(PYIM)_3^{2+}$ salts compared with those of their PYB analogues may arise from a greater distortion of the ligand field with consequent of the $^4T_{1g}$ level. However, these is no electronic spectral evidence for this (see below). Although it is, in principle, possible to obtain a quantitative measure of the ligand field distortions in six-coordinate cobalt(II) complexes from magnetic susceptibility data,[8] we have not attempted to do this for the compounds studied here, as the employment of average susceptibility measurements usually results in a good deal of ambiguity in the derived parameters.[8]

The nickel complexes are all high spin, and even in the case of $Ni(PYB)_2I_2$ the distortion of the ligand field from O_h symmetry is insufficient to cause the formation of a spin-singlet ground state.

The electronic spectra of the 3:1 nickel compounds show no measurable splitting of the bands arising from the spin-allowed transitions (Table II). In each case the ν_1 band ($^3A_{2g} \rightarrow {}^3T_{2g}$ in O_h) has a shoulder on

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Table II. Diffuse reflectance spectra (4000-25,000 cm^{-1}) and room temperature magnetic moments of some complexes of cobalt(II) and nickel with PYB and PYIM.

Compound	μ_{eff}	Band Max., cm^{-1}
$Ni(PYB)_3X_2$	(B.M.)	
$X=BF_4$	3.28	11,400, ~13,000 sh, 18,300, ~22,800 sh
ClO_4 [a]	3.17	11,500, ~12,900 sh, 18,000, ~22,600 sh, ~23,900 sh,
I	3.33	11,000, ~12,900 sh, 18,000, ~22,500 sh, ~23,700 sh,
Br	3.24	10,900, ~12,800 sh, 18,200, ~22,600 sh, ~23,800 sh,
Cl	3.20	11,200, ~12,900 sh, 18,200, ~22,500 sh, ~23,800 sh,
NCS	3.03	11,200, ~12,500 sh, 18,100, ~22,400 sh
$Ni(PYIM)_3X_2$		
$X=BF_4$	3.26	11,400, ~12,700 sh, 17,900
ClO_4	3.12	11,400, ~12,500 sh, 18,000
I	3.08	11,400,[b] 18,200
Br	3.15	11,400,[b] 18,300
Cl	3.03	11,400, ~12,500 sh, 18,100
NCS	3.13	10,600, ~12,900 sh, 17,500
$Ni(PYB)_2X_2$		
$X=Cl$	3.12	~8,900 sh, 9,800 15,400, ~25,000 sh, s
Br	3.12	~8,100 sh, 9,900, 15,900, ~25,000 sh, vs
I	3.22	~8,500 sh, 10,000, 16,600, ~25,000 sh, vs
NCS	3.22	10,200, 12,700 wsh, 17,200, ~21,600 sh, w.
$Co(PYB)_3X_2$		
$X=BF_4$ [a]	4.88	10,200, ~18,800 sh, ~20,700 sh, ~22,200 sh
ClO_4 [a]	4.92	10,300, ~18,500 sh, ~20,800 sh
I	4.81	10,000, ~18,500 sh, ~20,600 sh, ~ 22,100 sh
Br	4.88	9,900, ~18,500 sh, ~20,600 sh, ~22,200 sh
Cl	4.89	9,900, ~18,700 sh, ~20,600 sh, ~22,100 sh
$Co(PYIM)_3X_2$		
$X=BF_4$	4.47	10,600, ~18,300 sh, ~20,000 sh, ~23,300 sh
ClO_4	4.80	10,200, ~18,400 sh, ~19,900 sh, ~22,700 sh
I	4.67	10,500, ~18,200 sh, ~20,000 sh, ~23,200 sh
$Co(PYB)_2X_2$		
$X=Cl$	4.84	8,700, (14,800 wsh)[c], 19,300, 20,200 sh
Br	4.84	8,500, (13,900 wsh)[c] 19,000, 19,800 sh
I	4.62	8,700, (13,000w)[c], ~19,100 sh, 19,900
NCS	5.02	9,700, ~18,600 sh, 20,400, ~22,100 sh
$Ni(PYI)_3(ClO_4)_2$ [a,d]	3.14	11,400, ~12,700 sh, 18,300

[a] As monohydrate. [b] Asymmetric to higher energy. [c] Band probably due to tetrahedral cobalt(II) impurity (see text). [d] PYI = 2-(2′-pyridyl)imidazole.

