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FT-IR Spectroscopic and Some Thermal Properties of Hofmann-Type Clathrate and Transition Metal Complexes of 2-Aminothiazole

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In this study, new Hofmann type transition metal complexes of the form M(2-aminothiazole)$_2$Ni(CN)$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd) and Cd(2-aminothiazole)$_2$Ni(CN)$_4$·C$_6$H$_6$, Hofmann type clathrate, have been prepared in powder form and their infrared spectra and some thermal decomposition properties of the clathrate are reported. The spectral and thermal data show that the structures of these complexes and the clathrate are analogous with related Hofmann type complexes. The observed ν(C-N) wave numbers of the complexes are in good agrement with Irving-Williams natural stability series.

Key Words: Infrared spectrum, Hofmann type calthrates, 2-Aminothiazole(atz), Benzene, Thermal decomposition.

INTRODUCTION

Hofmann type inclusion compounds are given in general formula as $ML_2M'(CN)_4 \cdot nG$ where M is a transition metal ions having the valence of +2 in octahedral environment, M' is Ni^{2+}, Pd^{2+} or Pt^{2+} in square planar environment, L is either a bidentate or two monodentate ligand molecule, G is the guest molecule and n is the number of guest molecules depending on the empty space of host. Hofmann type clathrates have been a subject of many experimental and theoretical studies because of their significance in understanding the nature of host-guest systems[1-3].

Heterocyclic ligands such as pyridine, imidazole, thiazole and related molecules are better ligands due to the presence of possible coordination sites[4]. Thiazole and its derivatives have biological significance, *e.g.*, they found in the vitamin B_1 molecule and in coenzyme cocarboxylase[5]. The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazole is known mainly as biologically active compound with a broad range of activity and as intermediate in the synthesis of antibiotics[6].

Cobalt(II) complexes of 2-aminothiazole has been prepared and studied with two main interests. Firstly, because this is analogue of thiamine which has its enzymic action dependent upon metal ions. Secondly, this molecule has a number of possible bonding sites[7].

The extensive synthetic possibilities of this ligand holds promise for the preparation of new thiazole-transition metal complexes. The synthesis and characterization of

Hofmann type inclusion compounds of 2-aminothiazole have not been reported so far. The aim of this study is to give further examples of new Hofmann type clathrates and to examine the coordination behaviour of 2-aminothiazole.

In this study, Hofmann type transition metal complexes of M(2-aminothiazole)$_2$Ni(CN)$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn and Cd) and Cd(2-aminothiazole)$_2$ Ni(CN)$_4$·2C$_6$H$_6$, Hofmann type clathrate, have been prepared in powder form. Their infrared spectra and some thermal decomposition properties are reported. The partial loss of guest molecule from the host structure effects analytical composition of clathrate.

Thermal decomposition of Hofman type clathrates are occur in the three steps: (1) liberation of guest molecules, (2) that of ligands and (3) combustion of the CN groups to leave the host metals oxides, upon raising temperature[8].

EXPERIMENTAL

Commercially available chemicals were reagent grade and used as supplied. 2 mmol of 2-aminothiazole was solved in ethanol and excess of benzene were added into an aqueous solution contaning 1 mmol of $CdCl_2$ and $K_2Ni(CN)_4$ salts in 50 mL distilled water. The final mixture was stirred at a constant stirring rate for 2 days. The precipatate was collected by filtration and washed with water, ethanol and diethyl ether successively, then kept in a dessicator. On the other hand the host complexes were prepared in the same procedure given above except the addition of guest benzene. The calthrate was kept under benzene atmosphere in a desiccator.

Detection method: Elemental analysis of the clathrate compound were done by using LECO CHNS 932 model analyzer for C, H, N and S. The analytical results were found as: $Cd(C_3H_4N_2S)_2Ni(CN)_4$, [found (calculated) %] C: 25.29 (25.26); H: 1.93 (1.70); N: 23.08 (23.57); S: 12.83 (13.49).

These analytical results are changable because of partial decomposition of the clathrate compound as a result of weak interactions of bezene and host structure. Infrared spectra of the samples were recorded at room temperature on a Mattson 1000 FT-IR spectrophotometer in the range of 4000-400 cm^{-1} as mulls in Nujol (or fluorolube).

Thermal analysis were carried out by Perkin-Elmer Pyris Diamond TG/DTA to determine the composition temperatures of the clathrate. The TG curves were recorded in the temperature range of 28-1016 °C for 20 °C min^{-1} heating rate.

RESULTS AND DISCUSSION

The IR spectra of Cd(atz)$_2$Ni(CN)$_4$. Benzene clathrate and Co(atz)$_2$Ni(CN)$_4$ host are shown in Figs. 1 and 2, respectively. The spectral pattern of the compounds are found to be similar to each other. This sugests that they have similar structural properties. The results obtained from IR spectral data can be analyzed in three groups as usual: vibrations of ligand molecules, $Ni(CN)_4^{2-}$ group and guest molecule namely benzene.

