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Far-Infrared and Raman Studies of Mercury(II) Halide Donor-Acceptor Complexes with Pyridine 1-Oxide and Its Derivatives

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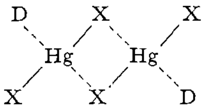
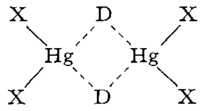
The infrared and Raman spectra between 400 and 30 cm^{-1} are reported for the mercury(II) halide complexes with pyridine 1-oxide and its α-, β-, and γ-monomethyl derivatives. Assignments are given for the symmetric and antisymmetric HgX_2 stretching modes. The mercury–oxygen stretching motion is believed to be coupled with the bridging mercury–halogen mode. These two fundamentals, however, have been assigned to frequencies below 200 cm^{-1}. The data are consistent with bridging halides.

Introduction

Recently, a number of papers have appeared which discuss the infrared spectra of pyridine 1-oxide and its derivatives in 1:1 donor–acceptor complexes of the mercury(II) halides.[2-4] Schmauss and Specker[2] reported ir data to 200 cm^{-1} for these complexes and concluded that the compounds contained dimeric units with bridged halogen atoms as in I where D is the donor.


I

They assigned bands between 400 and 200 cm^{-1} to mercury–halogen (bridging and terminal) and mercury–oxygen modes. Pappas, Villa, and Powell[3] observed two frequencies in the wave number range of 345–300 cm^{-1} in the ir spectrum of the mercury(II) chloride–pyridine 1-oxide adduct and concluded, therefore, that the structure contained bridging oxygen atoms as in II.


II

Ahuja and Rastogi[4] recorded the ir spectra down to 222 cm^{-1} in a number of mercury(II) chloride and bromide adducts of pyridine 1-oxide and concluded that the structures were dimeric as in I and contained tetrahedral mercury. However, on the basis of nqr studies,[5] tetrahedral mercury seems unlikely in these systems. Ahuja and Rastogi assigned only one mercury–halide mode and placed the mercury–oxygen frequency near 300 cm^{-1}. Mikawa, *et al.*,[6] have studied the ir and Raman spectra of the dioxane complexes of the mercury(II) halides. They placed the mercury–oxygen frequency near 100 cm^{-1}.

Thus, there is considerable disagreement among previous workers over the assignment of the skeletal vibrations of these complexes. In order to understand the vibrational spectra of these compounds better and, as a consequence, their structures, it was decided that an investigation of the far-infrared and Raman spectra was necessary.

Experimental Section

Compounds.—The compounds described here were prepared by dissolving the appropriate mercury(II) halide in hot ethanol and adding a slight excess of pyridine 1-oxide (pyO) and the picoline 1-oxides (picO). The crystalline precipitates were recrystallized from ethanol. The melting points of the compounds were in good agreement with those reported by Schmauss and Specker,[2] Pappas, *et al.*,[3] and Ahuja and Rastogi[4] except for the $HgCl_2 \cdot$ pyO. In this case, the melting point reported by Ahuja and Rastogi is about 40° lower than ours and those reported by the other workers.

Spectra.—The far-infrared spectra were recorded from 400 to 30 cm^{-1} on a Hitachi FIS-3 vacuum far-infrared spectrometer. Samples were run as Nujol mulls between polyethylene plates. The Raman spectra were obtained using a Jarrell-Ash 25-300 Raman spectrometer with 5145-Å excitation. The samples were run as powders in capillary tubes.

