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.

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$_5$H$_5$NO)$_m$(H$_2$O)$_n$Cl$_2$] and [M(C$_5$H$_5$NO)$_6$](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 in-

vestigation 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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Thermal Analysis.—The samples (25 mg) were mixed by grinding in a mortar and pestle with 25 mg of ground firebrick as diluent and packed in a 4-mm diameter Pyrex sample cup. The sample thermocouple was then inserted so that the end of the thermocouple was in the approximate center of the sample. The lower portion of the thermocouple was fitted through a ceramic sleeve which acted as a guide to center the thermocouple and as a loose stopper for the sample cup. The reference thermocouple was similarly embedded in 50 mg of pure firebrick in a second Pyrex sample cup. The two Pyrex cups were inserted into snug-fitted holes in an aluminum block within the furnace cavity to ensure even heating. The inertness of the firebrick was verified by obtaining thermograms of pure firebrick and of several of the compounds in the absence of firebrick. Either air or nitrogen at 1.0 atm was used as sample atmosphere during the differential analysis with no detectable differences. The thermograms exhibited peaks due to melting of the compounds, exothermic decomposition, and, in some cases, dissociation. The initial points for the peaks in these thermograms are listed in Table I.

TABLE I

Compound	Mp, °C	Exothermic dec pt, °C	Other, °C
Chlorides			
Hg(CH₃OC₅H₄NO)Cl₂	176	227	...[a]
Hg(CH₃C₅H₄NO)Cl₂	176	208	...
Hg(C₅H₅NO)Cl₂	166	228	...
Hg(CNC₅H₄NO)Cl₂	181	249	...
Hg(NO₂C₅H₄NO)Cl₂	171	235	...
Zn(C₅H₅NO)₂Cl₂	163	263	...
Cu(C₅H₅NO)₂Cl₂	...[a]	236	179[b]
Ni(C₅H₅NO)(H₂O)(Cl₂)	...	283	249[c]
Co(C₅H₅NO)(H₂O)(Cl₂)	230	262	215[c]
Mn(C₅H₅NO)(H₂O)Cl₂	314	306	177[c,d]
Mn(CH₃OC₅H₄NO)(H₂O)Cl₂	...	245	118[c]
Iodides			
Hg(CH₃OC₅H₅N)I₂	155	208	...
Hg(CH₃C₅H₄NO)I₂	154	192	...
Hg(C₅H₅NO)I₂	139	233	...
Tetrafluoroborates			
[Hg(C₅H₅NO)₆](BF₄)₂	166	216	...
[Zn(C₅H₅NO)₆](BF₄)₂	220	285	...
[Cu(C₅H₅NO)₆](BF₄)₂	186	244	197[b]
[Ni(C₅H₅NO)₆](BF₄)₂	282	296	...
[Co(C₅H₅NO)₆](BF₄)₂	267	281	...
[Mn(C₅H₅NO)₆](BF₄)₂	240	301	...
Free Ligands			
CH₃OC₅H₄NO	63	206	...
CH₃C₅H₄NO	190	272	...
C₅H₅NO	43	273[e]	...
CNC₅H₄NO	232	279	...
NO₂C₅H₄NO	164	265	...
Others			
Hg(C₅H₅NO)Br₂	125	221	...
Hg(C₅H₅NO)₂(CN)₂	125	291	...

[a] No other peaks were observed except that in some cases the organic residues from the exothermic decomposition undergo a further endothermic decomposition near 340°. The violence of the exothermic decomposition made this peak difficult to discern. [b] Loss of pyridine 1-oxide. [c] Loss of water. [d] This thermogram exhibited another peak at 238° which did not appear to be associated with a weight loss. [e] This peak was estimated since pyridine 1-oxide boils near this temperature causing the exothermic peak to be obscured.

Analysis of Decomposition Products.—In order properly to identify peaks observed in the above thermograms, weighed samples (approximately 0.2 g) of the compounds were placed at one end of an 8-mm diameter Pyrex tubing containing a constriction near the midpoint. The opposite end of the tube either

was sealed, leaving 0.7 atm of helium as the atmosphere in the tube, or was attached directly to a vacuum line equipped for gas analysis. The sample end of the tube was inserted in a furnace and heated at a temperature corresponding to a peak in the thermogram until any reaction was complete. At the conclusion of the heating, the tube was sealed at the constriction, each end weighed, and the materials subjected to chemical analysis. In this manner the loss of water or pyridine 1-oxide could be determined, as well as the elucidation of the nature of the exothermic decomposition.

