Nickel(II) Complexes of 2-(2-Pyridyl)imidazole

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The preparation, diffuse reflectance and i.r. spectra, and magnetic moments of complexes of the type [Ni(pyim)$_3$]X [pyim = 2-(2-pyridyl)imidazole; X = Cl$_2$,2H$_2$O or (NO$_3$)$_2$,3H$_2$O)], Ni(pyim)$_2$X$_2$ (X = Cl, Br, or I) and Ni(pyim)$_2$X$_2$,H$_2$O (X = Cl or Br) are described. The complexes Ni(pyim)$_2$X$_2$ and Ni(pyim)$_2$X$_2$,H$_2$O appear to have a dimeric halogen-bridged *cis*-octahedral structure.

THE stereochemical and spectroscopic properties of nickel(II) halide complexes of 2,2-bipyridyl (bipy) are well known [1,2] but studies on complexes of the related ligand 2-(2-pyridyl)imidazole (pyim) have been restricted to their formation in aqueous solution [3,4] and to the isolation, and determination of the magnetic moments, of just three complexes in the solid state.[5] Because of the important differences observed in the properties of the bipy and pyim complexes of Fe^{II} [6] and Cu^{II} [7] we have studied some Ni^{II} complexes of pyim in detail.

EXPERIMENTAL

The compound Ni(pyim)$_3$Cl$_2$,2H$_2$O was prepared by mixing ethanolic solutions of nickel(II) chloride hexahydrate (1 mol) and 2-(2-pyridyl)imidazole (8 mol) followed by precipitation with diethyl ether. Ni(pyim)$_3$(NO$_3$)$_2$,3H$_2$O was prepared in a similar manner except that a 3 : 1 mol ratio of pyim : Ni(NO$_3$)$_2$,6H$_2$O was used. Ni(pyim)$_2$Cl$_2$,H$_2$O, Ni(pyim)$_2$Br$_2$,H$_2$O, and Ni(pyim)$_2$I$_2$ were also prepared in this way using a 2 : 1 mol ratio of pyim to the appropriate metal salt. The anhydrous complexes Ni(pyim)$_2$Cl$_2$ and Ni(pyim)$_2$Br$_2$ were obtained by refluxing the hydrated complex with 2,2-dimethoxypropane for 8 h and filtering off the anhydrous complex in a dry-box. Ni(bipy)$_2$Cl$_2$,3H$_2$O was prepared as described previously.[2]

All the complexes were dried *in vacuo* over silica gel at room temperature. Analytical figures are given in the Table.

Diffuse reflectance and i.r. spectra (450—200 cm^{-1}) and magnetic measurements were determined as previously described.[6,7] I.r. spectra below 200 cm^{-1} were determined by the P.C.M.U. at Harwell.

	Analysis								Infrared (400—480 cm^{-1})			
	Found (%)				Required (%)							
	C	H	N	Ni	C	H	N	Ni	pyim bands	Ni–pyim band	Ni–X band	Other bands
Ni(pyim)$_3$Cl$_2$,2H$_2$O	48·3	4·2	20·9	9·7	47·95	4·2	21·0	9·8	422m,vb; 416m; 385w,b	162s		278m,vb; 243m; 205sh; 186s
Ni(pyim)$_3$(NO$_3$)$_2$,3H$_2$O	43·1	3·5	23·0	8·9	42·9	4·0	22·9	8·7	418m,b; 385w			282m,vb; 243m; 205vw †
Ni(pyim)$_2$Cl$_2$,H$_2$O	44·1	3·5	19·3	13·2	43·9	3·7	19·2	13·4	426m; 416m; 388w	175sbv	143s	292m,b; 245s; 240s; 216s
Ni(pyim)$_2$Cl$_2$	45·6	3·6	19·9	13·7	45·8	3·4	20·0	14·0	426m; 416m; 388w			292m,b; 245s; 240s,sh; 216s †
Ni(pyim)$_2$Br$_2$,H$_2$O	36·9	2·8	15·9	10·9	36·5	3·1	15·9	11·1	425m; 444m; 389vw	168m	128s, 110s	294m; 243s; 237s,sh; 209s
Ni(pyim)$_2$Br$_2$	37·6	2·7	16·7	11·4	37·8	2·8	16·5	11·5	424m; 413m; 388vm			294m; 242s; 237m,sh; 208s †
Ni(pyim)$_2$I$_2$	32·4	—	14·0	9·6	31·9	—	13·9	9·7	421m; 411m; 387w,b	161m	87s	294m,b; 241s; 230m; 206s; 180m; 130m

