Complexes of 2- and 4-Vinylpyridines with Cobalt(II) and Nickel(II) Halides and Pseudohalides

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Complexes of cobalt(II) and nickel(II) with 2-vinylpyridine (2-vpy) and 4-vinylpyridine (4-vpy) exhibit various stereochemistries according to their stoicheiometry and the anion X present: octahedral, $M(4\text{-vpy})_4X_2$ (M = Co, Ni; X = Cl, Br, I, NCO, NCS); polymeric octahedral, $M(4\text{-vpy})_2X_2$ [M = Co, X = Cl (mauve-form), N_3; M = Ni, X = Cl, Br, N_3, NCS]; and tetrahedral, $Co(4\text{-vpy})_2X_2$ (X = Cl, Br, I) and $Co(2\text{-vpy})_2X_2$ (X = Cl, Br, I, NCS). Structures have been assigned from the electronic, i.r., and far-i.r. spectra, and magnetic behaviour of the complexes. In several cases the assigned structures have been confirmed by *X*-ray powder investigations. The complexes $M(4\text{-vpy})_2(N_3)_2$ are antiferromagnetic while the complexes $Ni(4\text{-vpy})_2X_2$ (X = Cl, Br) are weakly ferromagnetic.

COBALT(II) and nickel(II) halides and pseudohalides react with a large range of substituted pyridines to form adducts of the types ML_nX_2 where $n = 2$ or 4. The stereochemistries are known, from *X*-ray and other physical measurements, to be octahedral monomeric ($n = 4$), polymeric octahedral ($n = 2$) with halogen or pseudohalogen bridging, or tetrahedral monomeric or planar. Previously,[1] the complex $Co(4\text{-vpy})_4Cl_2$ was shown to be octahedral while $Co(4\text{-vpy})_2Cl_2$ and $Co(2\text{-vpy})_2Cl_2$ were tetrahedral (2-vpy and 4-vpy are respectively 2- and 4-vinylpyridine). No polymeric octahedral species, similar to that formed by pyridine, was obtained from cobalt(II) chloride and 2-vinylpyridine. Here we report a further series of cobalt(II) halide and pseudohalide complexes with these ligands, including polymeric $Co(4\text{-vpy})_2Cl_2$, and also report a related series of nickel(II) complexes. Certain of the compounds were prepared in order to study their polymerisability in the solid state.[2]

Electronic Spectra.—Octahedral monomeric systems. In these complexes the stoicheiometric ratio of vinylpyridine to metal salt was 4 : 1. The results of previous workers have indicated that the symmetry of this species is not pure O_h but that tetragonal distortion along the *z* axis of the molecule leads to a symmetry closer to D_{4h}. This has been confirmed[3] by *X*-ray measurements, and it causes some modification of electronic spectra from that expected for O_h symmetry.

In O_h symmetry six-co-ordinate, high-spin cobalt(II) exhibits[4] three spin-allowed bands in the visible–u.v. region: ν_1, ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$; ν_2, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$; and ν_3, ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$. The assignments are given under these general headings in Table 1. However, in D_{4h} symmetry the ν_2 and ν_3 bands are usually found, as here, to be multiple.[4] The proximity and splitting of the ν_2 and ν_3 bands means that considerable overlap of the band envelopes occurs and a complex collection of bands, which cannot readily be assigned, is observed in the region 18 000—23 000 cm^{-1} (Table 1).

The position of ν_1 is in the region 8 000—9 000 cm^{-1}.[4] In D_{4h} symmetry this band is observed to split into two components (${}^4B_{2g}$ and ${}^4E_g$) to an extent dependent upon the amount of distortion present. Thus the complexes $Co(4\text{-vpy})_4(NCO)_2$ and $Co(4\text{-vpy})_4(NCS)_2$ show no splitting of this band, and this indicates that the pseudohalogen is *N*-bonded.

