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The FT-IR Spectroscopic Investigation of Two Dimensional Polymeric Complexes of 2-Aminopyrimidine

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Dedicated to Professor Yurij A. Dyadin.

Abstract—The coordination polymeric compounds, $M(2APM)_2Ni(CN)_4$ (where M = Mn, Co, Ni or Cd; 2APM = 2-aminopyrimidine) have been prepared for the first time and their FT-IR spectra are reported in the 400–4000 cm^{-1} region. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymeric compounds, formed with $Ni(CN)_4^{-2}$ ions bridged by $M(2APM)_2^{+2}$ cations. 2APM is coordinated to M(II) through one of the pyrimidine ring nitrogen atoms; the amino group is not involved in the complex formation. The coordination effect on the 2APM vibrational wavenumbers is analysed.

Introduction

Pyrimidine is the parent heterocycle of a very important group of compounds that have been extensively studied due to their occurrence in living systems.[1] Pyrimidine moieties are reported to have antibacterial, antifungal and anti-HIV activities.[2] Many pyrimidines, or their derivatives, possess remarkable biological activity and have been widely used in fields ranging from medicinal to industrial applications. The complexing ability of 2-aminopyrimidine with transition metal ions is of great interest, since 2-aminopyrimidine has endo- and exocyclic nitrogen donors for coordination. The amino nitrogen atom is known to be more basic in comparison to the pyrimidine ring nitrogens.[3] However, in some 2-aminopyrimidine complexes the coordination of the 2-aminopyrimidine with the metal occurs through the endocyclic ring nitrogen,[4,5] as shown by X-ray studies, whereas in others the 2-aminopyrimidine coordinates to the metal through the amino nitrogen.[3,6] Therefore the investigation of the coordination mode of 2-aminopyrimidine is of interest. This has stimulated us to study the two dimensional coordination polymeric compounds; the Hofmann type complexes of 2-aminopyrimidine.

The Hofmann type host complexes, $M(NH_3)_2Ni(CN)_4$ are built by stacking the two dimensional networks, in which M(II) takes an octahedral coordination, satisfied by four N-terminals of the cyano groups and two N atoms of ammonia molecules protruding above and below the network, and the square planar $Ni(CN)_4$ shares vertices with four M(II) octahedra to build up the 2D-network.[7,8] Based on this structure several metal (II) tetracyanonickelate complexes related to the Hofmann-type hosts have been developed by replacing the ammonia molecules by other N- or O-donor ligands (L), $ML_2Ni(CN)_4$.[7-9] In this paper we report the IR spectra (400–4000 cm^{-1} region) of four new tetracyanonickelate complexes of 2-aminopyrimidine, $M(2APM)_2Ni(CN)_4$ (where M = Mn, Co, Ni or Cd; 2APM = 2-aminopyrimidine, abbreviated hereafter as M–Ni–2APM). The aim of this study is to investigate the coordination ability of 2APM and to examine coordination sensitive ligand modes, by studying isostructural complexes of 2APM.

Experimental

All the chemicals used were reagent grade (Merck) and used without further purification. The complexes were prepared using the method given in the literature.[10] The C, H, N analyses were carried out for all the samples. The IR spectra of Nujol mulls or KBr discs were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution).

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Results and discussion

The FT-IR spectra of the Cd–Ni–2APM and Mn–Ni–2APM complexes are given in Fig. 1a and b, respectively. The IR spectra of the M–Ni–2APM complexes are very similar indicating that they have analogous structures. The vibrational wavenumbers of 2APM are tabulated in Table 1 together with the relevant data.[6,11,12]

2APM can exist in two tautomeric forms: one is the imine form, produced by a proton transfer from the NH_2 group to a ring nitrogen and the second is the unchanged amino form[6] (see Fig. 2). Based on a vibrational spectroscopic investigation, Contreras and Seguel[6] proposed that 2APM is in its amino form in the solid state. The IR spectroscopic investigation of M–Ni–2APM complexes also indicates that the molecule is in the amino form.