		Diffuse reflectance spectra				
		Band assignments (O_h symmetry, kK)				
	μ_{eff} (B.M.)	$^3A_{2g}(^3F) \rightarrow {}^1A_{1g}(^1G)$	$^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3F)$ (ν_2)	$^3A_{2g}(^3F) \rightarrow {}^1E_g(^1D)$	$^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3F)$ (ν_1)	Dq (cm^{-1})
Ni(pyim)$_3$Cl$_2$,2H$_2$O	3·11	22·6sh	18·2m	12·7sh	11·14m	1114
Ni(pyim)$_3$(NO$_3$)$_2$,3H$_2$O	3·19	22·7sh	17·9m	12·7sh	10·99m	1099

		Band assignments (C_{2v} symmetry, kK)			
	μ_{eff} (B.M.)	$^3A_2 \rightarrow {}^3B_1, {}^3B_2, {}^3A_2$	$^3A_2 \rightarrow {}^3B_2, {}^3B_1$	$^3A_2 \rightarrow {}^3A_1$	Other bands
Ni(pyim)$_2$Cl$_2$,H$_2$O	3·04	16·21m	9·90m	7·78sh	23·87sh; 22·80sh; 11·55sh
Ni(pyim)$_2$Cl$_2$	2·98	16·10m	9·86m	7·78sh	24·27sh; 22·57sh; 11·06sh
Ni(pyim)$_2$Br$_2$,H$_2$O	3·14	15·75m	9·59m	7·31sh	24·81sh; 22·78sh
Ni(pyim)$_2$Br$_2$		15·55m	9·63m	7·31sh	24·45sh; 22·68sh
Ni(pyim)$_2$I$_2$	3·03	16·50m	9·74m	7·52sh	20·92sh

† Spectra below 200 cm^{-1} not recorded for these samples; i.r. spectrum of pyim (ref. 7), 417w,b; 402m; 398sh; 385sh; 278w,b.

RESULTS AND DISCUSSION

Tris[*2-*(*2-pyridyl*)*imidazole*]*nickel*(II) *Complexes*.—The diffuse-reflectance spectra of Ni(pyim)$_3$Cl$_2$,2H$_2$O and

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$Ni(pyim)_3(NO_3)_2,3H_2O$ are very similar to one another and to that of $Ni(bipy)_3Br_2,6H_2O$.[8] The absorption bands can be satisfactorily assigned (see Table) on the basis of the Liehr and Ballhausen energy-level diagram for Ni^{II} complexes in O_h symmetry,[9] although the actual symmetry of the complex is D_3, and also by comparison with the work of Palmer and Piper for the bipyridyl complexes.[8] The band due to the $^3A_{2g}(^3F) \longrightarrow {}^3T_{1g}(^3P)$ transition is obscured by charge-transfer bands. The shoulder at *ca.* 12·7 kK, observed in both complexes, is assigned to the spin-forbidden $^3A_{2g}(^3F) \longrightarrow {}^1E_g(^1D)$ transition which is expected[10] to lie at a higher energy than the $^3T_{2g}(^3F)$ term in complexes where Dq is less than 1200 cm^{-1} {Dq for $[Ni(pyim)_3]^{2+}$ = 1107 cm^{-1}, see later}. The shoulder at 22·6 kK on the side of the charge-transfer bands may arise from a spin-forbidden transition to the $^1A_{1g}(^1G)$ term.

From the positions of the ν_1 band the average value of Dq is 1107 cm^{-1}, which is in excellent agreement with the value previously determined in aqueous solution[3] (1117 cm^{-1}) and is significantly less than the value of Dq found for $[Ni(bipy)_3]^{2+}$ (1279 cm^{-1}, single crystal;[8] 1265 cm^{-1}, aqueous solution[11]).

The magnetic moments of both complexes fall in the range normally observed for spin-free octahedral Ni^{II} compounds.[12]

Bis[2-(2-*pyridyl*)*imidazole*]*nickel*(II) *Complexes*.—There are no significant differences between the diffuse-reflectance spectra of the hydrated complex and the corresponding anhydrous complex indicating that the water present in the hydrate is not co-ordinated.

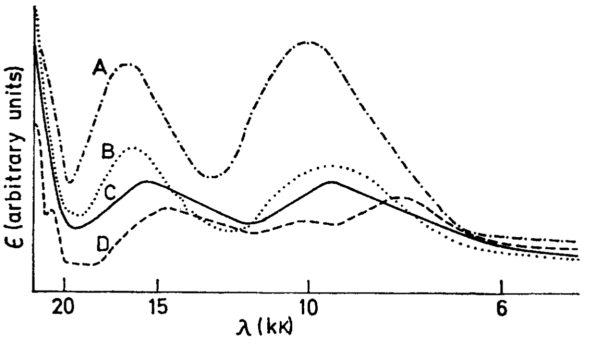

FIGURE 1 Diffuse reflectance spectra of (A) *cis*-$Ni(en)_2Cl_2$; (B) $Ni(bipy)_2Cl_2,3H_2O$; (C) $Ni(pyim)_2Cl_2$ and (D) *trans*-$Ni(py)_4Cl_2$

