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The Low-Frequency Infrared Spectra of Nitrogen-Ligand Complexes of Zinc(II) Halides[1]

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The low-frequency infrared spectra (650–50 cm^{-1}) of the pyridyl, 2,2′-bipyridyl, and 2,2′,2′′-terpyridyl complexes of Zn(II) halides are reported. The zinc–halogen vibration is followed as the halide changes from Cl to Br to I. The zinc–nitrogen vibrations are assigned. Differences in the position of these vibrations for the various complexes are discussed.

Introduction

The low-frequency assignments of nitrogen-ligand complexes of Zn(II) halides is far from complete. For the $Zn(py)_2X_2$ and $Zn(bipy)X_2$ complexes the far-infrared spectra have been measured only to 200 cm^{-1}.[3-6] Several vibrations occur in the region 200–220 cm^{-1}, and with use of instruments with a 200-cm^{-1} cutoff, assignment of bands in this region is very tenuous. To our knowledge only the chloro derivative of $Zn(terp)X_2$ complexes has been measured below 650 cm^{-1} and that to only 200 cm^{-1}. This paper reports the infrared spectra of nine complexes in the region 650–50 cm^{-1}. Low-frequency assignments are made for these compounds whenever possible.

Experimental Section

The solutions were prepared by the slow addition of ligand to a hot absolute alcohol solution of the zinc halide. After cooling, the compound was filtered and washed repeatedly with alcohol. The compounds were analyzed for C, H, and N by standard microanalytical techniques; halogen analysis was by either micro or wet chemical analysis. The analytical results for all of the complexes agreed with the calculated values to better than ±0.22% absolute for C, ±0.05% for H, ±0.13% for N, ±0.11% for Zn, and ±0.17% for halogen. The zinc analysis for the terpyridyl complexes and for the bipyridyl iodide were not obtained owing to interference. The spectra below 650 cm^{-1} were run as Nujol mulls between high-density polyethylene windows in a Perkin-Elmer Model 301 far-infrared spectrophotometer. KBr disks were run on a Beckman IR-12 infrared spectrophotometer from 4000 to 500 cm^{-1}.

Results and Discussion

The peaks in the 1700–650-cm^{-1} region, due to ligand vibrations, give evidence that the ligand is bound through the nitrogen to the metal. Further discussion will be omitted since our interest is in the M–X and M–N stretching modes. The tentative assignments of the low-frequency vibrations for the complexes reported in this paper are presented in Tables I–III.

(a) **Pyridine Complexes.**—The ligand is relatively free of absorption bands from 650 to 50 cm^{-1} and shows only two bands at 604 and 406 cm^{-1} in the free state. The band at 604 cm^{-1} is observed to shift to about 640 cm^{-1} in the complexes. This high-frequency shift has been observed by Gill, *et al.*,[7] for other complexes. For the free ligand, the 604-cm^{-1} vibration has been assigned as an in-plane ring deformation motion; the band at 406 cm^{-1}, as an out-of-plane ring deformation.[8-10] Upon complexation, the latter splits into two bands, both occurring at higher frequency, *i.e.*, 417 and 425 cm^{-1}. The degree of high-frequency shift of both bands appears to be independent of the halogen atom.

The strong vibrations at 326 and 293 cm^{-1} in the zinc chloride complex are assigned to the ν_{Zn-Cl} asymmetric and symmetric stretching vibrations. The vibrations are shifted in the bromide and iodide complexes. For the zinc bromide complex a new strong vibration occurs at 254 cm^{-1} with a shoulder on the high-frequency side at 260 cm^{-1}. These bands are assigned to the ν_{Zn-Br} stretching motions. Both vibrations shift in the iodide complex, and a strong band at 210 cm^{-1} is assigned to the ν_{Zn-I} stretching vibration.