Table III. Temperature dependence of magnetic moments.

	$Co(PYB)_3(BF_4)_2 . H_2O$			$Co(PYIM)_3(BF_4)_2$			$Co(PYIM)_3(ClO_4)_2$	
T°K	$10^3 . \chi_m$	μ_{eff} [a]	T°K	$10^3 . \chi_m$	μ_{eff}	T°K	$10^3 . \chi_m$	μ_{eff}
297	10.17	4.91	301	8.28	4.46	299	9.75	4.83
294	10.02	4.85	298	8.44	4.48	296	9.48	4.74
227	12.66	4.79	278	9.00	4.47	245	11.90	4.83
180	15.74	4.76	213	11.41	4.41	208	13.71	4.78
140	19.59	4.68	182	13.12	4.37	170	16.17	4.69
101	25.63	4.55	138	16.95	4.33	142	19.37	4.69
			100	21.99	4.19	106	25.31	4.63
	θ [b] $=26°$			$\theta=22°$			$\theta=12.5°$	

[a] B.M.; calc. from Curie Law. [b] Defined by $\mu_{eff} = 2.83\ [\chi_m(T+\theta)]^{1/2}$.

its higher energy side, but this is of very low intensity and almost certainly arises from a transition to the $^1E_g(D)$ level. Only two of the three spin-allowed bands were observed; that at highest-energy was obscured by very intense, electron transfer absorption above 26,000 cm^{-1}. (The $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition is expected to lie at *ca.* 29,000 cm^{-1} in these complexes). The Dq values of ca. 1120 cm^{-1} for $Ni(PYB)_3^{2+}$ and 1140 cm^{-1} for $Ni(PYIM)_3^{2+}$ are close to the critical values at which spin-crossover occurs for the analogous iron(II) complexes.[9] They are, however, at the low end of this critical Dq region (compare e.g. $Nien_3^{2+}$ has Dq 1120 cm^{-1} whereas $Feen_3^{2+}$ is high-spin).

In contrast to the 3:1 compounds the $Ni(PYB)_2X_2$ complexes, where X=Cl, Br, or I, show a splitting of the ν_1 electronic band (Figure 1, Table II). These splittings are much smaller than those found[10,11] for

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(11) D.A. Rowley and R.S. Drago, *Inorg. Chem.*, 6, 1092 (1967).

a range of *trans*-NiL_4X_2 compounds, where L = pyridine or a related amine ligand (in $Nipy_4Br_2$, for example the splitting of the $^3T_{2g}$ level is ca. 3000 cm^{-1}). Accordingly it seems likely that the 2-(2′-pyridyl)benzimidazole complexes have *cis*-configurations.

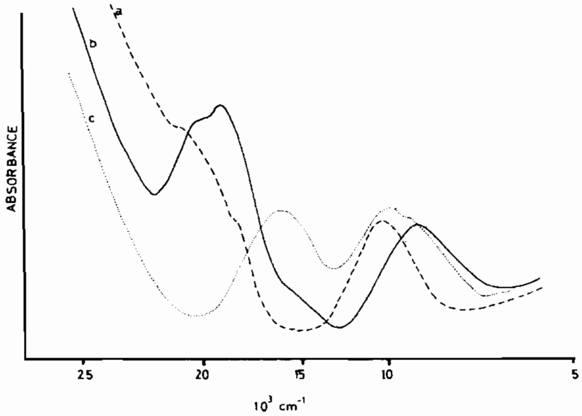

Figure 1. Reflectance Spetcra of: a) $Co(PYB)_3(ClO_4)_2 \cdot H_2O$; b) $Co(PYB)_2Cl_2$; c) $Ni(PYB)_3Cl_2$.