Results and Discussion

Table I lists the ir and Raman frequencies of the mercury(II) halide–pyridine 1-oxide compounds. The structures of these complexes are not known with certainty and thus standard symmetry considerations cannot be employed. The stoichiometry in acetonitrile[2] and benzene,[3] however, is known to be $Hg_2X_4D_2$, where X is the chloride, bromide, or iodide and D is pyridine 1-oxide. The mercury–oxygen bond is a weak donor–acceptor interaction. In a similar compound, the mercury(II) chloride adduct of 3,5-dibromopyridine 1-oxide, the Hg–O bond length has been found[7] to be 2.51 Å which is about 0.4 Å less than the sum of the atomic van der Waals radii. In much of the previous spectroscopic work, the halide atoms are considered to be bridging as in I.[2,4,8] There are at least two different types of mercury–halide bonds if this is the case. Based on previous X-ray data for mercury(II) chloride complexes with oxygen donor atoms,[7,9-12] one type of

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TABLE I

THE FUNDAMENTAL VIBRATIONS (CM^{-1}) OF THE MERCURY(II) HALIDE DONOR–ACCEPTOR COMPLEXES WITH PYRIDINE 1-OXIDE AND ITS DERIVATIVES

Pyridine 1-oxide			α-Picoline 1-oxide			β-Picoline 1-oxide			γ-Picoline 1-oxide			
Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I	Description
314^a 338^a	247	195	330^a	239	193	344^a	250	200	346^a	251	197	Antisym mercury–halide str
282	191	143	286	188	142	298	195	147	290	181	139	Sym mercury–halide str
163	138	98	144	142	95	155	136	97	192	190	175	Mercury–oxygen str and mercury–halide bridge str
139	100	80	120	105	73	120	106	73	119	106	98	
93	70	42	85	66	55	95	65	49	99	71	50	Mercury–halide bending

^{a} Ir frequencies; all others are Raman frequencies.

interaction is a typical Hg–Cl covalent bond of about 2.3 Å and the others are weak Hg–Cl interactions of about 2.9–3.2 Å. The mercury(II) bromide complex of tetrahydrofuran crystallizes in the same manner.[13] Although the interactions between the molecules are probably complicated such that the system is best described as weakly polymeric, we shall consider the vibrational spectra of these complexes as arising principally from dimeric units. Furthermore, if one makes the assumption that there is very little coupling between the two ends of the dimeric unit, then only nine skeletal modes are expected—all below 400 cm^{-1}. The skeletal fundamentals might be described as three mercury–halide stretching modes, a mercury–oxygen stretching vibration, and five bending frequencies.

Since it has been found that the halide bridge is a weak interaction,[5] one would expect only two mercury–halide stretching fundamentals at relatively high frequencies. In addition, most X-ray studies have shown[7,9–13] that the X–Hg–X covalent linkage is nearly linear, and, therefore, one of the mercury–halide modes, the antisymmetric stretching, should be very strong in the infrared but weak in the Raman spectrum. The other fundamental, the symmetric mode, will be at a lower frequency and show a reversal in intensities in the ir and Raman spectra. Schmauss and Specker[2] in their infrared study of these compounds assigned the mercury–chlorine stretching fundamental to 341 ± 1 cm^{-1} for the terminal chlorine atoms and 285 ± 7 cm^{-1} for the bridging chlorine atoms. Ahuja and Rastogi[4] reported only one ν(Hg–Cl) at 300 ± 15 cm^{-1}. Figures 1 and 2 show the infrared and Raman spectra below 400 cm^{-1} of the pyridine 1-oxide complexes of the mercury(II) halide. On the basis of the Raman spectrum, the symmetric $HgCl_2$ stretching vibration is readily assigned to a shift of 282 cm^{-1}. Two bands at 338 and 314 cm^{-1} appear in the infrared spectrum where the antisymmetric stretching mode is expected. Ahuja and Rastogi[4] assigned the 338-cm^{-1} peak to the mercury–oxygen stretching fundamental and the 314-cm^{-1} peak to an Hg–Cl stretching mode. The spectrum of the pyridine 1-oxide complex of mercury(II) chloride is, however, the only spectrum which shows two peaks in this region so we rule out the assignment of 338 cm^{-1} to

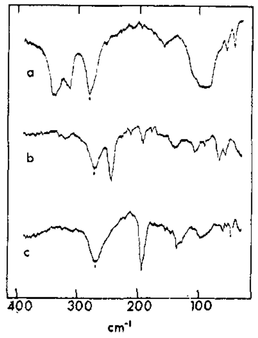

Figure 1.—The infrared spectra of the pyridine 1-oxide complexes of $HgCl_2$ (a), $HgBr_2$ (b), and HgI_2 (c). The starred peak belongs to pyridine 1-oxide.