The related nickel(II) complexes are similar. Nickel(II) complexes in O_h symmetry exhibit simple spectra with three spin-allowed transitions to the ${}^3T_{1g}(P)$, ${}^3T_{1g}(F)$, and ${}^3T_{2g}$ levels in the regions 19 000—27 000 cm^{-1} (ν_3), 11 000—20 000 cm^{-1} (ν_2), and 7 000—13 000 cm^{-1} (ν_1) respectively. Tetragonal distortion causes some splitting of certain levels,[5] in particular those arising from the ${}^3F$ and ${}^3P$ states. Because of this splitting more electronic transitions are possible and ν_2 and especially ν_1, may be observed to split into two components. As with the cobalt(II) complexes similar donor properties of pyridine and pseudohalogen result

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TABLE 1

Octahedral monomeric complexes (D_{4h})
Cobalt(II)

		Electronic reflectance spectra (kK) [a,b]			Absorption bands in the far-i.r. region (cm^{-1})			Assignments of pseudohalogen group bands (cm^{-1}) [e,g]			Analyses (%) Found (Calc.)				
		$^4T_{1g}(P)\nu_3$	$^4A_{2g}(F)\nu_2$	$^4T_{2g}(F)\nu_1$	ν(M-py)	ν(M-X)	Other modes (unassigned)	ν_{as}	ν_s	δ	Metal	C	H	N	Halogen
Co(4-py)$_4$(NCO)$_2$ (red)	RT	21·6s, 20·8ssh, 19·65ms,sh, 18·25ms	15·65m,sh	9·4ms	214ms, 201s, 195m,sh	308w,sh, 298s,[f] 290w,sh	262w,sh, 250ms	2210s	1325m	619ms	10·4 (10·4)	63·2 (63·9)	5·1 (5·0)	14·8 (14·9)	
	LT	22·0ms, 21·05ms,sh, 20·05ms, 19·7ms, 18·3ms	15·6w	9·8ms	215s, 202m,sh	307wm,sh, 301wm,sh, 294ms [f]	270m, 265w,sh, 253ms								
Co(4-vpy)$_4$(NCS)$_2$ (red)	RT	21·2s,sh, 20·35s, 18·6m,sh	15·6m,sh	9·6s	206s	276m [f]	266m, 252m,sh, 246s	2090s		481ms	9·9 (9·9)	60·4 (60·5)	5·3 (4·8)	14·2 (14·1)	
	LT	21·4s,sh, 20·5s, 19·8s,sh	15·6m,sh	9·9s	212s,sh, 208s	280s [f]	262m, 254m,sh, 246s, 229w, 172w								
Co(4-vpy)$_4$Cl$_2$ (red)	RT	19·8ms, 18·95ms, 18·2m,sh		9·35m,sh, 8·6m, 7·3m,sh	220s	198s	273m, 246wm, 132m				10·8 (10·7)	60·9 (61·1)	5·1 (5·1)	10·1 (10·2)	12·8 (12·9)
	LT	20·05ms, 19·05ms, 18·4m,sh		8·95m, 7·2m											
Co(4-vpy)$_4$Br$_2$ (purple)	RT	19·0ms, 18·45ms, 17·8m,sh		8·6m, 6·0m,sh	199ms	137ms,[f] 131m,sh, 109m, 101m	271wm, 253wm				9·4 (9·2)	49·1 (49·4)	4·4 (4·2)	8·3 (8·2)	20·9 (20·9)
	LT	19·2ms, 18·6ms, 17·8m,sh		8·8m, 6·2m	210s, 186ms	140ms,[f] 136m,sh, 109m	273wm, 258wm, 250w,sh								
Co(4-vpy)$_4$I$_2$ (olive green)	RT	18·4s, 17·4s,sh	15·05m,sh, 13·25m,sh	8·3m, 5·35m	204m,sh, 197m,sh, 171wm	104wm,sh, 92m [f]	267m, 246w,sh				7·9 (8·0)	52·4 (52·6)	4·4 (4·4)	8·3 (8·8)	24·8 (25·0)
	LT	18·5ms, 17·6ms	15·2m,sh, 13·05m,sh	8·55m, 5·4m	211ms, 203m,sh, 174m	108m,sh, 95m [f]	270m, 246w,sh								

Nickel(II) [e]

