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Some Tetrahedral Coordination Polymers of Zinc(II), Cadmium(II), and Mercury(II) Involving 4-Aminomethylpyridine

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ABSTRACT

Analytical data and infrared spectral measurements down to 200 cm^{-1} on the 1:1 compounds formed by the interaction of zinc(II) and cadmium(II) thiocyanates and mercury(II) chloride and bromide with 4-aminomethylpyridine indicate that the compounds are coordination polymers having tetrahedral stereochemistry with bidentate bridging 4-aminomethylpyridine molecules and terminally bonded halogen/pseudohalogen groups in the solid state.

INTRODUCTION

Many inorganic polymers of high molecular weights exist in solid state as crystals which are either three-dimensional infinite polymers or have lattices extending into two dimensions. Besides, there are inorganic materials of high molecular weight having a large number of

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simple monomeric units analogous to the organic polymers. Some high molecular weight products also result from condensation between simpler units such as polyphosphates, iso- and heteropolyacids and their salts, and the various classes of naturally occurring silicates [1]. The inorganic compounds are very often coordination polymers [1, 2]. The structures of a number of metal halides can also be explained in terms of electron pair donation from halogen to the metal atom as in palladium(II) chloride, the crystal of which has chains of double halogen bridges [3]. Structures of silver(I) and gold(I) cyanides can also be understood in terms of donation from the nitrogen atom to the metal atom [$\rightarrow$CN–M–CN$\rightarrow$], with the resulting chains arranged parallel to one another.

A number of coordination polymers have now been synthesized from organic ligands and various metal ions, and most of these show higher thermal stabilities than the organic substrates used in them. Polymerization in most such compounds is explained in terms of halogen bridges with terminally bonded organic ligands in the polymeric chain structures [1, 2]. The present communication describes the preparation and characterization of some coordination polymers of zinc(II) and cadmium(II) thiocyanates and mercury(II) chloride and bromide with 4-aminomethylpyridine (I).

EXPERIMENTAL

Hot ethanolic solutions of the metal(II) halide or thiocyanate and the ligand were mixed in a 1:2 molar ratio. The complexes, which precipitated, were suction-filtered, washed with ethanol, and dried.

The metal (zinc or cadmium) content was determined by decomposing the complex first with nitric acid and then with concentrated sulfuric acid and completing the estimations gravimetrically [4] as $ZnNH_4PO_4$ and $CdNH_4PO_4.H_2O$, respectively. Mercury was estimated by dissolving the complex in dilute hydrochloric acid and completing the estimation as mercury(II) sulfide gravimetrically. Chloride, bromide, and thiocyanate were estimated gravimetrically as silver salts [5].

Infrared spectra in the rock salt region were recorded as Nujol mulls (neat in the case of 4-aminomethylpyridine) supported between sodium chloride plates on a Perkin-Elmer 257 spectrophotometer. The 650-200 cm^{-1} region infrared spectra were recorded as Nujol mulls (neat with 4-aminomethylpyridine) held between thin polyethylene sheets on a Perkin-Elmer 621 spectrophotometer equipped with CsI optics.

RESULTS AND DISCUSSION

Analytical data of the compounds (Table 1) isolated indicate 1:1 mole ratios between the metal and ligand. No absorption bands were

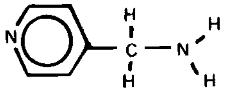
TABLE 1. Analytical Data

	Metal, %		Anion, %	
Compound[a]	Found	Calculated	Found	Calculated
$Hg(4\text{-}AMP)Cl_2$	53.0	52.8	18.9	18.7
$Hg(4\text{-}AMP)Br_2$	43.0	42.7	34.4	34.2
$Zn(4\text{-}AMP)(NCS)_2$	22.7	22.5	40.4	40.1
$Cd(4\text{-}AMP)(SCN)_2$	33.5	33.3	34.7	34.5

[a] 4-AMP = 4-aminomethylpyridine.

observed which could be attributed to water or ethanol in any of the IR spectra, thus establishing these compounds to be anhydrous and free from coordinated or lattice water/ethanol. All the compounds are quite stable and are insoluble in most of the common organic solvents, which precluded molecular weight determinations.