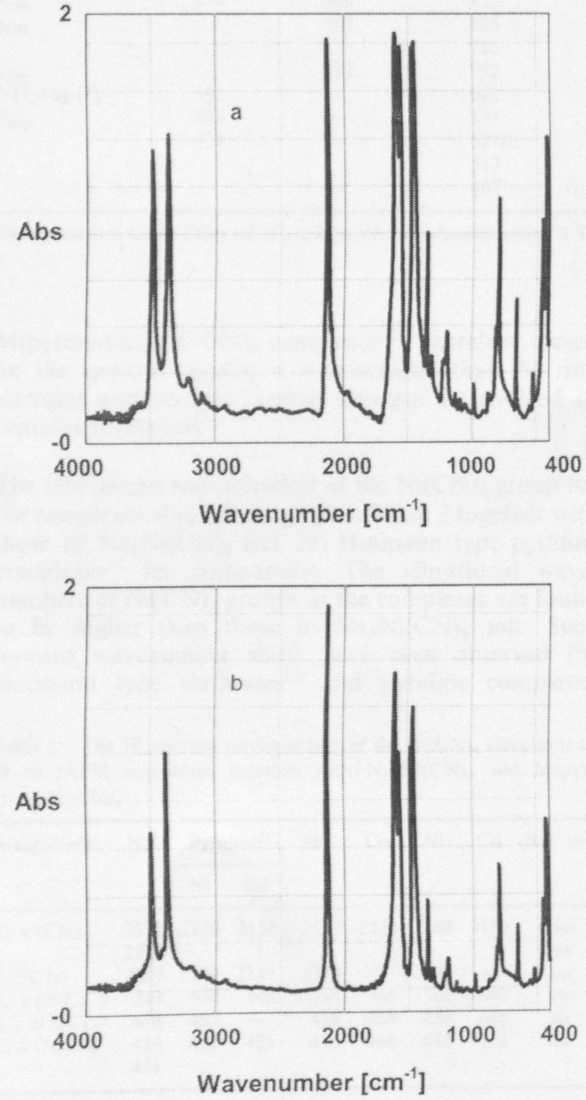

Figure 1. The FT-IR spectra of (a) $Cd(2APM)_2Ni(CN)_4$ and (b) $Mn(2APM)_2Ni(CN)_4$.

2APM has endo and exocyclic nitrogen donors available for coordination. In order to determine the coordination mode of 2APM, the vibrational wavenumbers are carefully investigated for effects arising from coordination through a pyrimidine ring nitrogen or through the amino group.

In the IR spectra of the 2APM complexes studied, the $\nu_a NH_2$ and $\nu_s NH_2$ modes are found to have higher frequencies than those of microcrystalline 2APM (see Table 1). Since it is well known that a coordinated amino group shows a negative shift, $\Delta = 150–220\ cm^{-1}$, in the NH_2 stretching vibrational modes, in comparison to the free ligand,[13–16] we can confirm that the amino group of 2APM does not take part in coordination. Similarly, the $\nu(C\text{-}NH_2)$ mode of aniline and aniline derivatives shows a negative shift, $\Delta = 50–60\ cm^{-1}$, upon coordination,[13–16] but we do not observe such a drastic red shift of this mode in the M–Ni–2APM complexes, [the red shift of the $\nu(C\text{–}NH_2)$ mode for M–Ni–2APM complexes is at most 4 cm^{-1}] which is further evidence of non-coordination through the amino nitrogen. In solid 2APM, amino group hydrogens are involved in H-bonding interactions.[17] Although the $\nu_a NH_2$ and $\nu_s NH_2$ modes of M–Ni–2APM complexes are found to be higher in frequency than those of microcrystalline 2APM, they are slightly lower in value than those of 2APM in a Ne matrix[12] and NH_2 scissoring mode frequency is lower than in solid 2APM and closer to that in Ne matrix,[12] indicating that the amino group hydrogens may be involved in a weak hydrogen bonding interaction, probably with guest water molecules, but H-bonding interaction must be weaker than in solid. It must be noted that samples are found to contain small amount of water as guest species [$\nu(H_2O)$ is observed around 3610 cm^{-1} as a weak intense band].

