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Raman spectroscopic study of two dimensional polymer compounds of 2-aminopyrimidine

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Abstract

The Raman spectra of the two dimensional layered polymer compounds, $M(2APM)_2M'(CN)_4$ {where M = Mn or Cd; and M′ = Ni or Pt; 2APM = 2-aminopyrimidine} are reported in the 70–4000 cm^{-1} region. Vibrational data suggests that compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $M'(CN)_4^{-2}$ ions bridged by $M(2APM)_2^{+2}$ cations. 2-Aminopyrimidine was coordinated to M(II) through one of the nitrogen atom of its heterocycle ring. Vibrational assignments are given for the bands arising from the tetracyanometallate layers and coordinated 2APM.

Keywords: Aminopyrimidine; Hofmann type complexes; Infrared and Raman spectra; Tetracyanonickelate; Tetracyanoplatinate; Transition metal

1. Introduction

Pyrimidine is the parent heterocycle of very important group of compounds that have been extensively studied due to their occurrence in living systems. Aminopyrimidines are of great biological importance. NH_2 groups substituted in pyrimidine rings are acidic components in hydrogen bonded interactions between pairs of nucleic bases responsible for formation of double helices in DNA and RNA [1,2]. Thus any information on their coordination properties is important as a means to understand the role of metal ions in biological systems.

The well known Hofmann type two dimensional complexes, $\{M(L)_2M'(CN)_4\}$, are build by stacking the two dimensional extended metal (M′) cyanide layers [3,4]. The two dimensional layer is constructed by the alternate linkage between square-planar M′(II) (M′ = Ni, Pd or Pt) and octahedral M(II) (M = Mn, Fe, Co, Ni, Cu, Zn or Cd) through the cyanide bridges. The octahedral coordination of M(II) is satisfied by four N-terminals of the cyano groups and two nitrogen atoms of the two N-donor ligands (L) in trans configuration, protruding above and below the network [3,4]. We have previously reported the IR spectra of $M(2APM)_2Ni(CN)_4$ complexes {where M = Mn, Co, Ni or Cd} [5] and shown that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer 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. We now report the Raman spectra of the $M(2APM)_2Ni(CN)_4$ {where M = Mn or Cd; 2APM = 2-aminopyrimidine, abbreviated hereafter as M–Ni–2APM} for the first time in the 70–4000 cm^{-1} region. In order to compare the vibrational modes of the polymeric layers, the $M(2APM)_2Pt(CN)_4$ (M = Cd or Mn) compounds were also prepared for the first time and their IR (400–4000 cm^{-1}) and Raman data are reported. The aim of this study is to investigate the coordination ability of 2APM and to examine the ligand modes, particularly the vibrational modes arising metal–ligand bonds.

2. Experimental

All the chemicals used were reagent grade (Merck and Reidel) and used without further purification.

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The complexes were prepared by adding slightly more than two moles of 2-aminopyrimidine and 1 mole of potassium tetracyanometallate aqueous solution to 1 mole of M(II) chloride solution using constant stirring. The C, H, N analyses were carried out for all the samples and the results were found to fit the proposed formulae well. The FT-Raman spectra of the powdered samples were recorded on a Bruker RFS 100/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector and 100 scans were accumulated. The IR spectra of nujol mulls or KBr discs were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution).

3. Results and discussion

The Raman spectra of the Mn–Ni–2APM and Cd–Ni–2APM complexes are given in Fig. 1a and b, respectively. The IR and Raman spectra of Mn–Pt–2APM complex are given in Figs. 2 and 3, respectively. The vibrational spectra of the M–Pt–2APM complexes are very similar to those of M–Ni–2APM, indicating that they have analogous structures.