The solid residues from the exothermic residue were treated with appropriate solvents in order to separate the metal salts from the organic residue. Mercury(II) chloride was successfully separated by prolonged extraction at reflux temperatures with either methanol or acetonitrile. Mercury(I) chloride was removed from the residue from the mercury(II) chloride extraction by oxidation with a nitric acid–hydrochloric acid mixture filtering to remove most of the organic residue, neturalizing the excess acid, and again filtering to remove the small amount of organic residue which had dissolved in the acid. Identification of mercury(I) chloride was aided by the successful mechanical extraction (using stainless steep forceps) of large (1 × 1 × 5 mm) single crystals of Hg₂Cl₂. Copper(II) chloride and copper(I) chloride were separated by prolonged extraction with water, alcohol, or acetonitrile. Cobalt(II) chloride was extracted by washing with water yielding a pyridine complex of cobalt(II) chloride (uv–visible spectra). Treatment of a small amount of the residue from the extraction of cobalt(II) with a large volume of dimethyl sulfoxide at 25° left a very small amount (<0.01 g) of a black solid which slowly dissolved in concentrated nitric acid, giving a solution in which cobalt ions could be detected. Attempts to extract nickel–manganese salts directly from the residue were unsuccessful. Small amounts of nickel as nickel(II) hydroxide were obtained by the following procedure. The light brown residue from the decomposition of Ni(C₅H₅NO)Cl₂ was dissolved in 12 M nitric acid (using 10 ml of acid for a 0.1-g sample of residue) yielding a golden yellow solution, which remained yellow upon making the solution strongly ammoniacal. Nickel(II) hydroxide was precipitated from the nitric acid solution upon addition of excess sodium hydroxide and filtering. A reasonably pure organic residue was obtained by neutralizing the filtrate, extracting with large volumes of dimethyl ether, and evaporating the ethereal solution to dryness. Both the yellow nitric acid solution and the ammoniacal solution exhibited visible spectra similar to the spectra observed for square-planar nickel-(II) moieties. Similar processes yielded manganese(II) and zinc(II) from their respective decomposition residues.

The individual metal ions isolated by the above processes were identified by standard qualitative tests and the ultraviolet–visible spectra. Where feasible, quantitative determinations were made using the methods described above.

The organic residues from these decompositions are intractable brown solids which were only slightly soluble (~1%) in 12 M nitric acid and dimethyl sulfoxide and even less soluble in other common solvents. The ultraviolet–visible spectra of all of these residues exhibit a single peak at 287 nm. The nmr spectra (as a 1% dimethyl sulfoxide solution) of the residues from the decomposition of Hg(C₅H₅NO)Cl₂ and Ni(C₅H₅NO)Cl₂ exhibited partially resolved multiplets at 7.70, 8.50, and 9.00 ppm and 7.70 and 8.10 ppm, respectively, downfield from tetramethylsilane. A later spectrum in perdeuteriodimethyl sulfoxide exhibited a further ill-resolved multiplet near 2.50 ppm. The infrared spectra of these residues, obtained as Nujol and/or perfluorokerosene mulls on a Beckman IR-10 spectrometer, contained bands characteristic of a pyridine ring and olefinic groups. In particular, the residue from Hg(C₅H₅NO)Cl₂ contained bands at 3110, 3086, 3060, 1630, 1511, 1470, 1210, 1190, 1173, 802, 770, and 670 cm⁻¹.

Results and Discussion

Ligand Dissociation.—Unlike other ligand–metal systems, the pyridine 1-oxide–metal system does not

exhibit loss of pyridine 1-oxide prior to thermal degradation of the pyridine 1-oxide. The only exceptions found in this investigation were the complexes with copper tetrafluoroborate and copper chloride which lost part of their pyridine 1-oxide at 179 and 197°, respectively.[6,12] A recent thermogravimetric investigation[12] of some pyridine 1-oxide coordination compounds yielded similar results but did report $Mn(C_5H_5NO)_{0.5}Cl_2$ and $Ni(C_5H_5NO)_{0.5}Cl_2$ which were not seen in this investigation. The failure of the corresponding zinc compounds to lose pyridine 1-oxide below 260° is counter to the usual trend[13] observed for the relative stability of first-row transition metal complexes. Such differences may well be expected for $Cu(C_5H_5NO)_2Cl_2$ and $Zn(C_5H_5NO)_2Cl_2$ because of the different structures of the two compounds;[14] however, this difference in the corresponding tetrafluoroborates probably reflects differences in the bonding patterns observed for the two metals.