It is well known that when the ring nitrogen of pyridine is involved in complex formation, certain vibrational modes, particularly the ring breathing mode and the two ring stretching modes around the 1500–1600 cm^{-1}, increase in value due to both coupling with M–N (pyridine) bond vibrations and alterations of the ring force field.[18–21] A glance at Table 1 clearly shows the presence of upward shifts relative to those of polycrystalline 2APM, for certain vibrational modes of 2APM in the IR spectra of M–Ni–2APM compounds, which are marked in bold. Similar shifts have also been predicted upon formation of H-bonding through one of the pyrimidine ring nitrogens[22] and were observed in the

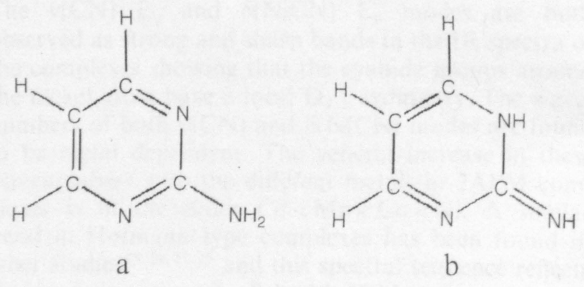

Figure 2. Amino (a) and imino (b) tautomeric forms of 2APM.

Table 1. The wavenumbers (cm^{-1}) of 2-aminopyrimidine in M–Ni–2APM complexes

Tentative assignment[a]	2APM				M–Ni–2APM			
	Solid[6]	Solid[11]	Ne Matrix[12]	This study	Mn	Co	Ni	Cd
$\nu(NH_2)$	3350	3350	3585	3348vs	3518s	3534s	3536s	3493vs
		3335		3330vs				
$\nu(NH_2)$	3240	3247	3469	3244m	3414vs	3418vs	3419vs	3373vs
	3170	3169		3168vs	3200w	—	3207m	3201m
ν(CH)				3050vw	3088w	3080w	3085w	3083w
ν(CH)	3030			3025w	3066vw	—	3067vw	—
ν(CH)	2960			2960w	3050w	—	3050vw	3051vw
$\delta(NH_2)$	1640	1642	1612	1648vs	1623vs	1624vs	1626vs	1606vs
			1606					
ν_{ring}	1575	1576	1571	1577s	**1590m**	**1590m**	**1594s**	**1590s sh**
ν_{ring}	1565	1559	1560	1559vs	**1566vs**	**1567vs**	**1568vs**	**1567vs**
ν_{ring}	1475	1479	1470	1479vs	1480vs	1480s	1480s	1478vs
ν_{ring} (*)	1449	1445	1454	1444s	**1458vs**	**1459s**	**1460s**	**1459vs**
ν_{ring}	—	1358	1356	1357m	1356m	1358s	1361m	1354m
ν(C–NH_2)	1225	1224	1219	1224m	1220m	1224m	1226m	1227m
ν_{ring}	1180	1179	1184sh	1179m	**1191s**	**1190m**	**1192w**	**1193m**
			1177					
δ (CH)		1128	1123	1130m	1131w	1130w	1131w	1127w
Ring breath.		1075		1078w	**1086w**	**1091w**	**1092w**	**1090w**
NH_2 twist		1038		1039m	1035w	1035w	1035w	1050m
δ Ring		997	991	999m	982m	978w	978w	983m
γ_{CH}	870	866	872	869w	873w	873vw	874vw	873w
γ_{CH}	—	803	805	803vs	798s	795m	795m	794m
			786	788m	771m	780m	780m	780sh
γ_{ring}	—	720	732	726m	721vw	720vw	721vw	722vw
NH_2wag.(*)	648	—	642	645m	652s	653m	658m	653m
δ_{ring}	608	—	593	602m	585w	—	—	602vw
	528	—	521sh	525s	521m	520m	521m	520m
			517					453m
	—	—	407	405s	408w	408w	410w	406vw

[a]Assignment is taken from ref. 11, except where indicated with (*). Coordination sensitive bands are marked in bold.