The electronic spectral behaviour of the cobalt(II) complexes resembles that of their nickel analogues. For both 3:1 and 2:1 compounds the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition remains unsplit. The lack of splitting for the $Co(PYB)_2X_2$ complexes again differs appreciably from the situation with other cobalt(II) halide compounds of the type *trans*-CoL_4X_2.[12] Assignment of the bands at higher frequencies in the 3:1 complexes is complicated by the presence of strong electron transfer absorption above ∼25,000 cm^{-1}, which causes the d-d bands in this region to appear only as shoulders, and also by the fact that for Dq values in the 10,000-12,000 cm^{-1} region the $^4A_{2g}$ and $^4T_{1g}$ levels cross.[13] Moreover, transitions to either, or both, of two levels ($^2\Gamma_6$,$^2\Gamma_8$) derived from spin-doublet free ion terms may be expected in this region, as they can gain intensity from nearby spin-allowed transitions.

For lingand fields of Dq ∼ 860 cm^{-1} the ν_2 transitions is expected[13] to be clearly on the low energy side of the ν_3 band, and the component at ca. 19,000 cm^{-1} for the halide complexes is within the energy range expected for this transition. However, the observed component seems to be too intense for this assignment as ν_2, as this transition is normally quite weak.

The visible bands of the 2:1 complexes are displaced to somewhat lower energies and they are better resolved from the electron transfer absorption (Figure 1).

The very weak shoulder or band found in the 13,000 - 15,000 cm^{-1} region for each of the halo-complexes $Co(PYB)_2X_2$ might correspond to spin-forbidden transitions to levels derived from the ^2G free ion term, which are expected at ca. 15.000 cm^{-1} in O_h symmetry. However, the energies of these weak bands increase in the order I < Br < Cl and this, and their position, suggest that they may be due to traces of tetrahedral cobalt(II) species (possibly CoX_4^{2-}) present as impurities.

Infrared Spectra

450-4000 cm^{-1} region. - Chelation has previously been shown[6] to have relatively little effect on the i.r. bands of PYB and PYIM in the region 650-5000 cm^{-1}, and the spectra of the free ligands and their complexes are also similar in the 450-650 cm^{-1} region. However we noted one discrepancy from the reported[6] spectrum of PYIM. The band at 1664 cm^{-1} assigned by Lane *et al* as the C=N stretch, was not present in the spectrum of the pure ligand. Since it apppeared in the spectrum of the crude ligand but disappeared after successive recrystallizations it was probably due to the strong ν(C=O) band of α-picolinic acid, used in the ligand preparation.

The ν_1 anion bands of the complexes $M(PYB)_2(NCS)_2$ are both markedly split (M = Ni 2122 vs, 2046 vs; M = Co 2110 vs, 2040 vs cm^{-1}). Such splitting is in accord with a *cis*-configuration, which is known to be present in $Fe(bipy)_2(NCS)_2$[14] and which was suggested above for the halide complexes $M(PYB)_2X_2$ (M = Co,Ni) from their electronic spectra.

150-450 cm^{-1} region - Assignment of low frequency i.r. spectra of compounds of this type, on an empirical basis, is complicated by several factors. Coordination may alter both the frequencies and the intensities of bands observed in the spectrum of the free ligand, and indeed, may activate a ligand mode. Moreover, particularly in systems involving chelating ligands, the absorption bands observed frequently originate from complex vibrational modes due to coupling between more than one simple metal-ligand, or internal ligand, mode. Thus the description M-N stretch for a band with marked M dependence in a series of $[ML_3]^{n+}$ ions is generally a convenient simplification implying that M-N stretching contributes appreciably to that particular mode. It is in this sense that the various assignments are made in the following discussion.

In the case of the $[ML_3]^{2+}$ (M = Co, Ni, L = PYB, PYIM) salts reported here, assignment has been aided by recent studies of the effect of metal isotope replacement in related species with 2,2′–bipyridine (bipy) and 1,10–phenanthroline (phen)[15] and by force constant calculations[16] for some $M(bipy)Cl_2$ compounds.

Three i.r. active M-N stretches are expected for a cation ML_3^{n+} where L is a bidentate, chelating amine of formal D_3 symmetry and for high-spin complexes of cobalt(II) or nickel these would be expected to lie below 400 cm^{-1} and probably below 350 cm^{-1}.