For all three halide complexes with pyridine, an intense band is observed at about 220 cm^{-1}, and this is assigned as the ν_{M-N} stretching vibration. Previous assignments for the ν_{M-Cl} vibrations agree with the present results;[3-5] however, previous investigators did not observe the shoulder on the 254-cm^{-1} Zn–Br band. Consequently, they list the 220-cm^{-1} band as a possible Zn–Br band which the present assignment rules out. High pressure has been shown[11] to decrease the intensity of the symmetric stretching band to a much greater extent than that of the antisymmetric; for $Zn(py)_2Br_2$ the intensity of the 220-cm^{-1} band is not decreased relative to that at 254 cm^{-1} which indicates that the symmetric Zn–Br band is not at 220 cm^{-1}. Less certain assignments for the ν_{Zn-I} and ν_{Zn-N} vibrations have been attempted,[3-5] but since the limit of the instrumentation was 200 cm^{-1} for these studies, near where these vibrations occur, some doubt must be cast on them. The present work clarifies the situation in the 200-cm^{-1} region.

The assignments in the region below 200 cm^{-1} are

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TABLE I

TENTATIVE ASSIGNMENTS FOR THE $Zn(py)_2X_2$ COMPLEXES (CM^{-1})

$Zn(py)_2Cl_2$	$Zn(py)_2Br_2$	$Zn(py)_2I_2$	Assignment	Pyridine
641(s)	641(s)	640(s)	Ligand	604
423(s) 417(m)	425(s) 418(m)	424(s) 416(m)	Ligand	406
326(vs) 293(vs)			ν_{ZnCl} antisym. sym.	
	260(sh) 254(vs)		ν_{ZnBr} antisym. sym.	
218(s)	219(vs)	222(vs) 210(vs)	ν_{ZnN} ν_{ZnI}	
200(m)	182(m)	167(m)	δ_{ZnCl} δ_{ZnBr} δ_{ZnI}	
154(sh)	153(w,br)	159(w), 147(w)	δ_{ZnN}	
141(m,br) 109(w,br)	136(w),130(w) 77(m)	126(w) 78(w,br)	Molecular Lattice Vibrations	

TABLE II

TENTATIVE ASSIGNMENTS FOR THE $Zn(bipy)X_2$ COMPLEXES (CM^{-1})

$Zn(bipy)Cl_2$	$Zn(bipy)Br_2$	$Zn(bipy)I_2$	Assignment	Bipyridyl
662(vw),656(vw) 640(vw)	662(vw),658(vw) 640(vw)	665(vw),656(vw) 638(vw)	Ligand	655(vw) 624(vw) 475(vw)
413(m) 365(vvw)	411(m) 364(vvw)	411(m) 363(vvw)	Ligand	405(m)
323(vs)			ν_{ZnCl}	
	261(s)		ν_{ZnBr}	
241(w)	250(s)	250(vs)	ν_{ZnN}	
	216(vw)	217(vs)	ν_{ZnI}	
192(vw) 170(w)	190(vw)	194(w)	δ_{ZnN}	164(s)
	158(m)			
135(m) 97(m) 67(w)	77(w) 55(m)	133(m) 62(m)	δ_{ZnX} molecular lattice vibrations ligand	136(vvw) 117(w) 93(m)

TABLE III

TENTATIVE ASSIGNMENTS FOR THE $Zn(terp)X_2$ COMPLEXES (CM^{-1})

$Zn(terp)Cl_2$	$Zn(terp)Br_2$	$Zn(terp)I_2$	Assignment	Terpyridyl
654(s) 638(s) 511(m) 430(s) 404(s) 354(vw)	652(m) 636(m) 510(m) 429(s) 405(s) 352(vvw) 305(vvw)	656(w) 640(m) 509(m) 429(s) 405(s) 354(vvw) 305(vvw)	↑ LIGAND ↓	658 624 509 424 406, 398 345
287(vs) 278(s,sh)	267(vvw)	261(vvw)	ν_{ZnCl} + Ligand	278(vvw)
244(m)	243(m)	245(m)	ν_{ZnN} + Ligand	244(vvw)
	222(sh) 213(vs)		ν_{ZnBr} + Ligand	222(vvw)
		204(m)	LIGAND	191(vs)
		187(vs)	ν_{ZnI}	
178(m)				
164(m)	167(m)	167(m)	δM-N	
124(m)	124(wn)	124(m)	LIGAND	129(sh)
110(s) 80(w)	89(m) 80(w)	83(m)	LIGAND Molecular lattice vibrations δ_{ZnX}	118