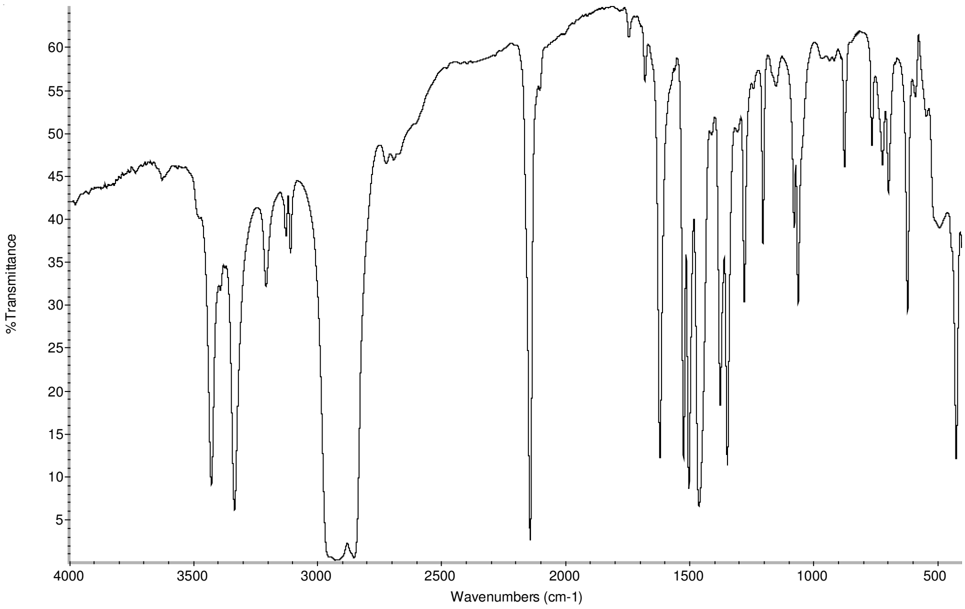


Fig. 1. IR spectrum of $Cd(atz)_2Ni(CN)_4{\cdot}C_6H_6$ (in Nujol)

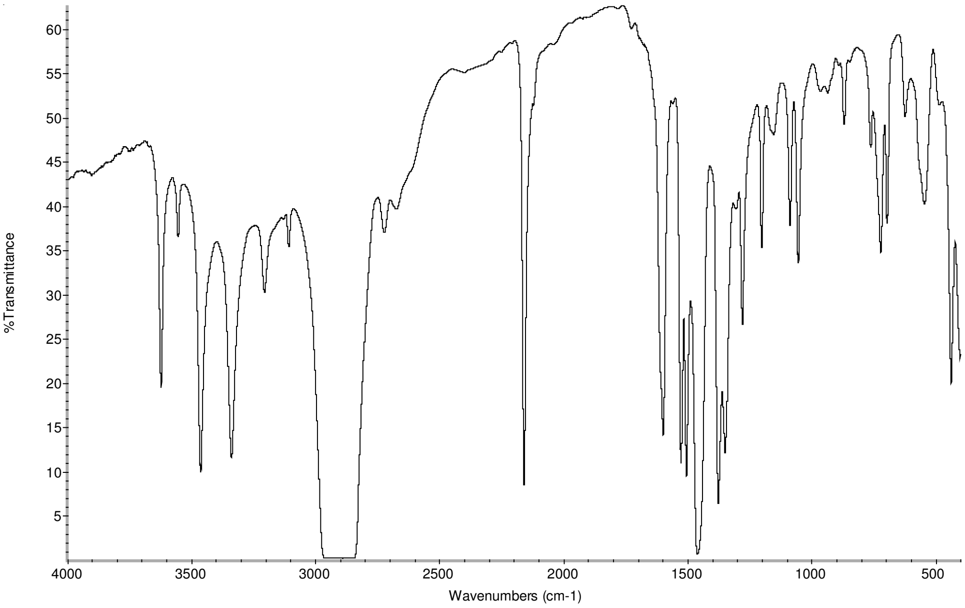
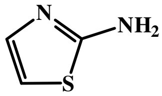


Fig. 2. IR spectrum of $Co(atz)_2Ni(CN)_4$ (in Nujol)

2-Aminothiazole (atz) vibrations: 2-Aminothiazole falls in the class of aromatic heterocyclic compounds and has a number of possible coordination sites. This molecule functions as a ligand to the transition metal ions *via* unshared pair of electrons of nitrogen and sulphur atom on the ring or amine nitrogen atom in outside of the ring.