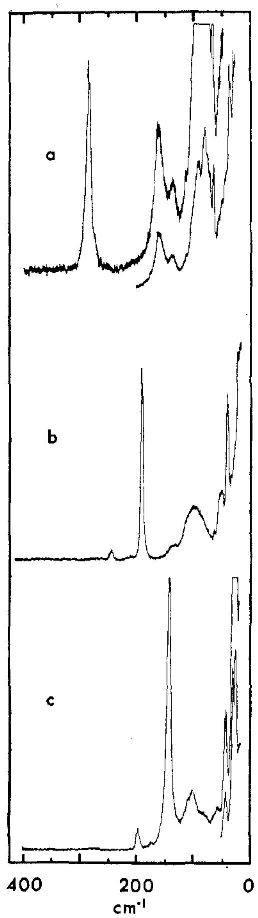

Figure 2.—The Raman spectra of the pyridine 1-oxide complexes of $HgCl_2$ (a), $HgBr_2$ (b), and HgI_2 (c). The spectra were recorded at a spectral slit width of ~1 cm^{-1}. The inserts in (a) and (c) were recorded with sensitivities decreased to bring the strong peaks on scale.

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ν(Hg–O). Schmauss and Specker[2] assigned the 338-cm^{-1} band to the terminal ν(Hg–Cl), whereas the peaks at 314 and 278 cm^{-1} were assigned to the bridging ν(Hg–Cl). In order to observe three Hg–Cl stretching fundamentals in this wave number range, the strength of the bridging interaction would have to be similar to that of the covalent bond. Contrary to this, recent nqr studies[5] show that two types of halogens do exist but by no means do they loose their character as covalently bound atoms to a *single* mercury atom. Even in the case of Al_2Cl_6, where the bridging interaction is thought to be quite strong, the force constants for terminal modes are almost twice those of the bridging modes.[14] Therefore, it would seem unlikely that the bridging halide motion would have so high a frequency. Pappas, Villa, and Powell[3] have stated that the presence of the two peaks at 338 and 314 cm^{-1} in $HgCl_2 \cdot pyO$ is indicative of the fact that the oxygen atoms are bridging in this complex. In addition, however, they stated that a mercury–chlorine mode in the range of 280–320 cm^{-1} would indicate bridging halides. On the basis of our Raman data, there is no doubt that there is indeed a mercury–chlorine stretching mode in this range and thus the explanation of Pappas, *et al.*, appears weak. It is not obvious why the antisymmetric mode is split in this spectrum; the numerous possible weak interactions are undoubtedly complicated and intermolecular forces may well cause distortions in the molecule, resulting in nonequivalent "terminal" halides.

All of the other spectra investigated here show only two bands at 330 ± 15 and 290 ± 8 cm^{-1} assignable to the covalent Hg–Cl stretching vibrations. These two bands display an alteration in intensity between the infrared and Raman spectra. The assignment of these bands to the strongly bound chloride motions can be made confidently, and they are in agreement with the numbers given by Schmauss and Specker.[2] However, we wish to stress the point that these are antisymmetric and symmetric stretching vibrations of the covalent $HgCl_2$ moiety and not terminal and bridging Hg–Cl motions as proposed by Schmauss and Specker. The bridging chloride motions are assigned a much lower frequency (*vide infra*). In the bromide compounds, both of the previous investigations[2,4] are in agreement that the infrared band at 245 ± 5 cm^{-1} is due to an Hg–Br mode. Our data leave no doubt that this band is indeed the antisymmetric $HgBr_2$ stretching mode. The intense Raman lines at 188 ± 7 cm^{-1} are then confidently assigned to the symmetric $HgBr_2$ mode.