$M(pyrimidine)_2M'(CN)_4$ complexes.[23] Therefore, based on the spectral results, it is concluded that the ring nitrogen and not the amino nitrogen is involved in complex formation.

The vibrational wavenumbers of the $Ni(CN)_4$ group for the complexes studied are given in Table 2 together with those of $Na_2Ni(CN)_4$ (ref 24) Hofmann type pyridine complexes[18] for comparison. The vibrational wavenumbers of $Ni(CN)_4$ groups in the complexes are found to be higher than those in $Na_2Ni(CN)_4$ salt. Such upward wavenumber shifts have been observed for Hofmann type clathrates[25] and pyridine complexes

Table 2. The IR spectral wavenumbers of the $Ni(CN)_4$ vibrations of M–Ni–2APM complexes together with $Na_2Ni(CN)_4$ and $M(pyridine)_2Ni(CN)_4$

Assignment	Na[a]	Pyridine[b]		Mn	Co	Ni	Cd	Rel. Int.
		Ni	Cd					
E_u ν (CN)	2132	2170	2154	2157	2158	2168	2136	vs
	2128							vs
ν (^{13}CN)	2087	2129	2111	2110	—	2128	—	vw
E_u ν (NiC)	543	550	543	547sh	560	562	543	vw
A_{2u} π(NiCN)	488	453	—	456	455	456	442	sh
E_u δ (NiCN)	433	441	425	436	440	445	423	vs
	421							

[a]$Na_2Ni(CN)_4$ complex taken from ref 24.
[b]$M(pyridine)_2Ni(CN)_4$ complexes (M = Ni or Cd) taken from ref 18.

$[M(py)_2Ni(CN)_4]$,[18] in which both ends of the CN group are coordinated, and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the M–NC vibrations.[18] The ν(CN) wavenumber of the Cd–Ni–2APM complex is found to be much lower than the other M–Ni–2APM complexes. This is probably due to a much longer M–NC bond in Cd–Ni–2APM than the others, which is an expected result; since from X-ray crystallographic studies[26] it is known that the M–NC bond distance increases with increasing ionic radius of the metal (M). Such a low wavenumber was also observed in one of the split pairs of the ν(CN) mode of the Hofmann type copper complexes,[27] in which non-equivalent trans pairs of Cu–NC bonds with different lengths were proposed [e.g., in Cu(4-methylpyridine)$_2$Ni(CN)$_4$ the IR active ν(CN) wavenumbers are 2164 and 2136 cm^{-1}].

The ν(CN) E_u and δ(NiCN) E_u modes are both observed as strong and sharp bands in the IR spectra of the complexes showing that the cyanide groups around the nickel atom have a local $D_{4\,h}$ symmetry. The wavenumbers of both ν(CN) and δ(NiCN) modes are found to be metal dependent. The general increase in these wavenumbers with the different metals in 2APM complexes is in the order Cd < Mn < Co < Ni. A similar trend in Hofmann type complexes has been found in other studies[18,20,21,25] and this spectral sequence reflects the increasing strength of the M–NC bond.

Conclusion

The IR spectroscopic study of four new complexes has shown that they have similar structures constructed by the linkage between the square planar $Ni(CN)_4^{2-}$ and the octahedral M(II) through cyano bridges. The six coordination of M(II) is satisfied by four N terminals of the cyano groups and two 2APM molecules. IR spectroscopy is found to be very useful for shedding light on the coordination mode of 2APM. It is concluded that the 2APM molecule is involved in coordination through one of the pyrimidine ring nitrogens as a monodentate ligand.

Acknowledgements

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