In the case of the $M(PYB)_3X_2$ compounds (Table IV) coordination raises the frequencies of the 399 and 342 cm^{-1} ligand bands and broadens or splits them, whereas the bands at 308 and 425 cm^{-1} remain relatively unaffected. Significant changes occur in the 200 – 300 cm^{-1} region. Comparison of the spectra

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Table IV. Low frequency spectra (150-450 cm^{-1}) of PYB and M(PYB)$_3$X$_2$ (M = Co, Ni, Zn).

PYB		M=Co					M=Ni						M=Zn		
R[a]	IR	X=BF$_4$	ClO$_4$	I	Br	Cl	BF$_4$	ClO$_4$	I	Br	Cl	NCS	BF$_4$	ClO$_4$	Assignment[d]
	425s	424	428	426	425	424	423	425	424	425	426	426	423	424	
			416sh		415sh		414sh	415sh	415sh	415sh		417sh			
404w	399s	406	406	408	410	409	410sh	410sh	408sh	409sh	412sh		403br	403br	L
350vw	342m	350br	356br	356br	355br	350br	365br	351br	361	361	358br	~358br	356	~356br	
									355	355			347		
					318w		323w	323w	324w	325w	323w				?
317vw	308w	306w	306	305	305w	303w	308w,sh	311w,sh	307w,sh	309w,sh	308w,sh	308w,sh	306w	308w	L
298vw							296s,sh	297s,sh	293s	297s	296s	296s			ν(Ni-N)
							290s	290s							
275m	279m	283s	284s	280	282	284	284s,sh	285s,sh	281s	287s	286s	287s	288sh	294sh	L+ν(Co-N) ?
	268m	277sh	276sh						271	274	273sh	275sh	279s	283s	
		253	253sh	250	250	244sh	258	259	248	249	253	255			ν(M-N)
206sh		244sh	242	233	232	234	219	220	218	219	218	~220	224s,br	224s,br	ν(M-N)
189s	197w	~195[c]	~190[c]	189[c]	190[c]	~200[c]	~200[c]	196[c]	194	195	~200[c]	192[c]	[d]	[d]	L
151m	151w	154	154br	153	157br	[d]	162br	164	161vs	160vs	178vs,br	168			L or X dep.
											140br				

[a] R = Raman; [b] L = ligand mode; [c] Very broad absorption, position ill-defined as near changeover point (200 cm^{-1}) between DM4 and GM3 spectrometers; [d] Not measured below 200 cm^{-1}.

Table V. Low frequency I.R. spectra (100-300 cm^{-1}) of some complexes M(PYB)$_2$X$_2$ (M = Co, Ni).

M=Ni				M=Co			
X=Cl	Br	I	NCS	Cl	Br	I	NCS
293s	292s	291	290	289s	286s	286s	286
284s	281s	281	281	279s	277sh	278s	276
			~260sh				~252sh
247s	245s	242	~252br	234s	235s	238	240br
			225		222sh		~228sh
208s	212sh	~200		202		208	206
			~185br		193	195	~185br
178br	160br	162w		170br	155br	155	
145		132w	125br	137	112		
100br	112br	~100w	110sh		103br		100br

of analogous nickel, cobalt, and, for two anions (ClO_4^- and BF_4^-), zinc, complexes, with one another and with i.r. and Raman spectra of PYB leads to the assignments shown in the final column of Table IV.

