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Low Frequency Infrared Studies of Metal Halide Complexes of 4,4'-Bipyridine*

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Complexes of the type M(bipy)X$_2$, where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, and X = halogen were prepared and examined in the region of 650-100 cm^{-1}. Assignments for the metal-halogen and the metal-ligand vibrations were made. On the basis of these assignments and from the magnetic moments and visible absorption data, the stereochemistry of the compounds was inferred. For the transition metals and cadmium, the data are indicative of a polymeric six coordinate complex with both halide and 4,4'-bipyridine bridging. For zinc the data are consistent with a polymeric tetrahedral complex involving 4,4'-bipyridine bridging.

Introduction

Relatively few investigations[1-3] have been made with complexes of 4,4'-bipyridine in comparison to the large effort made for the 2,2'-bipyridine complexes.[4-10] The most extensive study of the coordination chemistry of 4,4'-bipyridine was recently made by Musgrave and Mattson.[3] Complexes of the type M(bipy)(NO$_3$)$_2$ where M = Ag$^+$, Hg^{2+} and Cu^{2+}, and M(bipy)$_2$(NO$_3$)$_2$ where M = Ni^{2+}, Co^{2+}, Cu^{2+} were prepared. Only mid-infrared data was reported. Thus, no low frequency infrared data are available on complexes of this type. This paper reports on the preparation of several new complexes of the type M(bipy)X$_2$, where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}, and X = halogen. The low frequency infrared region has been examined, and where possible, metal-ligand vibrations have been tentatively assigned. The assignments together with magnetic moments and visible absorption measurements are discussed in terms of the possible sterochemistry involved. In view of the fact that these complexes precipitate as polymeric materials with limited solubility in various solvents, infrared data may be the only means at making an inference as to the nature of their structure.

Experimental Section

Preparation. A warm water solution of the metal halide was added slowly, with constant stirring, to a warm water solution of a slight 1:1 stoichiometric excess of the 4,4-bipyridine ligand. The complex precipitates immediately upon the addition of the halide. The mixture was allowed to cool, filtered and the complex washed repeatedly with absolute alcohol and stored in a vacuum desiccator. Elemental analyses for carbon, hydrogen, nitrogen and halogen were obtained by microanalytical techniques, and are tabulated in Table I.

For comparison purposes the 2,2'-bipyridine complexes of the type M(bipy)$_3$X$_2$ were prepared using the method of Inskeep.[10]

Infrared measurements. The spectra from 4000-200 cm^{-1} were obtained on a Beckman IR-12 spectrophotometer, using both Nujol and halocarbon oil mulls. KBr windows were used from 4000-650 cm^{-1}; polyethylene windows were used for the range 650-200 cm^{-1}. The far infrared spectra were obtained using a Beckman IR-11 and a Perkin-Elmer Model 301 spectrophotometer, and run as Nujol mulls between polyethylene windows.

Visible absorption measurements. The absorption spectra were obtained with a Cary No. 14 spectrophotometer, using Nujol mulls on filter paper,[11] or solid absorption experiments with the diamond cell.[12]

Magnetic moments. Magnetic susceptibility measurements were made using the Faraday technique.[13] Ferrous ammonium sulfate was used as a standard.

Results and Discussion

Stoichiometry and nature of the complexes. The complexes reported in this paper contain one mole

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Table I. Analytical Data for Metal Halide-4,4′-Bipyridine Complexes

	Analyses, %							
	C		H		N		X	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$MnCl_2 . L$*	42.59	42.66	2.86	3.06	9.93	9.91	25.15	25.00
$MnBr_2 . L$	32.38	33.75	2.17	2.31	7.55	8.06		
$FeCl_2 . L$	42.45	42.64	2.85	2.78			25.06	24.05
$CoCl_2 . L$	41.99	41.99	2.82	2.95			24.80	23.63
$NiCl_2 . L$	42.03	41.35	2.82	3.31	9.80	10.01	24.81	23.71
$NiBr_2 . L$	32.05	33.02	2.15	2.35			42.68	40.89
$CuCl_2 . L$	41.32	41.66	2.77	2.97			24.40	24.12
$CuBr_2 . L$	31.64	32.53	2.12	2.45	7.38	7.57		
$ZnCl_2 . L$	41.05	40.97	2.76	2.78	9.58	9.63		
$ZnBr_2 . L$	31.47	31.59	2.11	2.17	7.35	7.57		
$ZnI_2 . L$	25.25	25.39	1.70	1.69	5.90	6.17		
$CdCl_2 . L$	35.26	35.78	2.37	2.58	8.23	8.22		
$CdBr_2 . L$	28.02	28.30	1.88	2.07	6.54	6.57		
$HgCl_2 . L$	28.06	27.93	1.89	2.06	6.55	6.61		
$HgBr_2 . L$	23.23	22.98	1.56	1.66	5.42	5.42		