The iodide spectra have not been reported previously, but the HgI_2 stretching fundamentals are easily assigned to the strong infrared bands at 198 ± 2 cm^{-1} and the strong Raman lines at 143 ± 4 cm^{-1} for the antisymmetric and symmetric modes, respectively.

The mercury–oxygen stretching fundamental in $HgCl_2 \cdot pyO$ was assigned previously to a frequency of 278[2] and 340 cm^{-1}.[4] As mentioned above, the 340-cm^{-1} band was not observed in any of the other spectra. In addition, the other assignments of ν(Hg–O) to bands in the region of 280 cm^{-1} are also deemed unlikely, since these peaks also appear in the pure donor.

Although the mercury–oxygen stretching vibrations have usually been assigned to frequencies above 300 cm^{-1}, our data indicate that in these particular donor–acceptor adducts the frequency is much lower. Mikawa, Jakobsen, and Brasch[6] have investigated the dioxane complexes of the mercury(II) halides and have assigned ν(Hg–O) to frequencies of 128, 108, and 94 cm^{-1} in the infrared spectra of the chloride, bromide, and iodide, respectively. The spectra of the compounds under investigation here appear to be considerably more complicated than the corresponding dioxane systems. The Hg–O interaction in the dioxane complexes involves a mercury–ether adduct of bond length 2.66 Å[10] and is somewhat weaker than in the pyridine 1-oxides. The Hg–O and bridging Hg–X interactions are of comparable strength in the pyridine 1-oxide complexes. For this reason, the remaining skeletal modes will probably couple quite strongly. It is, therefore, impossible to talk about a pure Hg–O stretching frequency. However, there are some trends in the skeletal frequencies worth discussing.

If one examines the spectra of the pyridine 1-oxide complexes, there are two bands present in the region above that expected for the mercury–halide bending frequencies. In the Raman spectrum of the chloride, these peaks are observed at 163 and 139 cm^{-1}, whereas they appear at 138 and 100 cm^{-1} in the Raman effect of the bromide. One of the peaks is readily discernible at 98 cm^{-1} in the Raman spectrum of the iodide, and the other is a weak Raman shift at 80 cm^{-1}. Thus, there are two sets of peaks in the three complexes, one at 163, 138, 98 cm^{-1} and the other at 139, 100, 80 cm^{-1}. It is believed that these modes are, to a considerable degree, the mercury–oxygen and the bridging mercury–halogen modes. Table I shows that this pattern is the same in the α- and β-picoline 1-oxide complexes. In the γ-picoline 1-oxide adducts, however, the two sets of frequencies appear at 192, 190, 175 and 119, 106, 98 cm^{-1}. The first set is considerably higher in frequency than in the other complexes. Since the mercury–halogen symmetric and antisymmetric bands have been unambiguously assigned and the mercury–halogen bending modes are found much lower (*vide infra*), there appears to be no alternative but to assign these two sets of peaks to the coupled mercury–oxygen and bridging mercury–halogen modes. At present, we have no explanation for why the γ position of the methyl group would cause so drastic a change in the frequency of these absorptions. Upon changing the halogen from chlorine to bromine to iodine in all the compounds studied here, these absorptions do not form particularly smooth trends. For example, the bridge halogen stretching modes should be more sensitive to the variation of the halogen atom than the mercury–oxygen modes. Table I shows that in going from Cl to Br, the lower frequency set exhibits the greater amount of shift, but in the Br to I series, the trend is reversed.

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(14) W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956); T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, **20**, 325 (1964).

This fact would indicate that the vibrational coupling of the low-frequency fundamentals is probably very complicated.