Each of the hydrate complexes examined in this study lost its water of hydration forming anhydrous metal chloride–pyridine 1-oxide adducts. Careful heating at the dehydration temperature indicated by the thermogram yielded pure $Mn(C_5H_5NO)Cl_2$ and pure $Co(C_5H_5NO)Cl_2$. Pure $Ni(C_5H_5NO)Cl_2$ could not be prepared by this method because of some decomposition of the pyridine 1-oxide during the heating. Adducts of this type have been described in the recent literature.[12,15] The temperature at which this dehydration occurred increased in the expected[13] order: $Mn^{2+} < Co^{2+} < Ni^{2+}$. Since the hydrates were more stable than expected, thermograms of the simple metal chloride hydrates were obtained.[16] The next to last water molecule for these simple hydrates did dissociate earlier than the water molecule in the corresponding hydrated pyridine 1-oxide complex. The reason for the higher stability of the pyridine 1-oxide complexes is not readily apparent but, presumably, indicates a stronger water–metal ion bond. Since the water–metal ion bond can be described as an electrostatic interaction,[13] increasing bond strength would indicate an increased positive character of the metal ion. A difference in the positive charge felt by the water molecule in a complex of the type $ML(H_2O)Cl_2$ upon changing L from water to pyridine 1-oxide could be explained by donation of metal electrons to the pyridine 1-oxide ring which would not occur with water. However, a complete explanation of this phenomenon would have to take into account the

solid-state structures (the loss of water occurred before melting). Both $M(H_2O)_2Cl_2$ and $MH_2O(C_5H_5NO)Cl_2$ are polymeric in the solid state because of chloride bridging as well as pyridine 1-oxide bridging in the latter case.[14]

Thermal Decomposition.—The most prominent feature of all of these thermograms is a large, rather broad exothermic peak (Table I) which accompanies a complete decomposition (color changes to brown or black—gas is evolved) of the compound. Similar but much sharper exothermic peaks were observed in thermograms of the free ligands (Table I). The initial point for this peak exhibited the following trends.

1. The decomposition temperature (Table I) for a series of 4-substituted pyridine 1-oxides increased in the order: $CH_3O < CH_3 < H < CN$. Similar trends were observed for the decomposition temperature of these 4-substituted pyridine 1-oxides when coordinated to a particular metal salt except that 4-methoxypyridine 1-oxide sometimes decomposed at a higher temperature than the 4-methylpyridine 1-oxide.

2. The decomposition temperatures for a series of metal tetrafluoroborate complexes of pyridine 1-oxide increased in the order: $Hg^{2+} < Cu^{2+} <$ free ligand $< Co^{2+} < Zn^{2+} < Ni^{2+} < Mn^{2+}$. A similar order was found for a series of metal chloride complexes of pyridine 1-oxide except that the free ligand is between Co^{2+} and Ni^{2+}.

3. For the series of complexes $HgX_2 \cdot n(C_5H_5NO)$ the decomposition temperature for different anions increased in the order: $BF_4^- < Br^- < Cl^- < I^- \ll CN^-$. The products of this decomposition can be divided into three parts: (1) a nonvolatile brown residue, (2) a colorless volatile liquid, and (3) carbon dioxide.

The volatile liquid was a mixture of water, pyridine, small amounts of unreacted complex, which sublimed during the decomposition, and hydrogen chloride, when metal chlorides were used. The nonvolatile residue consisted of the metal salt and a brown organic residue which appeared as a brown powder for some complexes (*e.g.*, manganese complexes) and as a dark brown gum for others (*e.g.*, mercury complexes). Both mercury and copper were reduced to the +1 oxidation state. Cobalt appeared in the reaction products as a tetrahedral chloro complex (ultraviolet–visible spectra) and possibly as cobalt metal. The nickel and manganese appeared to be in the +2 oxidation state with no evidence for the formation of appreciable amounts of free metal; however, these metals were combined with the organic residue and could be separated only by fairly vigorous means.

The organic residue appeared to be a high molecular weight material containing some pyridine rings (as a pyridinium salt), carbonyl groups, and an unsaturated hydrocarbon chain. Since the pyrolysis of pyridine 1-oxide is known to give derivatives of glutaconic dialdehyde[17] and since the above data are compatible

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(13) H. Irving and R. J. P. Williams, *ibid.*, 3192 (1953).

(14) W. H. Watson, *Inorg. Chem.*, **8**, 1879 (1969).

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(16) Thermograms of the commercial metal chloride hydrates were determined under the same conditions used for the pyridine 1-oxide complexes. In all cases the hydrates lost their water of hydration in two or more steps, ultimately giving the anhydrous metal chloride. However, the water of hydration was not always lost in a completely stepwise manner and in those cases the step which must have included the loss of the next to last molecule was used for the correlation. The next to last molecule dissociated at 155, 180, and 183° for hydrated manganese chloride, cobalt chloride, and nickel chloride, respectively.