		$^3T_{1g}(F)$			$^3T_{2g}(F)$												
		^3E_g	$^3A_{2g}$	$^1E_g(D)$	$^3B_{2g}$	^3E_g	ν(M-py)	ν(M-X)	Other modes (unassigned)	ν_{as}	ν_s	δ	Metal	C	H	N	Halogen
Ni(4-vpy)$_4$(NCO)$_2$ (blue)	RT	17·05m		12·95w,sh	10·2m		228s, 222m,sh	310m,[f] 304m,sh	271m,sh, 262s	2210s	1314m	615ms	10·4 (10·4)	63·9 (64·0)	5·0 (5·0)	15·0 (14·9)	
	LT	17·5m		12·95w,sh	10·6m		233s, 223m,sh	314m, 308m	272s,sh,268s, 210wm								
Ni(4-vpy)$_4$(NCS)$_2$ (violet)	RT	17·4m		12·85m,sh	10·4m		226m	293m [f]	266ms, 253m,sh	2080s		488ms	9·9 (10·0)	59·5 (60·5)	4·9 (4·8)	14·0 (14·1)	
	LT	17·6m	16·3m,sh	12·8m,sh	10·8m												
Ni(4-vpy)$_4$Cl$_2$ (pale blue)	RT	15·7ms		10·35w,sh	12·2m	8·55ms	234w,sh, 220m,sh	209s, 184m,sh, 178m [f]	278wm, 256wm, 144m, 140m				11·1 (11·2)	60·8 (61·1)	5·1 (5·1)	10·0 (10·2)	13·0 (12·9)
	LT	16·2ms	14·8m,sh	10·9w,sh	12·0m	8·6ms											
Ni(4-vpy)$_4$Br$_2$ (blue green)	RT	15·9ms	13·5m,sh	11·45m,sh	12·4m,sh	7·6ms	208s	132m,[f] 113m	276m, 263m,sh				9·0 (9·2)	51·8 (52·6)	4·3 (4·4)	8·7 (8·8)	24·7 (25·0)
	LT	15·4ms	13·6m	11·6m,sh	12·25m,sh	8·0ms											
Ni(4-vpy)$_4$I$_2$ [d] (olive green)	RT	15·75ms	12·4m	10·9m,sh	12·4m	7·2ms	219m, 208s, 186m	110m,[f] 100w, 86m	276m, 256w				8·0 (8·0)	45·4 (45·8)	3·8 (3·9)	7·8 (7·6)	31·6 (34·6)
	LT	16·3m	12·6m	11·0m,sh	12·6m	7·4ms											

Octahedral polymeric complexes (C_i)
Cobalt(II)

		$^4T_{1g}(P)$	$^4A_{2g}(F)$	$^4T_{2g}(F)$	ν(M-py)	ν(M-X)	Other modes (unassigned)	ν_{as}	ν_s	δ	Metal	C	H	N	Halogen
Co(4-vpy)$_2$Cl$_2$ (mauve)	RT	19·8m,sh, 18·9ms, 18·05m,sh	15·9m	8·0br, 6·1m	216m	170m, 164m	152wm,sh				17·0 (17·3)	49·1 (49·4)	4·4 (4·2)	8·3 (8·2)	20·9 (20·9
	LT	19·9m,sh, 19·05ms, 18·35m,sh	16·15ms, 15·1m,sh	8·8m, 6·2m											
Co(4-vpy)$_2$(N$_3$)$_2$ (pink)	RT	20·2m,sh, 18·8m, 18·1m,sh, 17·4m,sh		8·05m				2135m	1349m, 1297m	665m, 620wm, 602wm	16·4 (16·7)	48·1 (47·6)	4·3 (4·0)	31·7 (31·7)	
	LT	20·2m,sh, 19·0ms, 18·2m,sh, 17·45m,sh		8·15m											

TABLE 1 (*Continued*)