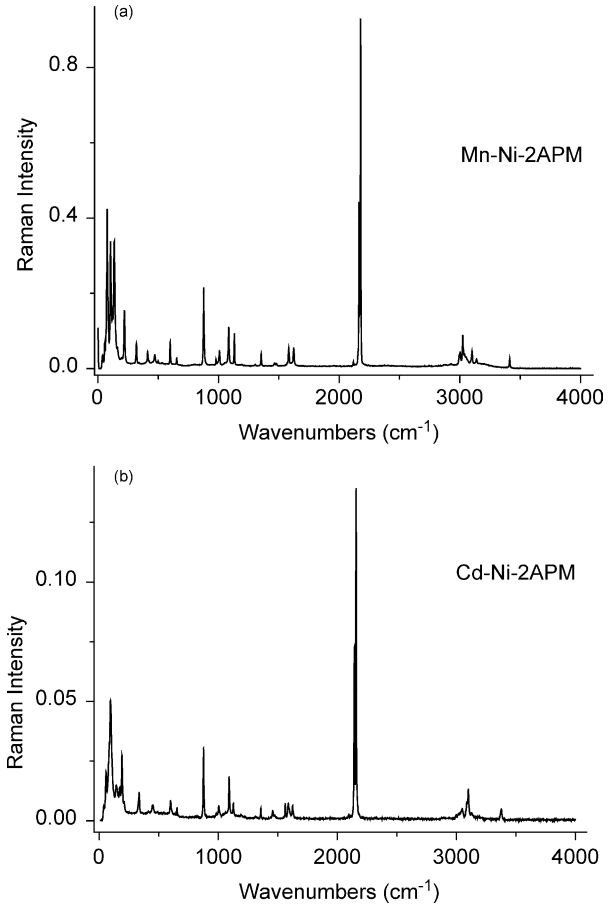

Fig. 1. FT-Raman spectra of $Mn(2APM)_2Ni(CN)_4$ (a) $Cd(2APM)_2Ni(CN)_4$ and (b) compounds.

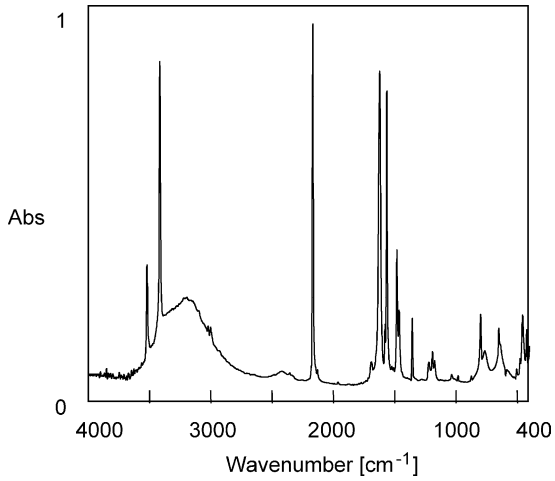

Fig. 2. FT-IR spectrum of $Mn(2APM)_2Ni(CN)_4$ compound.

3.1. Vibrations of 2-aminopyrimidine

2-Aminopyrimidine has *endo*- and *exo*-cyclic nitrogen donors for coordination. The amino nitrogen atom is known to be more basic in comparison to the pyrimidine ring nitrogens [6]. However, in some 2-aminopyrimidine complexes the coordination of the 2-aminopyrimidine with the metal occurs through the endocyclic ring nitrogen [7–9], whereas in others the 2-aminopyrimidine coordinates to the metal through the amino nitrogen [6,10]. The vibrational wavenumbers of 2APM are tabulated in Table 1 in comparison with those of microcrystalline 2APM [5,11] and 2APM in a Ne matrix [12]. In our previous study based on IR spectroscopic results it was concluded that the 2APM molecule in Mn–Ni–2APM and Cd–Ni–2APM complexes, is coordinated to metal through one of the pyrimidine ring nitrogen atoms as a monodentate ligand [5] and the amino group nitrogen is not involved in the complex formation. Raman spectra support the previous findings. We clearly observed the symmetric stretching mode of NH_2 group at 3378–3415 cm^{-1} in the Raman spectra of the compounds

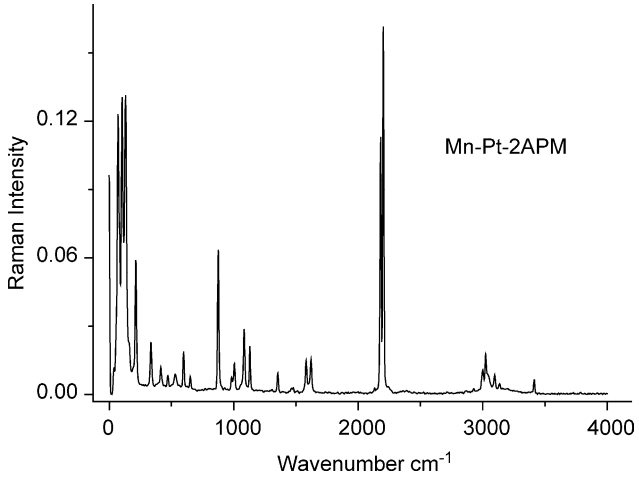

Fig. 3. FT-Raman spectrum of $Mn(2APM)_2Ni(CN)_4$ compound.