4-Aminomethylpyridine possesses two potential donor sites: (i) pyridyl ring nitrogen, and (ii) amino nitrogen of the $-CH_2NH_2$ group, which raises the possibility of linkage isomerism. This ligand may act as a monodentate ligand bonding through either of the two donor sites or may act as a bidentate ligand bonding through both of its donor sites simultaneously. As a bidentate ligand, the two sites may coordinate to the same metal ion and thus act as a chelating ligand, or to two different metal ions, resulting in polymeric chain structures. It should be possible to distinguish between the likely modes of ligand bonding with IR spectroscopy by observing the effect that the complex formation has on the fundamental vibrations (i) of the pyridine ring or (ii) of the amino group. Coordination through the pyridine ring nitrogen would lead to significant perturbations in the fundamental frequencies of the pyridine part of the molecule [6]. A negative shift of the NH and CN stretching vibration frequencies (due to $-CH_2NH_2$) would be expected when coordination takes place through the amino group [7]. The amino group as well as the pyridine ring vibrations suffer significant negative and positive shifts, respectively, when both the donor sites coordinate simultaneously with the metal ion (bidentate chelating or bridging ligand). Moreover, the chelating or bridging forms of the same ligand can be distinguished by IR spectroscopy. The bridging form, being more symmetrical, gives rise to fewer absorption bands in the infrared, while a multiplicity of bands due to lowered symmetry indicates the chelating form of the same ligand [8-13].



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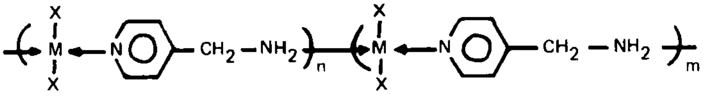
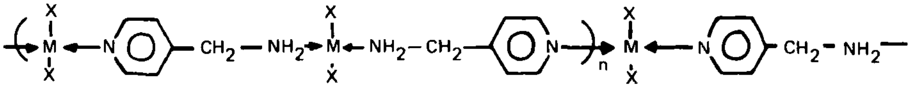


Unsymmetrical structure 1



Symmetrical structure 2
X=Cl, Br or NCS

Infrared spectra of the metal(II) complexes with 4-aminomethylpyridine indicate the bidentate bridging behavior of the organic ligand [6-13]. This is evident from the fact that the fundamental vibrations of the pyridine ring [6] and those of the amino group [7] suffer significant shifts in all these complexes. The pyridine ring vibrations at 998, 584, and 390 cm^{-1} in the uncoordinated 4-aminomethylpyridine undergo significant positive shifts. Further, the formation of a coordinate bond between $-CH_2NH_2$ and the metal(II) ions is apparent in the NH and CN stretching regions (Table 2). Both these modes suffer negative shifts. It is thus clear that 4-aminomethylpyridine is acting as a bidentate ligand bridging between two metal ions, resulting in polymeric chain structures. Stereochemically, 4-aminomethylpyridine cannot act as a bidentate chelating ligand. Moreover, since IR absorption bands due to coordinated 4-aminomethylpyridine do not exhibit any multiplicity, it is considered that the ligand molecules are equivalently head-to-head coordinated in all the complexes studied here. However, the splitting, if any, anticipated for the random coordination of 4-aminomethylpyridine is not resolvable, and such a structure will not contribute.

TABLE 2. Selected Infrared Spectra Data (cm^{-1})

Compound	νNH	δNH	$\nu C\overset{\cdots}{-}C$ $\nu C\overset{\cdot\cdot}{-}N$	Ring vibrations	Coordinated anionic modes	
4-AMP	3 350 3 280	1 560	1 600	998, 584, 390		
Hg(4-AMP)Cl_2	3 260 3 150	1 552	1 610	1 020, 615, 414	νHg-Cl	301
Hg(4-AMP)Br_2	3 260 3 200	1 552	1 610	1 020, 615, 414	νHg-Br	230
Zn(4-AMP)$(NCS)_2$	3 250 3 200	1 570	1 610	1 035, 633, 440	νCN	2 090
					νCS	783
					δNCS	476
					νZn-NCS	260
Cd(4-AMP)$(SCN)_2$	3 215 3 160	1 575	1 612	1 005, 611, 418	νCN	2 100
					νCS	733
					δSCN	447
					νCd-SCN	255