The diffuse-reflectance spectra of all five complexes are similar in shape to one another and consist of two main bands in the regions 17·7—16·5 and 9·6—10·0 kK, the latter band possessing a pronounced shoulder on its low-energy side (see Figure 1). These spectra and the magnetic moments of these complexes (2·98—3·20 B.M.) indicate a pseudo-octahedral stereochemistry around the nickel(II) ion.[12]

It has been suggested[13,14] that *cis*- and *trans*-octahedral nickel(II) complexes can be distinguished by the much greater splitting of the band system in the *trans*-complex and also by the higher intensity of the absorption bands associated with the *cis*-complex. The splitting of the band system of the pyim complexes is comparable to that observed[14,15] for $NiCl_2(en)_2$, which possesses[16] a dimeric *cis*-octahedral structure, suggesting a *cis*-configuration for the pyim complexes. The intensity of the spectrum is less than that observed for $NiCl_2(en)_2$ but is comparable to that of $Ni(bipy)_2Cl_2,3H_2O$ for which a *cis*-octahedral structure has been suggested on steric grounds.[2] The assignment of the principal absorption bands in C_{2v} symmetry is given in the Table. The transitions arising from the ν_3 (O_h symmetry) band are obscured by charge-transfer bands.

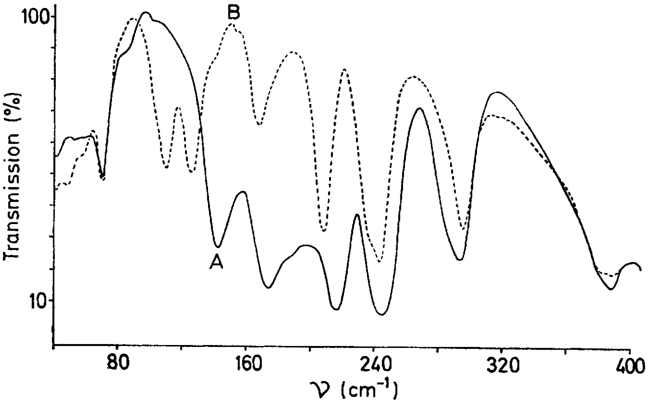

FIGURE 2 I.r. spectra of (A) $Ni(pyim)_2Cl_2,H_2O$ and (B) $Ni(pyim)_2Br_2,H_2O$

The i.r. absorption bands (400—80 cm^{-1}) are listed in the Table. The band at 160—175 cm^{-1}, present in all the four complexes studied below 200 cm^{-1}, cannot be assigned to a Ni–X mode because the position of the band in the chloro- and iodo-complexes differs by only 14 cm^{-1}. This band does not appear to be due to an internal mode of the pyim ligand as it appears at a different frequency (190 cm^{-1}) in the corresponding Co^{II} complexes[17] and is therefore tentatively assigned to a Ni–pyim mode. There do not appear to be any halogen-dependent bands above 200 cm^{-1} although the presence of several strong bands in the 200—300 cm^{-1} region makes the detection of Ni–X bands difficult. Below 200 cm^{-1} several strong halogen-dependent bands are observed (see Figure 2). In the chloro-complex the Ni–Cl band occurs at a much lower frequency than those found for octahedral Ni^{II} complexes containing terminal Ni–Cl bonds.[18] In all three complexes studied in this region the Ni–X band is at a lower frequency than those

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observed for octahedral Ni^{II} complexes containing planar $[NiX_2]_n$ chains.[19] Thus it appears likely that the $Ni(pyim)_2X_2$ complexes contain bridging rather than terminal Ni–X bonds. Although only one of the two expected ν(Ni–X) bands has been assigned in the chloro- and iodo-complexes, the presence of the second band may be obscured by the broadness of the observed band or by the presence of other strong bands in this region of the spectrum.

The presence of bridging halogen suggests a *cis*-octahedral dimeric structure for these complexes similar to that found previously[16] for $NiCl_2(en)_2$. Both the i.r. and diffuse reflectance spectra indicate a *cis*- and not a *trans*-configuration about the nickel(II) ion.

In the sequence of ligands 2,2′-bipyridyl, 2-(2-pyridyl)-imidazole, and 2,2′-bi-imidazolyl, the first ligand is incapable of forming a *trans*-complex with first-row divalent transition metal ions because of steric interactions[20] whereas the latter ligand is known to occupy *trans*-positions in the pseudo-octahedral complex Ni-$(2,2'\text{-bi-imidazolyl})_2(H_2O)_2(NO_3)_2$.[21] From our results it appears that 2-(2-pyridyl)imidazole is similar to 2,2′-bipyridyl and prefers to adopt a *cis*- rather than a *trans*-position in pseudo-octahedral complexes of nickel(II).

We thank the S.R.C. for a research studentship (to R. J. D.).

[1/1788 *Received, 29th September,* 1971]

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