		Electronic reflectance spectra (kK) [a,b]							Absorption bands in the far-i.r. region (cm^{-1})			Assignments of pseudohalogen group bands (cm^{-1}) [e,g]			Analyses (%) Found (Calc.)				
		$^3T_{1g}(P)$			$^3T_{1g}(F)$		$^3T_{2g}(F)$												
		^3E_g	$^3A_{2g}$	$^1T_{2g}(D)$	$^3A_{2g}$	^3E_g	^3E_g	$^3B_{2g}$	ν(M-py)	ν(M-X)	Other modes (unassigned)	ν_{as}	ν_s	δ	Metal	C	H	N	Halogen
Octahedral polymeric complexes (C_i) Nickl(II)																			
Ni(4-vpy)$_2$Cl$_2$ (yellow)	RT	24·15s	22·8m,sh	19·9w,sh	13·75m	12·35m,sh	8·15m	5·95m	233s	184s, 178m, 167m	291w				17·2 (17·3)	48·9 (49·5)	4·1 (4·2)	8·0 (8·2)	20·5 (20·6)
	LT	24·4m	23·0m,sh	20·5w	14·2m	12·6m,sh	8·35m	6·05m											
Ni(4-vpy)$_2$Br$_2$ (yellow)	RT	22·45m	22·15m,sh	19·45w	12·4m	11·95	7·8m	5·65m	224m, 212m,sh	154s, 143sh	288m, 260m				13·5 (13·7)	39·1 (39·2)	3·3 (3·3)	6·5 (6·5)	36·4 (37·3)
	LT	23·6m	22·6m,sh	20·1m,sh	13·9m	12·4m,sh	8·1m	5·95m											
Ni(4-vpy)$_2$(N$_3$)$_2$ (green)	RT			21·1w,sh	15·6m		9·25m		201m	294ms	344m, 263ms, 248ms, 166m	2070s	1365m, 1305m	677w, 670w,sh, 623w, 604w	16·6 (16·6)	47·5 (47·6)	4·2 (4·0)	32·0 (31·8)	
	LT	23·2m,sh		21·5m,sh	16·15m	14·45	9·65m	8·65m,sh											
Ni(4-vpy)$_2$(NCS)$_2$ (green)	RT			20·55m	16·6m		8·4ms		224ms	293ms	249m, 264ms	2110ms	790wm, 782w	470ms	15·1 (15·2)	48·6 (49·9)	3·6 (3·7)	14·9 (14·6)	
	LT			20·95m	17·1m		8·75ms												
Tetrahedral monomeric complexes (C_{2v}) Cobalt (II)																			
		$^4T_1(P)$			$^4T_1(F)$														
Co(4-vpy)$_2$Cl$_2$ (blue)	RT									342ms, 313ms						49·2 (49·4)	4·1 (4·2)	8·0 (8·2)	20·9 (20·9)
Co(4-vpy)$_2$Br$_2$ (blue)	RT	16·8s,sh, 16·05s, 14·9s,sh			9·2ms, 6·2s,sh, 5·75s,sh, 5·2s				233m,sh, 224m,sh	257m, 244m,sh	281ms				14·1 (13·7)	39·0 (39·2)	3·3 (3·3)	6·5 (6·5)	37·3 (37·3)
	LT	16·8s,sh, 15·9s, 15·05s,sh			9·4ms, 7·25s, 7·0s,sh, 6·05s				240ms, 224ms	258m, 252m,sh	285s, 271m								
Co(4-vpy)$_2$I$_2$ (green)	RT	15·95s,sh, 15·05s,sh, 14·6s			8·95ms, 6·85ms, 5·9m,sh				226ms, 220m,sh	248m, 214m,sh	269wm, 137wm				11·3 (11·3)	33·7 (32·2)	2·8 (2·7)	5·3 (5·4)	
	LT	16·1s,sh, 15·2s,sh, 14·7s			9·15ms, 6·85ms, 5·8ms				234m,sh, 230s	252m, 214m	272wm, 140wm								
Co(2-vpy)$_2$Cl$_2$ (blue)	RT	17·4s,sh, 16·0s, 15·2s,sh			9·0ms, 7·2s, 6·05s				230wm, 225w,sh	334m, 314m	304m,sh, 285wm, 122w,sh, 115wm				17·9 (17·3)	49·3 (49·4)	4·3 (4·2)	8·1 (8·2)	21·5 (20·9)
	LT	17·4s,sh, 16·0s			9·2ms, 7·35ms, 6·05s														
Co(2-vpy)$_2$Br$_2$ (blue)	RT	16·65s,sh, 15·4s			8·7s, 7·3s,sh, 7·0s, 5·85s				248ms, 230ms	285m, 264ms	174w, 142w, 107w, 94wm, 77wm				13·9 (13·7)	39·2 (39·2)	3·1 (3·3)	6·2 (6·5)	37·5 (37·3)
	LT	16·7s,sh, 15·5s			8·5s, 7·3s,sh, 6·8s, 5·9s														
Co(2-vpy)$_2$I$_2$ (green)	RT	16·3s, 15·2s, 14·5s			8·1s, 6·7s, 5·8s,sh				242wm,sh, 235m	216m	284wm, 277w,sh				11·4 (11·3)	32·2 (32·2)	2·7 (2·7)	5·4 (5·4)	48·6 (48·5)
	LT	16·25s,sh, 15·2s, 14·55s			8·2s, 6·8s, 5·75s														
Co(2-vpy)$_2$(NCS)$_2$ (blue)	RT	16·95s, 15·4s,sh			9·05s,sh, 7·55s, 6·8s,sh, 5·65m,sh				248wm, 220w	322m, 303ms	293m,sh, 163m, 80wm,sh	2078s 2055s	847w, 833w	477m	15·1 (15·3)	49·6 (49·9)	4·0 (3·7)	14·4 (14·5)	
	LT	17·1s, 15·8s,sh			8·25s,br, 7·0m,sh, 5·6ms														