* L = 4,4′-bipyridine

Table II. Magnetic Moments and Visible Absorption Spectra for Several Transition Metal Halide-4,4′-Bipyridine Complexes

Compound	Color	$\mu_{eff.}$ at 25°C B.M.	E_{max}, Absorption Spectra (mμ) (Solid)*
$MnCl_2 . L$**	Pink-white	5.78	400 (sh), 1200 (V, Br), 1480 (V, Br)
$MnBr_2 . L$	Pink-white	5.88	380 (sh), 1200 (V, Br), 1480 (V, Br)
$FeCl_2 . L$	Brown	5.56	980 (V. Br), 1475 (V. Br)
$CoCl_2 . L$	Violet	5.22	350 (VBr), 528, 550 (sh), 620
$NiCl_2 . L$	Light-green	3.23	405, 690, 1200 (VBr)
$NiBr_2 . L$	Yellow-green	3.10	720, 770, 1220 (VBr)
$CuCl_2 . L$	Blue	1.63	672, 1200, 1460 (VBr)
$CuBr_2 . L$	Green	1.85	480 (sh), 643, 1480 (V. Br)

* Obtained by Nujol mull on filter paper, or in a diamond cell. ** L = 4,4′-bipyridine. Sh = shoulder; V. Br = very broad.

of 4,4′-bipyridine ligand per mole of metal halide. The analytical results of Table I, and the infrared spectra indicate that water is not present in these complexes.

The complexes are insoluble in common solvents and appear to be polymeric in nature.

Absorption spectra. The absorption spectra for the complexes studied are recorded in Table II. The spectra for the transition metal (II) halide-4,4′-bipyridine complexes are in agreement with those for other complexes existing in an octahedral environment.[14-16]

Magnetic susceptibility studies. The magnetic moments for the complexes are tabulated in Table II. The moments are consistent with an octahedral environment for spin-free complexes.[17-19]

Infrared spectra (4000-650 cm^{-1}). The infrared results obtained in the region of 4000-650 cm^{-1} will only be briefly discussed, as emphasis in this paper will be placed on the low-frequency region of the spectrum. The observations made in this region for the 4,4′-bipyridine complexes are as follows: (1) No evidence for coordinated water was found. (2) The vibration in the pure ligand at ~ 1540 cm^{-1}, attributed to the $>C=C<$ ring vibration, remains unchanged with complexation. (3) The 1600 cm^{-1} band in the pure ligand, attributed to the $>C=N$ ring vibration, shifts toward higher frequency with complexation. The results are consistent with complexation of the ligand.

Comparison with the 2,2′-bipyridine complexes, where chelation of the ligand occurs, show that some differences in the spectra are present. Table III compares results for $Co(4,4'\text{-bipy})Cl_2$ and $Co(2,2'\text{-bipy})_3Cl_2$, which are typical of the complexes studied. The 2,2′-bipyridine complexes appear to have a richer spectra; major differences are noted between 1100 and 1312 cm^{-1}. Schildt and Taylor[20] have discussed the spectra of related complexes in terms of ligand perturbations.

Infrared spectra (650-100 cm^{-1}). Low frequency spectra of several transition complexes of 2,2′bipyridine have been measured to 250 cm^{-1}. Similar studies for 4,4′-bipyridine are unkown. Table IV presents the low-frequency data for the 4,4′-bipyridine complexes. The spectrum of the uncomplexed ligand is also presented. Vibrations occurring from 400

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Table III. Comparison of the Mid-Infrared Spectra of Co(bipy)$_3$Cl$_2$[a] and Co(bipy)Cl$_2$[b]

Co(bipy)$_3$Cl$_2$[a] (cm^{-1})	Co(bipy)Cl$_2$[b] (cm^{-1})
1650 (sh)	1625 (sh)
1600 *	1610 *
1570	1570
	1537
1490	1493
1470 *	
1442	
	1417 *
	1370
	1343
	1330
1312 *	1305
1284	
1249	
1230	1220*
1179	
1160 *	
1100	1109
1062	1080
1040	1048
1018 *	1010
908	857
778 *	818
765 (sh)	
737 *	730
651	

[a] 2,2'-bipyridine; [b] 4,4-bipyridine; * strongest vibration.

