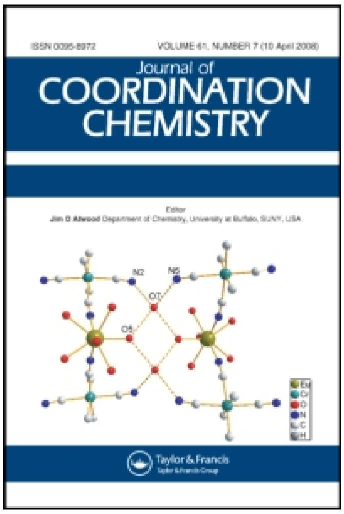

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Bidentate Bridged Morpholine Complexes with Zinc(II) and Cadmium(II) Cyanides

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SHORT COMMUNICATION

Bidentate Bridged Morpholine Complexes with Zinc(II) and Cadmium(II) Cyanides

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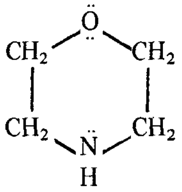
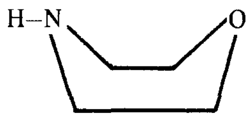
Coordination compounds formed by zinc(II) and cadmium(II) cyanides with morpholine have been prepared and characterized by infrared spectral measurements down to 200 cm^{-1} in the solid state. Possible structures for the compounds isolated in the solid state are discussed. Morpholine is shown to act as a terminal N-bonded ligand in the 1:2 zinc(II) cyanide-morpholine complex and a four-coordinated, monomeric pseudotetrahedral structure is suggested for the complex. The 1:1 zinc(II) and cadmium(II) cyanide-morpholine complexes are considered to have four-coordinated polymeric chain structures with bidentate bridged morpholine. The trans or chair configuration of the uncoordinated morpholine is retained in all the complexes.

INTRODUCTION

Recent X-ray structural[1] and infrared spectroscopic[2–6] studies have established that morpholine, with two potential donor sites – nitrogen and oxygen – in 1,4 positions, coordinates with metal ions via its nitrogen atom only and that the chair or trans conformation of the uncoordinated ligand[7] is retained in these complexes. The present i.r. spectral studies on the complexes of zinc(II) and cadmium(II) cyanides with morpholine show that it may bond through both the sites and act as a bidentate ligand bridging between two metal atoms retaining its trans configuration in these complexes.



Morpholine



Boat configuration

Chair configuration

EXPERIMENTAL SECTION

The 1:2 zinc(II) and 1:1 cadmium(II) cyanide–morpholine complexes were synthesized by heating the respective metal(II) cyanide with an excess of morpholine. The compounds formed were filtered, washed with ethanol then with ether and finally dried in air. The 1:1 zinc(II) cyanide–morpholine complex was obtained by heating the 1:2 compound at ~100°C. Stoichiometry of the compounds isolated was established by metal and cyanide estimations gravimetrically.[8]

$\mathit{Zn(Morpholine)}_2(\mathrm{CN})_2$

Found: Zn = 22.4, CN = 17.8; Calc.: Zn = 22.4, CN = 17.8%.

$\mathit{Zn(Morpholine)}(\mathrm{CN})_2$

Found: Zn = 31.8, CN = 25.4; Calc.: Zn = 32.0, CN = 25.4%.

$\mathit{Cd(Morpholine)}(\mathrm{CN})_2$
Found: Cd = 44.8, CN = 20.7; Calc.: Cd = 44.7, CN = 20.7%.

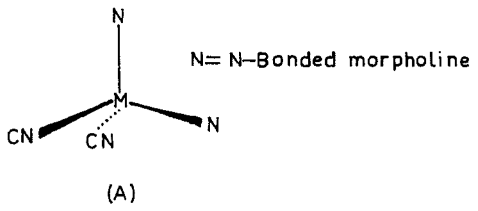
Infrared spectra were recorded as NUJOL mulls supported between sodium chloride plates (rock salt region) and thin polythene sheets (15–50μ) on a Perkin–Elmer 621 spectrophotometer equipped with caesium iodide optics.

RESULTS AND DISCUSSION

Morpholine gave two complexes with zinc(II) cyanide but only one with cadmium(II) cyanide. Infrared spectral data of the uncoordinated morpholine and the complexes studied here are listed in Table 1. Assignment of the observed bands in the present study has been made from a comparison of the vibrational modes assigned in closely related molecules like tetrahydropyrane, piperidine, 1,4-dioxane and 1,3,5-trioxane.[9] Insolubility of the compounds isolated here in suitable organic solvents precluded molecular weight and conductivity measurements.