[a] RT = room temperature, LT = liquid-nitrogen temperature. Near i.r. overtone bands of the substituted pyridines occurred at 5·9 kK and 6·05 kK in the spectra of all 2-vpy and 4-vpy complexes. [b] Some very weak bands occurred between the strong, assigned bands in a number of the complexes. These were considered to be spin-forbidden and are not reported in detail. [c] The $^3T_{1g}(P)$ band and (ν_3) was obscured by charge-transfer absorptions in these complexes. [d] A medium intensity band was found at 19·2 kK at liquid-nitrogen temperature. [e] In some complexes notably Ni(4-vpy)$_4$Cl$_2$ and ' blue ' Co(4-vpy)$_2$I$_2$ the positions of the ν(metal–pyridine) and ν(metal–halogen) vibrations were found to overlap. [f] These are the bands assigned to metal-halogen or pseudohalogen stretching frequencies. Other bands in this column also show halogen dependence. [g] In some cases ν_s is obscured by ligand absorptions.

in smaller distortion and spectra approximately as expected for O_h symmetry.[6]

The data (Table 1) show that the splitting of the bands, especially ν_1, increases in the order NCO $\approx$ NCS $<$ Cl $<$ Br $<$ I as expected from the positions of the ligands in the spectrochemical series. *X*-Ray powder investigations * show that $Ni(4\text{-vpy})_4Cl_2$ and $Co(4\text{-vpy})_4Cl_2$ are isomorphous.

Polymeric octahedral systems. Two forms of cobalt(II) halogeno-complex containing a 2 : 1 ratio of pyridine to metal have been shown to exist in the solid state,[7] a mauve polymeric octahedral form and a blue tetrahedral monomeric form. As in the case of $Co(py)_2Cl_2$ (py = pyridine), it is found that the two forms of $Co(4\text{-vpy})_2Cl_2$ can be readily distinguished by their colour and electronic spectra and also by their magnetic behaviour and far-i.r. spectra. The electronic spectrum of the mauve compound resembles more closely the spectra of the 4 : 1 monomeric systems than those of the blue form and the other 2 : 1 complexes. The 2 : 1 azido-complex also shows a similar spectrum, indicating an octahedral polymeric structure.

The mauve form of $Co(4\text{-vpy})_2Cl_2$ is stable at room temperature. As with $Co(py)_2Cl_2$ on heating, to 98°, a rapid solid-state rearrangement [8] to the blue complex occurred. The same transformation occurred on prolonged exposure to sunlight, but the *X*-ray powder pattern indicated that the change was not quantitative. The complexes, mauve $Co(4\text{-vpy})_2Cl_2$ and $Ni(4\text{-vpy})_2Cl_2$ have very similar *X*-ray powder patterns and are isomorphous, or nearly so. The powder diffractogram of the tetrahedral blue form of $Co(4\text{-vpy})_2Cl_2$ is quite different.

To interpret the spectra of the 2 : 1 nickel(II) complexes the approximation to D_{4h} symmetry is again made and the bands assigned as for the 4 : 1 complexes, but since the positioning of the pyridine and halogen ligands is reversed with respect to the 4 : 1 complexes, the splittings of the bands are inverted.