The assignments and the wave numbers of the fundemental vibrations arising from 2-aminothiazole in the clathrate and complexes are tabulated in Table-1. Several authors have studied the vibrational assignments of 2-aminothiazole[9,10]. This molecule has planar structure and belongs to the C_s point group. The 24 normal modes of vibration can be classified as 17A' + 7A'' both active in the infrared spectra as well as in the Raman one[11].

TABLE-1
VIBRATIONAL WAVENUMBERS (cm^{-1}) OF THE 2-AMINOTHIAZOLE IN $Cd(atz)_2Ni(CN)_4 \cdot C_6H_6$ CLATHRATE AND $M(atz)_2Ni(CN)_4$ COMPLEXES

Assignments[a]	atz (Nujol)[a]	$Co(atz)_2Cl_2$[a]	$Cd(atz)_2Ni(CN)_4 \cdot C_6H_6$	$M(atz)_2Ni(CN)_4$					
				Co	Cu	Ni	Mn	Fe	Zn
ν(N-H) asym	3400 s	3300 s	3428 s	3465 s	3478 m	3468 m	3483 vw	3464 s	3463 w
ν(N-H) sym	3270 s	3195 s	3335 s	3341 s	3365 m	3343 m	3343 m	3343 s	3339 w
$\delta(NH_2)$	1620 s	1612 s	1619 vs	1600 vs	1618 s	1610 m	1613 s	1600 s	1618 m
Ring skeletal	1515 s	1520 s	1524 s	1527 m	1520 m	1532 m	1523 m	1526 s	1524 w
Ring skeletal	1490 s	1495 s	1503 s	1507 m	1459 s	1506 m	1504 m	1506 vs	1506 w
ν(C-N) out of ring	1322 s	1355 m	1348 s	1349 m	1347 m	1347 m	1345 m	1345 m	1347 w
Ring skeletal	1200 s	1200 s	1204 m	1201 m	1202 w	1202 s	1199 w	1201 m	1199 w
ν(C-S)	690 s	692 s	698 m	697 m	703 vw	696 s	698 w	696 m	698 w

[a] Taken from ref.[7].

Werner type cobalt(II) complexes of 2-aminothiazole have been reported in the literature previously[7]. It is very clear to observe from the Table-1 that most of the vibrational modes of 2-aminothiazole in the clathrate and complexes have increased in wave numbers when compared with free ligand. The positive shift of exocyclic ν(C-N) can be explained the evidence in favour of bonding through amino nitrogen because, after coordination, the polarization of the π electrons from the atz ring towards nitrogen of the amino group will increase the double-bond character of C-N in the $C-NH_2$ group. The positive shift in ν(C-S) rules out the possibility of coordination through sulphur.

In conclusion, atz is coordinated to the metal ion *via* exocyclic nitrogen and not the nitrogen or sulphur atoms of the ring. One possible reason for this might be that the lone pair electrons on the nitrogen of the amino group are more exposed whereas those present on the ring nitrogen or sulphur are sterically hindered by the presence of the amino group at the 2-position thus favouring the coordination through exocyclic nitrogen[7].

$Ni(CN)_4^{2-}$ group vibrations: Cyano metal complexes can be identified by IR spectroscopic techniques easily since they exhibit sharp ν(CN) at 2200-2000 cm^{-1}. Upon coordination to a transition metal ion, the ν(CN) shift to higher frequencies. The CN^- ion acts as a σ-donor by donating electrons to the metal and also as a π-acceptor by accepting electrons from the metal[12] (Table-2).

TABLE-2
IR VIBRATIONAL WAVENUMBERS (cm^{-1}) OF CN GROUP IN $Cd(atz)_2Ni(CN)_4 \cdot C_6H_6$ CLATHRATE AND $M(atz)_2Ni(CN)_4$ COMPLEXES

Assignments	$Na_2(NiCN)_4$*	$Cd(atz)_2Ni(CN)_4 \cdot 2C_6H_6$	$M(atz)_2Ni(CN)_4$					
			Co	Cu	Ni	Mn	Fe	Zn
ν(C-N)	2132 s	2143 vs	2160 vs	2184 vs	2166 vs	2155 vs	2157 vs	2189 s

*Taken from ref.[14].

In Hofmann type clathrates and Hofmann type transition metal complexes, the Ni atom in $Ni(CN)_4^{2-}$ ion is square planer environment. In this structure Ni atom is coordinated to CN groups *via* carbon atoms. In order to assign the bands arising from $Ni(CN)_4^{2-}$ ion in the spectra of the compounds, we used the work done by McCullough and co-workers in the $Na_2Ni(CN)_4$ salt[13]. Since the ion is not coordinated to cations, it can be treated as an isolated unit.