made with less assurance because crystal lattice modes may occur in this region. However, a set of medium-intensity bands at 200, 182, and 167 cm^{-1} for Cl, Br, and I, respectively, are assigned to the δ_{Zn-X} vibrations. In all of the complexes studied in this work, a weak band is observed at about 155 cm^{-1}, and this is assigned to the δ_{M-N} vibration. The vibrations below 141 cm^{-1} are generally broad and weak to medium in intensity and are assigned to the molecular lattice vibrations.

(b) **Bipyridyl Complexes.**—The two bipyridyl bands (655 and 624 cm^{-1}) become three bands upon complexation (662–665, 656–658, and 638–640 cm^{-1}) which are independent of the halide in the complex. The 401-cm^{-1} band shifts to 411–413 cm^{-1} with some intensification occurring. All of these bands can be attributed to ring vibrations, and this behavior upon complexing with a metal is quite typical.[12]

The intense band at 323 cm^{-1} in the chloride is assigned to the ν_{Zn-Cl} vibration because it shifts to 261 cm^{-1} in the bromide and 217 cm^{-1} in the iodide. Thus, the latter two bands are assigned to the ν_{Zn-Br} and ν_{Zn-I} vibrations, respectively. The band at about 250 cm^{-1} in all of the presently studied halide complexes is assigned to ν_{M-N}. Coates and Ridley[4] observed a separation of the Zn–Cl bands [331, 323 (sh) cm^{-1}] while we observe only a broad band at 323 cm^{-1}. They assigned the bands at 263 and 256 (sh) cm^{-1} to ν_{Zn-Br}. Although we also observe two bands in this region [261 (sh), 250 cm^{-1}] we assign the higher frequency band to ν_{Zn-Br} and the lower to $_{M-N}$. Since the separation of symmetric and antisymmetric modes usually decreases as the mass of the halogen increases, it seems unlikely that the separation of Zn–Br would be seen in view of the small separation for the chloro[4] or lack of separation as observed in this work. All of the complexes have a band at about 190 cm^{-1}, which is assigned to the δ_{M-N} vibration. It is difficult to assign the δ_{Zn-X} vibrations because of the complication of ligand bands and the overlap with the molecular lattice region.

(c) **Terpyridyl Complexes.**—The assignments made for the terpyridyl complexes are not so clear-cut as the previous cases because of the many low-frequency vibrations in the ligand itself. The ligand doublet at 624 and 658 cm^{-1} occurs at 636–640 cm^{-1} upon complexation for the lower frequency band and at 651–656 cm^{-1} for the higher frequency band. The 509-cm^{-1} band shows very little change with complexation. The 424-cm^{-1} band shifts to 429–430 cm^{-1}, while the doublet at about 400 cm^{-1} becomes a singlet in the complexes at about 404 cm^{-1}. The ligand vibrations in this region can all be attributed to ring-type vibrations.[13]

The ligand vibration at 345 cm^{-1} shows a small shift to 352–344 cm^{-1} in the complexes. The intense pair of bands in the 280-cm^{-1} region in the chloride is as-

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signed primarily to the ν_{Zn-Cl} vibration. This vibration shifts to 214 cm^{-1} (ν_{Zn-Br}) in the bromide and 187 cm^{-1} in the iodide (ν_{Zn-I}). None of these vibrations is pure, since ligand vibrations are probably also involved. A medium-intensity band which is present in all three complexes occurs at 243–245 cm^{-1} and is assigned to the ν_{Zn-N} vibration, while a medium band at 164–167 cm^{-1} present in all of the complexes is assigned to the δ_{Zn-N} vibration. Assignments for the δ_{Zn-X} vibrations involve the same complications discussed for the bipyridyl complexes.