Monomeric tetrahedral systems. These complexes were also of pyridine to metal ratio 2 : 1, but of symmetry C_{2v}. Tetrahedral, four-co-ordinate cobalt(II) complexes exhibit two broad and split absorption bands in the near-i.r. and visible regions: ν_3, the ${}^4T_2(P) \leftarrow {}^4A_2$ transition, and ν_2, the ${}^4T_1(F) \leftarrow {}^4A_2$ transition.[9,10]

The tetrahedral [11a] and polymeric bridged [11b] structures assigned to blue and to mauve $Co(4\text{-vpy})_2Cl_2$ respectively have been confirmed by *X*-ray investigations.[11] The metal–ligand bond lengths are very similar to those in $Co(py)_2Cl_2$.

All the complexes of 2-vinylpyridine prepared with cobalt(II) were tetrahedral. The *X*-ray powder pattern of $Co(2\text{-vpy})_2Cl_2$ was very similar to that of $Zn(2\text{-vpy})_2Cl_2$ which is also expected to be tetrahedral. Bivalent cobalt readily takes up a tetrahedral stereochemistry. Tetrahedral nickel(II) halide pyridine complexes are less common [12] than the octahedral forms and attempts to prepare such complexes with 2-vinylpyridine resulted in failure, anhydrous nickel halides being obtained in every case. 2-Substituents favour the formation of tetrahedral nickel(II) complexes, *e.g.* $Ni(2\text{-Mepy})_2Cl_2$ but with 2-vinylpyridine and nickel(II) the steric effect is perhaps too large to permit complex formation except in solution. Construction of molecular models indicates that the steric effect of 2-vinylpyridine is greater than that caused by 2-methylpyridine in this type of system.

Far-i.r. Spectra.—The metal-substituted pyridine vibrations have been assigned on the assumption that for a series of complexes of equivalent stereochemistry, the vibrations will occur at approximately the same frequencies [13,14] if significant coupling with other vibrational modes is absent. Some coupling between vibrations of the same symmetry would be expected to occur and this would cause some variation in the band positions. It has been shown, for example, by normal co-ordinate analysis, that in $Si(py)_2Cl_4$ the purity of the metal–nitrogen mode is in the region of 40—67%.[15] However, since the vibrations are primary stretchings the variations would be expected to be small.

Since several sets of compounds of the same stereochemistry were available in which the halogen varied from Cl to Br to I it was possible to assign the metal–halogen stretching vibrations (Table 1) with reasonable certainty. For the tetrahedral complexes the ratios: $\nu(M\text{–}Br)/\nu(M\text{–}Cl)$ and $\nu(M\text{–}I)/\nu(M\text{–}Cl)$, from these assignments, were about 0·75 and 0·65 as usual,[14] but the values of terminal $\nu(M\text{–}Br)$ were sometimes slightly below the lower limit of the quoted [14] range (300—200 cm^{-1}). As in the pyridine complexes, the ν(M–Halogen) frequencies diminished as the co-ordination number increased, but the frequencies of the octahedral monomers and polymers were similar.

In the 4 : 1 monomeric octahedral species only one i.r.-active stretching vibration would be expected, but in the polymeric octahedral, and tetrahedral species two bands are expected (Table 1). This was found to be the case in the tetrahedral (2 : 1) complexes studied, but

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only partially true in the spectra of polymeric (2 : 1) and monomeric (4 : 1) complexes. Metal–pseudohalogen vibrations, although not as well characterised as the metal–halogen vibrations, were found in the 250—300 cm^{-1} region.[16]

TABLE 2

Magnetic data [a,b]

Co(4-vpy)$_2$(N$_3$)$_2$			Ni(4-vpy)$_2$(N$_3$)$_2$		
T/K	χ_A	μ_e	T/K	χ_A	μ_e
296	9 620	4·77	296	3 840	3·01
263	10 530	4·71	263	4 177	2·96
230	11 690	4·63	230	4 559	2·90
199	13 020	4·53	199	5 037	2·83
167	14 620	4·41	167	5 641	2·74
136	16 340	4·21	136	6 286	2·59
104	17 990	3·85	104	7 160	2·45
90	18 540	3·63	90	7 839	2·36
$\theta = 86°$, $\chi_L = 148$			$\theta = 110°$, $\chi_L = 148$		