All the complexes show strong absorption at 270 – 300 cm^{-1}, either as a single, broad band or as two or three well-resolved bands. The free ligand has medium intensity i.r. bands at 268 and 279 cm^{-1} (the latter having Raman activity) but the nickel complexes all show an additional well-defined strong band, split in two cases, near 295 cm^{-1}. As this is not present for the cobalt and zinc complexes it is reasonably assigned to a ν(Ni–N) mode. On the basis of the usual trend of metal donor stretching frequencies for octahedral first-row M^{2+} complexes, the corresponding absorption for the cobalt complexes probably overlaps the ligand bands at 270-280 cm^{-1}. The band for the zinc analogues is expected to be at much lower frequencies,[15] and, in agreement with this, there is a strong band at 224 cm^{-1} for each of the Zn(PYB)$_3$X$_2$ compounds. The cobalt and nickel complexes each show two other ν(M-N) bands, at ~220 and 248-259 cm^{-1} for nickel, and at 232-244 and ~250 cm^{-1} for cobalt. These assignments of ν(M–N) for the M(PYB)$_3$X$_2$ complexes correspond well with those[15] for Ni(phen)$_3$X$_2$ (243, 260, and 300 cm^{-1} when X = ClO_4[15]).

One feature of the spectra of the nickel complexes which remains unexplained is the weak band near 324 cm^{-1}. This has a counterpart in only one of the other complexes, Co(PYB)$_3$Br$_2$. It is possibly an activated ligand band corresponding to the weak Raman band at 317 cm^{-1} but this does not explain why it appears more consistently with the nickel complexes than with the others.

In the case of the M(PYB)$_2$X$_2$ compounds the bands involving M-donor atom stretches are found below 300 cm^{-1} (Table V) but their assignment is not clear-cut. Instead of the strong, and frequently complex, absorption found at 270-300 cm^{-1} for the M(PYB)$_3$X$_2$ compounds the 2:1 complexes all show a well resolved doublet in this region quite similar in relative intensity to the pair of bands observed at 268 and 279 cm^{-1} for the free ligand. However, in view of the small, but consistent metal dependence of the observed frequencies, and the ν(M–N) values found for the M(PYB)$_3$X$_2$ compounds, it seems likely that these bands arise from modes with both ligand and ν(M–N) character.

All the M(PYB)$_2$X$_2$ compounds show strong, and generally broad, absorption at 230-250 cm^{-1}. Identification of one of the two expected (if *cis*-octahedral) ν(M–NCS) bands for the isothiocyanates is relatively straightforward as each shows a strong shoulder at ~260 (Ni) or ~252 cm^{-1} (Co) in addition to the main band at lower energy. There is also another component in each case at ~225-230 cm^{-1} which may be the other ν(M–NCS) absorption, but a similar band is observed for Co(PYB)$_2$Br$_2$. An alternative possibility would be the strong, broad band at ~185 cm^{-1} for each of the isothiocyanates.

For the chlorides the broad band at 234 (Co) and 247 (Ni) is much stronger than for the other halides and it may contain ν(M–Cl). The Ni–Cl stretch in Nipy$_4$Cl$_2$ has been reported[17] to be at 246 cm^{-1} but lower values (~190-200 cm^{-1}) have been observed[18]

Table VI. Low frequency spectra (200-400 cm^{-1}) of PYIM and (M(PYIM)$_3$X$_2$.

PYIM		M=Co			M=Ni						
R^a	IR	X=BF$_4$	ClO$_4$	I	BF$_4$	ClO$_4$	I	Br	Cl	NCS	
375s		368w	~370w	~370w	~370w	372w	373w	372w	372w		L
		352w			~370vw						$\nu_2(BF_4^-)$
					291s		292s	292s	294s		ν(Ni-N)
265s	258s, br	267s, sh	260s, br	270s	281s	283s, br	279s	276s	280s	274s, br	ν(M-N) or L
		254s, br	246s, sh	256s	268s, sh		268s, sh	264s, sh	272s, sh		
		220w, sh	224	223	240w	241w	239w	238w	239w	240	ν(M-N)

^{a} Raman.

for some other *trans*-NiL$_4$Cl$_2$ compounds. Other, strong X-dependent bands were found for the M(PYB)$_2$X$_2$ complexes at ~170-180 cm^{-1} (X = Cl) and ~150-160 cm^{-1} (X = Br).

The i.r. and Raman spectra of PYIM are much simpler than those of PYB (Table VI) in the region 200-400 cm^{-1}. The strong 375 cm^{-1} Raman band appears weakly in the i.r. spectra of the complexes, and the assignments of the M—N stretches for these last follow closely those of the analogous PYB compounds (Table VI).

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