Table IV records all of the assigned metal to ligand vibrations for the three series of complexes. In the pyridine and bipyridyl complexes the frequency of the ν_{Zn-X} vibrations is very similar. This is understandable since both series of complexes have a tetrahedral structure[14] and a coordination number of four. These complexes differ only in the fact that the pyridine is monodentate while the bipyridyl is bidentate. Thus, differences ought to be observed in the metal–nitrogen vibrations, and this is confirmed. The added stabilization through chelation is reflected by the shift of the ν_{Zn-N} vibration to higher frequencies for the bipyridyl complexes. Chelation also causes the N–Zn–N bend in the bipyridyls to be at a higher frequency than for the monodentate complexes. For the terpyridyl complexes, several changes occur. The structure changes to a trigonal bipyramid,[15] the coordination number becomes five, and the ligand is now terdentate. This is reflected by a shift to lower frequencies of the ν_{Zn-X} vibrations as expected for an increase in coordination number.[16] The shift of the ν_{M-N} vibration is the net result of two opposing factors: a shift to lower frequencies due to the increase in coordination number and to higher frequencies due to an increase in chelation. Actually, the ν_{M-N} occurs at slightly lower frequencies than for the bipyridyl complexes indicating that the influence of change in coordination number is the predominant factor.

TABLE IV
COMPARISON OF METAL–LIGAND VIBRATIONS FOR Zn(II) HALIDE COMPLEXES (CM^{-1})

Complex	ν_{ZnCl}	ν_{ZnBr}	ν_{ZnI}	ν_{MN}	δ_{ZnCl}	δ_{ZnBr}	δ_{ZnI}	δ_{ZnN}
$Zn(py)_2Cl_2$	326,293			218	200			154
$Zn(py)_2Br_2$		260sh,254		219		182		153
$Zn(py)_2I_2$			210	222			167	147,159
$Zn(bipy)Cl_2$	323			241				192
$Zn(bipy)Br_2$		261		250				190
$Zn(bipy)I_2$			217	250				194
$Zn(terp)Cl_2$	287,278			244				167
$Zn(terp)Br_2$		222,213		243				167
$Zn(terp)I_2$			187	245				167

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Metal Complexes of N,N,N′,N′-Tetramethylated Diamines. II.[1] Copper(II) and Iron(II) Complexes

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Complexes of N,N,N′,N′-tetramethylated ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn) with copper(II) and iron(II) halides of the type $M(diamine)X_2$ have been prepared and investigated. The Fe(diamine)Br_2 and $Cu(Me_4tn)Br_2$ complexes are pseudo-tetrahedral, but the Me_4en and Me_4pn derivatives of copper(II) are essentially planar in solution and probably also in the solid state. The ligand field spectra of the compounds have been discussed on the basis of their stereochemistry.

Introduction

In a previous paper[1] the complexes formed by Co(II) and Ni(II) halides with some N,N,N′,N′-tetramethylated alkylenediamines, those of ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn), were described and characterized: $(CH_3)_2NCH_2CH_2N(CH_3)_2$, Me_4en; $(CH_3)_2NCH(CH_3)CH_2N(CH_3)_2$, Me_4pn; $(CH_3)_2NCH_2CH_2CH_2N(CH_3)_2$, Me_4tn. Most of these complexes, which have the formula $M(diamine)X_2$, were assigned a pseudo-tetrahedral structure with C_{2v} microsymmetry. In the solid state only the complexes $Ni(Me_4en)Cl_2$ and $Ni(Me_4pn)Cl_2$ attain six-coordination by polymerization, and in inert solvents such as dichloromethane and dichlorobenzene there is an equilibrium between associated six-coordinated species and tetrahedral species. The formation of pseudo-tetrahedral complexes was attributed to steric hindrance about the donor atoms of these ligands.

In this paper the preparation and study of the complexes formed by copper(II) and iron(II) halides with Me_4en, Me_4pn, and Me_4tn are reported. Complexes of the general formula $M(diamine)X_2$, where X = Cl or Br, were obtained. Of these only $Cu(Me_4en)Br_2$ had previously been described,[2] and on the basis of its absorption spectrum it had been assigned a tetragonal

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