	Co(4-vpy)$_2$Cl$_2$ (mauve)		Ni(4-vpy)$_2$Cl$_2$		Ni(4-vpy)$_2$Br$_2$	
T/K	χ_A	μ_e	χ_A	μ_e	χ_A	μ_e
295	11 700	5·26	4 895	3·40	4 720	3·34
262	13 180	5·24	5 543	3·42	5 280	3·33
230	15 050	5·26	6 370	3·43	6 077	3·34
199	17 370	5·25	7 532	3·42	7 091	3·35
166	20 480	5·21	9 187	3·49	8 549	3·37
136	24 600	5·16	11 696	3·57	10 802	3·41
104	31 160	5·08	15 975	3·64	14 330	3·44
90	35 370	5·03	19 111	3·71	16 802	3·48
	$\theta = 14°$, $\chi_L = 166$		$\theta = -17°$, $\chi_L = 166$		$\theta = -11°$, $\chi_L = 195$	

Co(4-vpy)$_4$(NCO)$_2$			Ni(4-vpy)$_4$(NCO)$_2$		Ni(4-vpy)$_4$Cl$_2$		
T/K	χ_A	μ_e	χ_A	μ_e	T/K	χ_A	μ_e
295	10 350	4·94	4 211	3·15	306	4 082	3·17
263	11 550	4·92			287	4 356	3·18
198	15 070	4·88	6 486	3·20	271	4 586	3·17
167	17 750	4·86			229	5 407	3·16
103	26 870	4·70			189	6 504	3·15
95	28 750	4·67			150	8 225	3·15
					121	10 180	3·14
					101	12 130	3·14
			132 K 9295	3·17			
$\theta = 18°$, $\chi_L = 293$			$\theta = 0°$, $\chi_L = 293$		$\theta = 3°$, $\chi_L = 332$		

Room-temperature results (compounds above excluded)

	μ_e	χ_L		μ_e	χ_L
Co(4-vpy)$_4$Br$_2$	5·10	320	Ni(4-vpy)$_4$Br$_2$	3·22	320
Co(4-vpy)$_2$I$_2$	4·49	227	Ni(4-vpy)$_4$I$_2$	3·21	352
Co(2-vpy)$_2$Br$_2$	4·62	195	Ni(4-vpy)$_4$(NCS)$_2$	3·18	313
			Ni(4-vpy)$_2$Br$_2$	3·33	195
			Ni(4-vpy)$_2$(NCS)$_2$	3·07	188

[a] Curie–Weiss law taken as $\chi_A \propto 1/(T + \theta)$. [b] χ_A in c.g.s.u. $\times 10^6$; μ_e in B.M.; χ_L = diamagnetic correction $\times 10^6$.

Difficulty was experienced with the assignments of the spectra of monomeric octahedral complexes because of the unexpected multiplicity of bands. Examples can be seen in the Figure which shows the spectra obtained for the compounds Ni(4-vpy)$_4$X$_2$ (X = Cl, Br, or I). The spectra are similar in the 200 cm^{-1} region; hence the bands here are assigned to metal–pyridine vibrations. The main halogen-dependent vibrations seem to be at 184 and 176 cm^{-1} (chloride), 132 and 113 (bromide), and 110 and 86 cm^{-1} (iodide). The higher frequency band in each case is assigned to the metal–halogen stretching vibration. This agrees with recent work [14b] on Ni(py)$_4$X$_2$ (py = pyridine), except that ν(Ni–Cl) was placed at 207 cm^{-1} where in our spectra intense halogen-insensitive bands occur.

Ligand and Internal Pseudohalogen Vibrations.—The i.r. spectra of the co-ordinated organic ligands show only relatively small differences from the spectra of the free ligands.

Three pseudohalogen frequencies can be of use in determining the bonding mode of the group; these are the symmetric and asymmetric vibrations, ν_s and ν_{as}, and the deformation, δ. These are respectively found in the regions 1 400—600, 2 200—2 000, and 800—600 cm^{-1} (Table 1). The increase in frequency of ν_{as} in going from Ni(4-vpy)$_4$(NCS)$_2$ to Ni(4-vpy)$_2$(NCS)$_2$ is as commonly found for terminal and bridged NCS.[17] The medium intensity of the ν_s vibration in all the azido-complexes indicates that it forms a single-atom bridge [18] since for a linearly bridged complex the vibration should be i.r. inactive as in the azide ion. In this limited series of compounds i.r. evidence alone does not lead to an unambiguous assignment of the donor atoms of the pseudohalides.