Table IV. Low Frequency Absorptions for Metal Halide-4,4'-Bipyridine Complexes (cm^{-1})

4,4'Bipyridine = L	618 (s, br), 575 (sh), 508 (s, sp), 369 (m, sp), 322 (vw), 302 (vvw), 280 vvw), 244 (w), 180 (m), 178 (sh), 168 (w), 148 (w), 137 (w), 112(w)
ZnCl$_2$. L	646 (vs, sp), 596 (vw, br), 486 (vs), 403 (w), 337 (vs), 288 (w), 219 (s), 199 (m), 168 (s), 146 (m), 121 (s, br)
ZnBr$_2$. L	648 (vs, sp, 600 (w), 572 (vw), 496 (m), 401 (w), 267 (vs), 212 (vs), 180 (sh), 159 (w), 120 (vw)
ZnI$_2$. L	648 (vs, sp), 612 (sh), 568 (s, sp), 505 (vs, sp), 392 (m), 239 (vs), 206 (vs), 200 (vs), 161 (vw), 146 (m)
CdCl$_2$. L	635 (vs, sp), 597 (w, sh), 565 (m, sp), 501 (vs, sp), 386 (m, sp), 279 (vw), 212 (vs), 192 sh), 174 (vs), 144 (vs), 134 (vs), 120 (m, sh)
CdBr$_2$. L	632 (vs, sp), 565 (m, sp), 491 (vs, sp), 393 (m, sp), 206 (m), 165 (s), 158 (s), 120 (s, br), 100 (m)
HgCl$_2$. L	640 (s, sp), 600 (vw, br), 563 (w, sp), 498 (vs, sp), 390 (w, sp), 203 (sh), 183 (s, br), 171 (s), 142 (m), 117 (vs, br), 96 (m, br)
HgBr$_2$. L	636 (s, sp), 600 (vw, br), 501 (w, sp), 492 (s, sp), 395 (m, sp), 208 (w), 166 (m), 143 (m), 132 (m, br)
MnCl$_2$. L	631 (vs, sp), 565 (m, sp), 500 (vs, sp), 389 (vw), 244 (s), 208 (s), 194 (s), 150 (s), 126 (vw), 113 (vw)
MnBr$_2$. L	633 (vs, sp), 567 (m, sp), 489 (vs, sp), 400 (vs, sp), 233 (s), 208 (vs), 180 (s), 150 (vs), 142 (vs), 127 (sh), 118 (m), 106 (vw)
FeCl$_2$. L	636 (m, sp,), 600 (sh), 566 (m, sp), 501 (s, sp), 398 (m, sp), 390 (m, sh), 386 (m, sp), 337 (vw), 251 (m), 211 (m), 205 (m), 172 (w), 120 (vw)
CoCl$_2$. L	638 (vs, sp), 501 (vs, sp), 401 (s, sp), 366 (s, sp), 295 (w, sh), 258 (vs), 218 (vs, br), 190 (vs, br), 126 (m, br)
NiCl$_2$. L	640 (vs, sp), 565 (m, sp), 501 (vs, sp), 409 (m, sp), 300 (vw), 277 (s), 231 (sh), 219 (vs), 201 (vs), 132 (vw, br)
NiBr$_2$. L	640 (vs), 629 (sh), 571 (vw), 490 (vs), 423 (w), 355 (vvw), 278 (s), 231 (vs), 215 (vs), 185 (s), 166 (vs), 149 (s, br)
CuCl$_2$. L	648 (vs, sp), 630 (sh), 567 (m, sp), 508 (vs, sp), 470 (vw), 410 (w, sp), 295 (vs), 264 (m), 255 (m), 215 (vs), 185 (m), 114 (m, br)
CuBr$_2$. L	650 (vs, sp), 565 (vw), 506 (w), 470 (vs), 476 (vw), 408 (vw), 208 (w), 261 (m), 231 (vs), 215 (vs), 130 (m, br)

Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, sp = sharp.

cm^{-1} and higher may be assigned to ligand vibrations. The metal-ligand vibrational region for metal(II) complexes is expected at frequencies lower than 350 cm^{-1}. This region is observed to be halogen-sensitive in the 4,4'-bipyridine complexes as contrasted to the insensitivity found in the 2.2'-bipyridine complexes. This is in agreement with the conclusions previously reached that the 2,2'-bipyridine complexes are hexacoordinated with the three ligands being chelated and the halogens being ionic; the complexes being water soluble.[4-10] Figure 1 illustrates the halogen insensitivity in Cu(bipy)$_3$X$_2$. It would be expected that for the insoluble 4,4'-bipyridine complexes with a stoichiometry of MX$_2$. L, the halogens would be coordinated, and therefore, the far infrared spectrum should be halogen-sensitive. Figure 2 illustrates this for the Zn(bipy)X$_2$ complexes.