The observed wave numbers of the CN groups are found to be similar those of Hofmann type clathrates[14] and tabulated in Table-1 for comparison. These results indicate that the $[M\text{-}Ni(CN)_4]_\infty$ layers have been preserved in a local D_{4h} symmetry. The vibrational frequencies of the $Ni(CN)_4^{2-}$ group in the complexes are much higher than isoleted one. The ν(CN)(E_u) modes are observed strong bands in all the IR spectra of the compounds. The observed ν(CN) wave numbers of the divalent transition metals ions in the complexes are in a good agrement with Irving-Williams natural stability series.

Guest molecule (benzene) vibrations: The assignments of the wave numbers of the vibrational modes related with benzene molecules observed in the spectra of the clathrate is tabulated in Table-3 together with the frequencies of benzene in the liquid phase[15] and in the clathrate $Cd(dahxn)Ni(CN)_4 \cdot C_6H_6$[16] for comparison.

The vibrational modes of benzene molecule are weakly afected by enclatration due to very weak host-guest interaction. The important exception is CH out of plane vibrations of aromatic benzene ring. The out of plane mode of benzene in the clathrate was observed at higher frequency than liquid benzene. Similar observation has been reported in Hofmann-type clahrates[17] and explained by the the presence of special type weak hydrogen bonding between delocalized π electrons of benzene ring and the hydrogen atoms of the ligand molecules in the host lattice.

TABLE-3
IR VIBRATIONAL WAVENUMBERS (cm^{-1}) OF BENZENE IN
$Cd(atz)_2Ni(CN)_4{\cdot}C_6H_6$ CLATHRATE

Assignment*	Liquid benzene*	$Cd(dahxn)Ni(CN)_4{\cdot}C_6H_6$**	$Cd(atz)_2Ni(CN)_4{\cdot}C_6H_6$
$\nu_8 + \nu_{19}$	3075	3078	3070
$\nu_{20}E_{1u}$	3073	–	3089
$\nu_{13}B_{1u}$	3062	3022	3034
$\nu_5 + \nu_{17}E_{1u}$	1955	1979	1965
$\nu_{10} + \nu_{17}$	1815	1830	–
$\nu_{19}E_{1u}$	1479	1474	1477
$\nu_{14}B_{2u}$	1309	1309	–
ν_5B_{2u}	1149	–	–
$\nu_{18}E_{1u}$	1036	1034	–
$\nu_{11}A_{2u}$	670	690	690

*Taken from ref.[15], **Taken from ref.[16].

Thermal decomposition properties of the clathrate: Fig. 3 shows the thermal decomposition of the clathrate. As it can be seen from the Fig. 3, the clathrate is stable at lower temperatures. The thermal decomposition of the clathrate has been occured in the three steps. In the first step: liberation of benzene molecules, in the second step: liberation of aminothiazole and in the third step: combustion of the CN groups to leave the mixture of nickel and cadmium oxides, upon raising temperature. Thermal decomposition of double transition metal complexes have been reported in the literature[8,18].

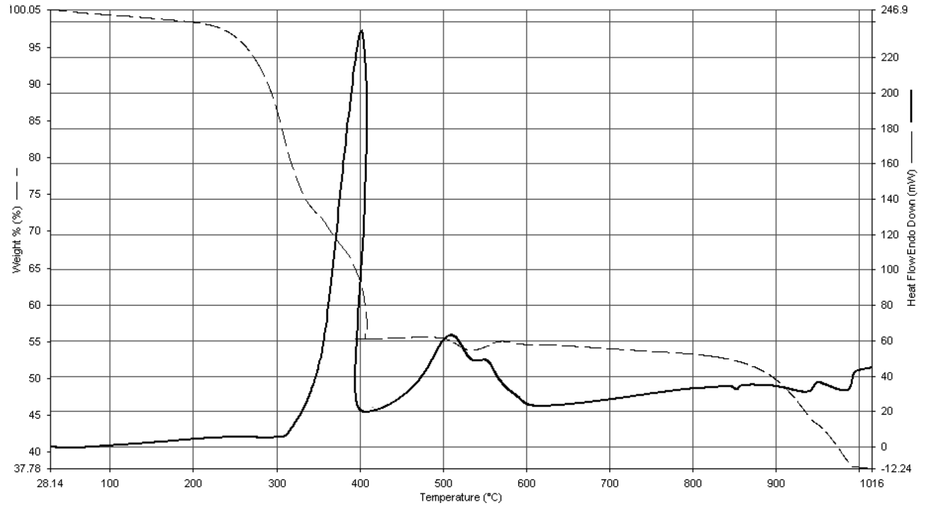


Fig. 3. TGA of $Cd(atz)_2Ni(CN)_4{\cdot}C_6H_6$

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