Far-i.r. spectra: a = Ni(4-vpy)$_4$Cl$_2$, b = Ni(4-vpy)$_4$Br$_2$, c = Ni(4-vpy)$_4$I$_2$

Magnetochemical Results.—The magnetic moments of the cobalt(II) compounds of the stoicheiometry Co(4-vpy)$_4$X$_2$ are of the magnitude expected [19] for high-spin, six-co-ordinate cobalt(II) compounds, and Co(4-vpy)$_4$(NCO)$_2$ obeyed the Curie–Weiss law with a moderate θ value, showing the usual temperature variation of magnetic moment arising from varying orbital contribution in this type of compound. The mauve form of Co(4-vpy)$_2$Cl$_2$ also behaved magnetically as an octa-

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hedral complex in agreement with the polymeric structure assigned from spectral data. The azido-complex $Co(4\text{-vpy})_2(N_3)_2$ obeyed the Curie–Weiss law with a large θ value of 86° and a magnetic moment of 4·77 B.M. at room temperature which is reduced even below the spin-only value (3·87 B.M.) at 90 K. The reduction would indicate that unlike in polymeric octahedral $Co(4\text{-vpy})_2Cl_2$ considerable antiferromagnetic interactions are present in addition to the normal orbital contribution. The magnetic moments of $Co(2\text{-vpy})_2Br_2$ and $Co(2\text{-vpy})_2I_2$ are as expected[19] for tetrahedral complexes (4·4—4·8 B.M.).

The magnetic moments of the nickel(II) complexes at room temperature are compatible[19] with octahedral structures, tetrahedral structures being excluded by the reflectance spectra. The halide-bridged compounds $Ni(4\text{-vpy})_2Cl_2$ and $Ni(4\text{-vpy})_2Br_2$ show weak ferromagnetic interactions as has been found[20] in some similar compounds. The failure of the reflectance and far-i.r. spectra to alter significantly on cooling showed that the magnetic results were not affected by stereochemical changes. The corresponding azido-nickel(II) compounds have low, temperature-dependent magnetic moments arising from antiferromagnetic interactions, and this would suggest that, as in related manganese(II) complexes,[18] the azido-groups form bridges through a single nitrogen atom.

EXPERIMENTAL

Most complexes were prepared by the addition of the stoicheiometric amount of ligand in alcoholic solution to an aqueous alcoholic or aqueous solution of the metal halide or pseudohalide. Ethanol was used in the preparation of the nickel complexes and propan-2-ol in the preparation of the cobalt(II) complexes since the latter were very soluble in ethanol. Except in the cases of cobalt iodide and thiocyanate, metal iodides and pseudohalides were not used directly but were prepared by metathesis of the transition-metal nitrate with the appropriate alkali-metal salt in ethanolic or aqueous ethanolic solution.

Several attempts were made to prepare the 2-vinylpyridine complexes of nickel halides. Ethanolic solutions of the pyridine and the metal salt were vacuum distilled, and benzene added to replace the ethanol removed. This method, proved successful with related systems,[21] gave only anhydrous nickel halides. A blue oil was obtained by the addition of ether to a solution of the reactants in dimethylformamide, but this rapidly decomposed to the anhydrous chloride in the atmosphere.

Pyridine complexes of nickel iodide are often planar, but attempts to prepare similar complexes of 4-vinylpyridine failed. When 2 : 1 ratios of amine and iodide were mixed in ethanol only the 4 : 1 complex separated. Complete removal of the ethanol and treatment with benzene left an intractable mixture. Similarly only $Co(4\text{-vpy})_4(NCS)_2$ could be obtained.

All materials were of reagent grade or purer. Ligands were purified as before.[1] Analyses were carried out by standard procedures.[22]

Electronic spectra (40 000—5 000 cm^{-1}) were recorded at room and liquid nitrogen temperatures by the diffuse reflectance technique on a Unicam SP 700 C spectrophotometer. Far-i.r. spectra (400—30 cm^{-1}) of the solid complexes as Nujol mulls between Polythene plates were determined at room and liquid-nitrogen temperatures on an R.I.I.C. FS 720 Fourier spectrometer. Magnetic moments from room to liquid-nitrogen temperature were measured by the Gouy method using a Newport Instruments Gouy balance. The susceptibilities of all the compounds investigated were independent of field strength.

[3/313 *Received*, 12*th February*, 1973]

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