Mikawa, *et al.*,[6] have assigned bands at 92 and 74 cm^{-1} to $HgCl_2$ and $HgBr_2$ antisymmetric bending modes in the mercury(II) halide–dioxane adducts. These assignments are in agreement with our data so we have assigned the infrared bands at 90, 68, and 49 cm^{-1} to the $HgCl_2$, $HgBr_2$, and HgI_2 antisymmetric bending modes in the pyridine 1-oxide complexes. Similar frequencies are also found in the picoline 1-oxide–mercury halide complexes. Although we have observed many Raman lines at much lower frequencies, we were not able to distinguish internal modes from those of the lattice and thus no further assignments were attempted. Our data are consistent with bridging halogen atoms, but the vibrational spectra are complicated and complete X-ray analyses will be needed before the exact nature of all the interactions in these complexes is understood.

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Differential Thermal Analysis of Some Pyridine 1-Oxide Coordination Compounds

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Differential thermograms were determined for two series of compounds $[M(C_5H_5NO)_m(H_2O)_nCl_2]$ and $[M(C_5H_5NO)_6](BF_4)_2$, where m is 1 or 2, n is $2 - m$, and M^{2+} is Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, or Hg^{2+}. The principal features of the thermograms were melting points, endothermal peaks due to loss of water (when present as coordinated water), and an exothermic peak due to decomposition. The decomposition involved oxidation of the pyridine ring and in some cases reduction of the metal. Variation of the decomposition temperatures as well as the temperatures of dehydration is discussed.

Introduction

Differential thermal analysis has been a useful tool in the study of coordination compounds.[2] The pyridine–transition metal compounds are typical of many metal–ligand systems.[3,4] In this system endothermic peaks resulting from the loss of pyridine molecules were observed for all of the adducts investigated.[3,4] The dissociation temperatures of these compounds then proved useful in elucidating their bonding and structure.[3,4]

As a part of an investigation of the interaction of pyridine 1-oxides with Lewis acids, the thermal behavior of a series of pyridine 1-oxide transition metal coordination compounds was examined. Initially it had been hoped that the pyridine 1-oxide system would behave in a manner analogous to the pyridine system; however, the thermal behavior of the two systems proved to be markedly different. In order to obtain a more thorough understanding of the pyridine 1-oxide system several Lewis acids (including both metal tetrafluoroborates and metal halides) and a series of substituted pyridine 1-oxides were used.

Experimental Section

Preparations.—The coordination compounds used in this investigation were prepared by precipitation from alcoholic solution upon mixing solutions of the metal salts and pyridine 1-oxide, as described in the literature.[5-7] Recrystallization from alcohol and drying at 120° gave pure crystals having melting points, color, magnetic susceptibilities, and metal analysis which agreed with the literature values.[5-7] Metals, except mercury, were determined titrimetrically with standard ethylenediaminetetraacetic acid.[8] Mercury was determined spectrophotometrically in 1 *M* potassium iodide solution.[9] Room-temperature magnetic moments were obtained on a Gouy balance equipped with a 5000-G magnet.

Instrumentation.—The differential thermal analyzer used for this investigation was constructed in this laboratory. Differential temperatures were detected with a matched pair of glass encased chromel–alumel thermocouples, a Leeds and Northrup Model DC amplifier, and a Sargent SR recorder. This system was capable of detecting differential temperatures of less than 0.01°. The furnace was equipped with a cam-driven variable-voltage supply which provided linear heating rates from 30 to 450° of 4, 8, or 12°/min (other heating rates can be obtained but were not used in this investigation). The initial points of peaks in the thermograms were found to be reproducible to ±3°.[10] Comparison of thermograms obtained in this laboratory with literature values for silver nitrate, barium chloride dihydrate, and potassium nitrate[2,11] indicated that the accuracy of the peak initial points was ±3°.

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[10] It is the initial point of a peak in a differential thermogram rather than the peak maximum which correlates with other data. See for example ref 2.

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