Mercury(II) Chloride and Bromide Complexes

In the 650-200 cm^{-1} IR spectral region, strong absorption bands are observed at 301 cm^{-1} in the chloro and 230 cm^{-1} in the bromo complex. Since the frequency of these bands is halogen dependent and in fair agreement with terminal Hg-Cl and Hg-Br stretching modes in several mercury(II) chloride and bromide complexes known to have tetrahedral environments about the mercury(II) ions [14, 15], these bands are identified at IR active νHg-Cl (301 cm^{-1}) and νHg-Br (230 cm^{-1}) modes, respectively. The bidentate bridging nature of 4-aminomethylpyridine molecules (vide supra) and the frequencies of νHg-Cl and νHg-Br modes consistent with terminally bonded Hg-Cl and Hg-Br bonds in tetrahedral mercury(II) complexes suggest that both these compounds are coordination polymers (Structure 2) in which the metal atoms have a polymeric tetrahedral environment of two nitrogen atoms of the head-to-head coordinated 4-aminomethylpyridine molecules and two terminal halogens in the solid state. Moreover, since only one band due to νHg-X (X = Cl or Br) is observed in the low-frequency IR spectra of the mercury(II) chloride and bromide complexes, it is clear that these complexes are highly symmetrical tetrahedral structures. One could postulate polymeric chain octahedral structures with bridging 4-aminomethylpyridine molecules as well as bridging Cl and Br groups for the 1:1 mercury(II) chloride and bromide complexes [13]. However, such structures are ruled out because the νHg-Cl and νHg-Br modes observed suggest the exclusive presence of terminal Hg-Cl and Hg-Br bonds in tetrahedral structures. The νHg-Cl and νHg-Br modes in polymeric chain octahedral structures with only bridging Hg-Cl and Hg-Br bonds would be expected to absorb much below 200 cm^{-1}, the lower frequency limit of the far IR spectrophotometer used in this study.

Zinc(II) and Cadmium(II) Thiocyanate Complexes

Zinc(II) and cadmium(II) thiocyanates gave 1:1 complexes with 4-aminomethylpyridine. Rock salt as well as low-frequency IR spectra of both these complexes are consistent with the presence of bidentate 4-aminomethylpyridine molecules bridging between two metal ions (head-to-head coordination), resulting in polymeric chain structures.

Thiocyanates of zinc(II) and cadmium(II) offer interesting examples of the mode of metal-thiocyanate bonding. Whereas zinc(II) forms Zn-NCS complexes, cadmium(II) is intermediate in character because both Cd-NCS and Cd-SCN species have been observed [16, 17]. Stereochemically, zinc(II) forms tetrahedral complexes while cadmium(II) has a tendency to result in polymeric octahedral structures built from chains of octahedra with halogen bridges. Thiocyanate bridges may, therefore, be expected to occur in cadmium(II) thiocyanate complexes. (A few monomeric four- and six-coordinated cadmium(II) thiocyanate complexes with terminally S-bonded thiocyanate groups have recently been reported [12, 13, 18].) The mode of metal-thiocyanate bonding can be distinguished from the frequency ranges for the fundamental vibrational modes of the thiocyanate group [16, 19, 20], i.e., νCN, νCS, and the doubly degenerate δNCS.

IR spectra due to coordinated 4-aminomethylpyridine in the 1:1 zinc(II) and cadmium(II) thiocyanate complexes with this ligand are consistent with the exclusive presence of bidentate bridging 4-aminomethylpyridine (head-to-head coordinated) molecules. In addition to this, the IR spectrum of the zinc(II) complex exhibits absorption bands at 2 100, 783, 476, and 260 cm^{-1} which are assigned as νCN, νCS, δNCS and νZn-NCS modes, respectively, due to coordinated thiocyanate groups. The frequencies of these modes are consistent with terminally N-bonded NCS groups in this complex. The bidentate bridging nature of 4-aminomethylpyridine molecules and terminally N-bonded NCS groups suggest that the 1:1 zinc(II) thiocyanate complex with 4-aminomethylpyridine is a coordination polymer with a tetrahedral environment of four nitrogen atoms (two from bidentate bridging, head-to-head coordinated, 4-aminomethylpyridine molecules, and two of the terminally N-bonded NCS groups) around zinc(II) ions in the solid state.

The IR spectrum of the 1:1 cadmium(II) thiocyanate complex shows absorption bands at 2 100, 733, 447, and 255 cm^{-1}, which are assigned as νCN, νCS, δSCN, and νCd-SCN modes, respectively, due to coordinated SCN groups. The frequencies of these modes suggest the exclusive presence of terminally S-bonded SCN groups in this compound [16, 19, 20]. With bidentate bridging, head-to-head coordination of 4-aminomethylpyridine molecules and terminally S-bonded SCN groups, the 1:1 cadmium(II) thiocyanate complex is considered to be a coordination polymer with a tetrahedral coordination of two nitrogen atoms of the head-to-head coordinated bidentate bridging 4-aminomethylpyridine molecules and two sulfur atoms of the terminally S-bonded SCN groups around cadmium(II) in the solid state. One could postulate coordination polymers with octahedral environments for these 1:1 zinc(II) and cadmium(II) thiocyanate complexes with bridging 4-aminomethylpyridine molecules as well as bridging thiocyanate groups. However, such structures are ruled out since the IR spectra suggest the exclusive presence of terminally bonded thiocyanate groups (N-bonded in the zinc(II) complex and S-bonded in the cadmium(II) complex) in both these complexes.

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