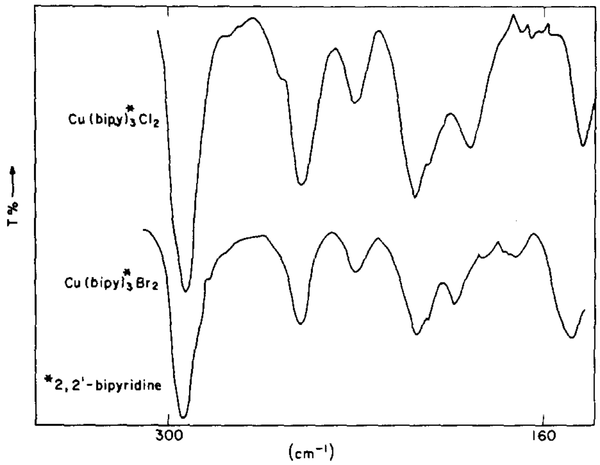

Figure 1. Comparison of Spectra for Cu(bipy)$_3$X$_2$, where X = Cl and Br and bipy = 2,2'-bipyridine.

Tentative assignments for the complexes are made and are recorded in Table V. The assignments are made not without difficulty, since 4,4'-bipyridine contains absorption in this region. Further, it is not to be inferred that these are pure vibrations, because

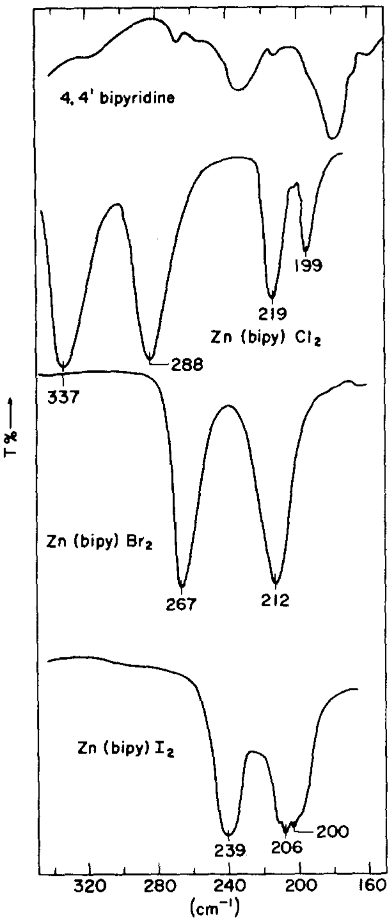

Figure 2. Spectra of Zn(bipy)X_2, where X = Cl, Br, and I and bipy = 4,4'-bipyridine.

Table V. Tentative Assignments for ν_{MX} and ν_{MN} in Various MX_2-4,4'Bipyridine Complexes

Complex	(cm^{-1}) ν_{MX}	ν_{MN}
$ZnCl_2$. L *	337, 288	219, 199
$ZnBr_2$. L	267	212
ZnI_2 . L	239	206, 200
$CdCl_2$. L	212	192 (sh), 174
$CdBr_2$. L	165	206
$MnCl_2$. L	244	208, 194
$MnBr_2$. L	180	208
$FeCl_2$. L	251	211
$CoCl_2$. L	258	218, 190
$NiCl_2$. L	219	201
$NiBr_2$. L	185	215
$CuCl_2$. L	295	215
$CuBr_2$. L	231	215

* 4,4'-bipyridine

of the possible coupling with ligand and metal-ligand bending vibrations. The assignments are made based on the following criteria: (1) The assignments for the ν_{MX} and ν_{MN} are consistent with those made for similar vibrations in related O_h or T_d complexes. (2) The intensity of the ν_{MX} and ν_{MN} are usually the strongest in this region for these complexes. (3) Vibrations in the pure ligand occurring in this region, and which are generally weak, are followed in the complexes. Although some of these vibrations can shift upon complexing and perhaps intensify, it would be in-appropriate to consider that all the strong bands that appear in this region are due to this cause. (4) Shifts toward lower frequency as one changes the halogen from Cl→Br→I are observed. (5) The self consistencies of the assignments are considered.

Stereochemistry for the complexes. The assignments for the ν_{MX} and ν_{MN} vibrations are consistent with the data obtained from other physical measurements, such as the magnetic susceptibility data and absorption studies. The data taken together suggest an octahedral environment for the 4,4'-bipyridine complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, involving halide and ligand bridging. A similar conclusion was reached for the Ni^{2+} complexes of 4,4'-bipyridine.[3] The zinc complexes appear to be tetrahedral with ligand bridging. The far infrared spectra of the mercuric halide complexes are too broad and diffuse, and thus no inference in structure is suggested.

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