An examination of the i.r. spectra of the complexes indicates clearly that the chair conformation of the uncoordinated morpholine is retained in all the complexes studied here. In liquid morpholine the NH asymmetric and symmetric stretching vibrations occur at 3400 and 3300 cm^{-1}, respectively. These vibrations absorb at 3258 and 3208 cm^{-1}, respectively, in the 1:2 zinc(II) cyanide–morpholine complex. This weakening of the NH bond can be explained as resulting from the electron drainage from the nitrogen atom on account of its coordination to the metal atom. The C–O–C stretching mode at 1095 cm^{-1} in uncoordinated morpholine, however, does not suffer any shift at all in this complex. It is thus clear that the morpholine acts as a monodentate N-bonded ligand in this complex.[2–6] Strong bands are also observed at 2204, 440, 333 and 325 cm^{-1} in the i.r. spectrum of this complex but not in the uncoordinated ligand. Infrared spectra of the 1:2 zinc(II) halide complexes with morpholine show a band at ~317 cm^{-1} due to νZn–N (morpholine) mode.[3] The observed additional bands are, therefore, assigned as νCN(2204 cm^{-1}) and νZn–C(440 cm^{-1}) modes due to coordinated cyano groups. One of the two bands at 333 and 325 cm^{-1} is assigned as δZn C N and the other as νZn–N (morpholine) mode. However, it is difficult to assign definite frequencies for these modes as both are expected to absorb in the same region. The observed frequencies of νCN, νZn–C and δZn C N modes are consistent with the presence of terminal cyano groups (vide infra) in this complex. With unidentate terminal N-bonded morpholine and terminal cyano groups it is suggested that the 1:2 zinc(II) cyanide–morpholine complex is a four-coordinated monomeric structure with pseudotetrahedral environments around the zinc atoms (structure A). The observed frequencies due to coordinated cyano groups rule out the possibility of cyano-bridged polymeric octahedral structure for the complex.

In addition to the shift of NH stretching vibrations to lower frequencies (Table 1) the C–O stretching mode suffers a significant negative shift in the 1:1 zinc(II) and cadmium(II) cyanide complexes with morpholine. The band at 1095 cm^{-1} due to C–O–C stretching mode in uncoordinated morpholine occurs at ~1020 cm^{-1} in these complexes. This decrease in the C–O–C stretching mode may be attributed to a change in the nature of C–O–C bond as a result of oxygen-to-metal coordination. The formation of oxygen-to-metal bond increases electron demand of the donor oxygen atom which thereby brings about a decrease of the C–O–C bond order resulting in a lowering of C–O–C stretching vibration frequency. Lowering of NH and C–O–C stretching vibration frequencies suggests that the morpholine is coordinated through both nitrogen and oxygen and thus acts as a bidentate ligand in these complexes. Except for the shift of NH and C–O–C stretching modes to lower energies, on account of coordination, the i.r. spectra due to coordinated morpholine in these 1:1 complexes are almost identical with those of uncoordinated morpholine and the N-bonded morpholine complexes. N-bonded morpholine complexes are known to retain the chair configuration of the uncoordinated ligand. I.R. spectra of 1:1 zinc(II) and cadmium(II) cyanide complexes indicate clearly that the trans configuration of morpholine is retained in these complexes and that the two donor sites must be bonded to different metal atoms. It is thus clear that the morpholine must be bridging between two metal atoms in these complexes and may be compared with the bidentate bridging nature of 1,4-dioxane in the 1:1 mercury(II) chloride–dioxane complex. Hg(dioxane)Cl$_2$ has been shown from infrared[10,11,12] and Raman[13] spectroscopic as well as X-ray diffraction[14] studies to have the constituent molecules linked together by weak O–Hg–O bonds to make a planar chain and that the mercury(II) chloride and dioxane molecules retain practically similar configurations to those in the free molecules even in the crystalline state. The interaction between the constituent molecules in Hg(dioxane)Cl$_2$ is considered to be so small[14] that the original frequencies of both the free molecules appear in the i.r. spectrum of the complex.[12] Moreover, i.r. spectral studies have shown

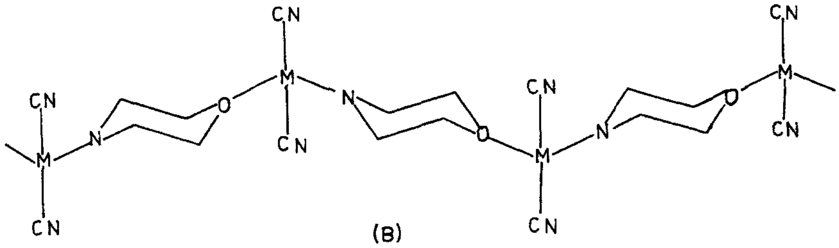


(A)