(17) E. Ochai, "Aromatic Amine Oxides," American Elsevier, New York, N. Y., 1967.

with this conclusion, the organic residues are assumed to be various glutaconic dialdehyde derivatives. The major decomposition product for $Hg(C_5H_5NO)Cl_2$ is tentatively identified as 5-hydroximino-1,3-pentadienyl-pyridinium chloride. Mixtures of different glutaconic dialdehyde derivatives would be expected from a process of this type and the composition of the mixture would be expected to vary with the reaction temperature. The pyridine which is present in the volatile material is thought to arise from a small amount of deoxygenation of pyridine 1-oxide which is a slow reaction at these temperatures but becomes more rapid with increasing temperatures.[17] The exothermic decomposition is essentially an oxidation–reduction reaction in which the pyridine ring is oxidized to a glutaconic dialdehyde derivative either by the metal ion in the complex or by autoxidation. Air oxidation is unlikely since the reaction occurred as readily in a nitrogen atmosphere as in air.

Ease of oxidation of the pyridine ring would be expected to depend on the π-electron density of the pyridine ring, as well as the strength of the oxidizing agent. Two factors which should affect the π-electron density of the pyridine ring were examined: (1) varying the electron-withdrawing ability of a substitutent in the 4 position on the pyridine 1-oxide ring and (2) coordination of the pyridine 1-oxide. The decomposition temperature for a series of 4-substituted pyridine 1-oxides either as the free ligand or in two different coordinated environments appeared to increase with increasing electron-withdrawing capacity of the substituent (Table I), except that 4-methoxy- and 4-methylpyridine 1-oxide were sometimes reversed. 4-Nitropyridine 1-oxide decomposed at lower temperatures than expected from the above. This lower temperature may be due to the ability of the nitro group to act as an oxidant. Coordination of the pyridine 1-oxide to the various metal ions by donation of a pair of oxygen electrons would make the oxygen more positive and cause it to pull some of the electron density from the ring decreasing the tendency of pyridine to be oxidized. Indeed, the decomposition temperatures of the manganese, zinc, and nickel tetrafluoroborate complexes are higher than the free ligand although their decomposition temperatures are not in the expected order of increased σ-bond strength.[13] The rather marked decrease in the decomposition temperature for the mercury and copper tetrafluoroborate complexes is inconsistent with this simple electron-donor picture. The decreases observed for mercury and copper tetrafluoroborate could be related to the ability of these metal ions to act as oxidizing agents. The order of increasing decomposition temperatures, $Hg <$ $Cu < Co < Zn < Ni < Mn$, is similar to the order of decreasing electron affinity for these ions; however,

the positions of mercury and copper are interchanged. The position of the copper complex in this series could be due to the difference in its structure since some pyridine 1-oxide is lost prior to the decomposition; however, all of the others appear to remain octahedrally coordinated until decomposition occurs. The metal chloride complexes of pyridine 1-oxide exhibit a similar trend in decomposition temperatures. Possibly the trends in the metal chloride series can be explained by the above factors, but structural differences in the chlorides[14] make this series more ambiguous.

Another factor which could also contribute to the variations in the decomposition temperatures and which we believe leads to a more complete explanation of the observed trends is back-donation of metal electrons onto the pyridine ring *via* the oxygen atom. The importance of back-donation in pyridine 1-oxide has been disputed in recent communications.[18–20] Back-donation would increase the electron density of the ring and, thus, should decrease the decomposition temperature. The order of increasing decomposition temperatures (*vide supra*) for the different metal ions is similar to the expected order of decreasing π-electron-donor ability[21] of the metal ions. Including some back-donation in the bonding scheme provides an explanation for the lower decomposition temperatures of the mercury(II) complexes compared to the corresponding copper(II) complexes and for the higher decomposition temperature of the manganese complexes compared with the nickel and zinc complexes. The strong π-electron-acceptor ability of the cyanide ion, by removing electron density from the mercury atom and, thus, decreasing its ability to donate electrons to the pyridine 1-oxide, could explain the unexpectedly high decomposition temperature (291°) of the mercury(II) cyanide–pyridine 1-oxide complex.

Differential thermal analysis indicates that coordination compounds of pyridine 1-oxide do not readily dissociate upon heating but, instead, undergo a complex ligand decomposition similar to the pyrolysis of pyridine 1-oxide. Variation in the decomposition temperature is consistent with an initial oxidation of the pyridine ring and with the presence of some back-bonding in the metal–oxygen bond.

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