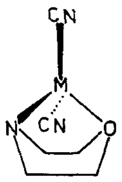
TABLE I
Infrared spectral data (cm^{-1})

M	$ZnM_2(CN)_2$	$ZnM(CN)_2$	$CdM(CN)_2$	Tentative assignment
3400 s	3258 s	3216 s	3287 m	NH stretch
3300 s	3208 s	3186 sh	3224 s	NH stretch
	2204 s	2200 vs	2180 vs 2158 m	CN stretch (M–CN)
1645 sbr	1650 sbr	1654 mbr	1650 mbr	NH deformation
1435 s	1441 s	1441 s	1458 s 1441 m	CH_2 scissor
1360 sh	1370 s	1370 s	1375 s	CH_2 wagging
1345 s	1325 w	1358 sh	1364 sh	CH_2 wagging
1314 vs	1308 m	1308 m	1312 m	CH_2 twist
1302 sh	1300 w	1300 sh	1304 w	CH_2 twist
1275 s	1254 vs	1250 vs	1254 m	CN stretch
1245 s				
1220 m	1204 s			
1190 m	1191 ms 1183 ms	1192 vs	1187 s	CH_2 twist
1130 s			1135 ms	ring vibration
	1109 m	1106 vs	1102 vs	
1095 s	1095 s	1027 s	1025 s	C–O–C stretch
1058 m	1084 m 1066 s	1083 s 1059 s		ring vibration
1028 s	1030 s			CC ring vibration
990 m	1012 m		1016 sh	
885 s	887 m	888 s	888 s	CH_2 rocking
850 s	875 s	872 s	866 s	CH_2 rocking
805 s	820 s	820 m	820 m	NH rocking
740 w	716 w	712 w	758 ms 717 ms	CH out-of-plane deformation
647 w	641 m 625 m	636 s 608 w	625 m	ring bending
	441 s	436 s	366 s	νM–C
	333 m	328 ms	285 m	δMCN/νM–N$^{(@)}$
	325 m	316 ms	300 m	(morpholine)
$Zn(CN)_2$	νCN 2216,	νZn–C 454,	δZnCN	345
$Cd(CN)_2$	νCN 2200,	νCd–C 392,	δCdCN	300

M = Morpholine; (@) = see text
νM–O mode in polymeric chain structures could not be observed as it is expected to absorb[1 2] below 200 cm^{-1}.



(B)



(C)

that the planar chain arrangement of the two oxygens and the two pseudohalogen groups is retained in the 1:1 mercury(II) pseudohalide–dioxane complexes as well.[15]

The observed frequencies of νCN, νM–C and δMCN modes in the 1:1 zinc(II) and cadmium(II) cyanide–morpholine complexes (Table 1) suggest the presence of only terminal cyano groups (vide infra). From a consideration of the terminal cyano groups and the bidentate bridged nature of morpholine it is suggested that both these compounds are four-coordinated polymeric chain structures with the trans or chair configuration of morpholine (structure B). The bidentate bridged nature of morpholine has also been reported in the 1:1 mercury(II) cyanide–morpholine complex.[6]

One could postulate that the two donor sites of morpholine in these 1:1 zinc(II) and cadmium(II) cyanide–morpholine complexes are coordinated to the the same metal atom (chelated morpholine) and monomeric four-coordinated structures for these complexes (structure C). If chelated, the morpholine must have the cis or boat configuration. If the coordinated morpholine molecules have the boat rather than the chair configuration i.r. spectra of such compounds would be anticipated to exhibit multiplicity of bands owing to the increased number of infrared active fundamentals (cf. chelated 1,4-dioxane).[16]

It may be pointed out that the frequencies of νCN, νM–C and δMCN modes in simple zinc(II) and cadmium(II) cyanides[17] suffer significant negative shifts in the morpholine complexes studied here (Table 1). Zinc(II) and cadmium(II) cyanides are isostructural and have the metal atoms linked into infinite chains and networks by means of –C–N– bonds.[18] The lowering of νCN, νM–C and δMCN modes in the present complexes compared with the corresponding modes in the simple cyanides of zinc(II) and cadmium(II) (Table 1) is consistent with the presence of terminal cyano groups (cf. lowering of νCN, νHg–C and δHgCN modes in mercury(II) cyanide complexes with only terminal cyano groups[19–21] as compared with those in pure mercury(II) cyanide[22] and cyano-bridged compounds[23]).

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