Solid-state Vibrational Spectroscopy. Part V.[1] An Infrared and Raman Spectroscopic Study of Metal(II) Halide Pyridine Complexes

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Infrared (200—4 000 cm^{-1}) and Raman (300—3 500 cm^{-1}) spectra are reported for metal(II) halide pyridine complexes of the following stoicheiometries: $[MX_2(py)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, or Hg); $[MX_2(py)_4]$ (M = Fe, Co, or Ni); $[MX_2(py)]$ (M = Co, Cu, Cd, or Hg); and $[Hg_3X_6(py)_2]$ (X = Cl or Br). Structure–spectra correlations have been found for the dipyridine complexes whose structures are either monomeric tetrahedral {M = Zn or Co; X = Cl or Br; $[HgBr_2(py)_2]$ and $[CdI_2(py)_2]$}, polymeric octahedral (M = Mn, Ni, or Cd; X = Cl or Br; M = Fe or Co; X = Cl), or distorted polymeric octahedral {M = Cu, X = Cl or Br; and $[HgCl_2(py)_2]$}. For a given series of isomorphous complexes there is a correlation between the sum of the difference between the liquid and ligand values of ν_2, ν_3, ν_4, ν_5, ν_6, ν_7, ν_8, ν_9, ν_{10}, ν_{17}, ν_{27}, and $(\nu_9 + \nu_{10})$ and the strength of the metal–nitrogen bond as measured by the ν(M–N) value.

In this paper we report an infrared and Raman study of a range of mono-,di-, and tetra-pyridine-metal(II) halide complexes, with the aim of detecting any relation between the ligand frequencies and the metal. We believe that we have improved on an earlier study [2] by (*i*) studying halide complexes only, and (*ii*) comparing the spectra of compounds known to be isomorphous. The previously reported Raman spectra [3-7] covered the low-wavenumber regions only.

RESULTS AND DISCUSSION

The Dipyridine Complexes.—The dipyridine complexes are of three main structures: monomeric tetrahedral, polymeric octahedral, and distorted polymeric octahedral.

Monomeric tetrahedral complexes. The dipyridine complexes of zinc(II) chloride and bromide,[8] cobalt(II) bromide, mercury(II) bromide,[7] cadmium(II) iodide,[6] and the β-polymorph of $[CoCl_2(py)_2]$ are reported to have a monomeric tetrahedral structure. In this paper we will be concerned principally with the pyridine vibrations in the complexes. The correlation for these vibrations between the C_{2v} molecular point group, the C_1 site group, and the C_{2h} factor group indicates that site-group splitting would result in 27 coincident i.r. and Raman bands, while factor-group splitting would result in no coincidences between the i.r. and Raman bands, and each band should be split into a doublet.

The observed i.r. and Raman spectra of all the complexes studied are collected in Supplementary Publication No. SUP 21804 (9 pp.) † and will be discussed later. In addition to these pyridine vibrations, bands arising from metal–halide and metal–nitrogen stretching modes were also observed. There is good agreement between the values obtained by us and those reported in previous i.r.[7,9,10] and Raman [4-7] studies.

Polymeric octahedral complexes. The i.r. and Raman spectra are collected in SUP 21804. The symmetry correlations for these complexes are the same as for the tetrahedral complexes. The dipyridine complexes of the copper(II) halides [11] and of mercury(II) chloride [7] are reported to have a distorted polymeric octahedral structure.

DISCUSSION

The i.r. spectra are better resolved than those obtained by Gill *et al.*[2] For example, those workers reported no

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† For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full size copies).

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split bands for $[CuBr_2(py)_2]$ whereas we found four of the bands to be doublets. The observation of some split bands in the i.r. and Raman spectra indicates that factor-group splitting is operative in these complexes. As outlined above, there should also be a non-coincidence of i.r. and Raman bands. There are, in most cases, small differences between the i.r. and Raman values of a given mode, but the occurrence of non-coincidence can be clearly seen in the ν_6 mode of the polymeric octahedral complexes. Factor-group splitting should also result in the A_2 modes appearing in both the i.r. and Raman spectra, but in practice these modes give rise to very weak bands. It is interesting to note that, although several doublets have been observed in the present study, no splitting of the pyridine bands was observed in the series of isomorphous complexes $[M^{II}(py)_2][Ni(CN)_4]$ even under conditions of high resolution.[12]

The differences between the liquid-phase and ligand values are very small for some modes (*e.g.* ν_{19}) while for others (*e.g.* ν_{10}) they are relatively large. The sum of the shifts of the ν_2, ν_3, ν_4, ν_5, ν_6, ν_7, ν_8, ν_9, ν_{10}, ν_{17}, ν_{27}, and $(\nu_9 + \nu_{10})$ modes has been calculated for each complex. These 12 modes have been chosen since they can be observed in the i.r. and Raman spectra of all the complexes studied. It is thus possible to compare the shift values of isomorphous complexes as well as the values for the different pyridine complexes of the same metal. It is immediately apparent that there is a regular metal dependency for the series of polymeric octahedral complexes, with the total shift value progressively increasing across the period from manganese to copper (Figure and Table). Far-i.r. studies[8,9] have also shown that the ν(M–N) mode displays a similar trend (Figure). The increasing total shift value can thus be correlated with the increasing strength of the metal(II)–nitrogen bond. In this context it is worth noting that the two polymorphs of $[CoCl_2(py)_2]$ have very different total shift values. The value for the tetrahedral form is 24 cm^{-1} higher than that for the polymeric form and this can also be correlated with the greater strength of the Co–N bond in the tetrahedral form, as deduced from far-i.r. studies.[13]

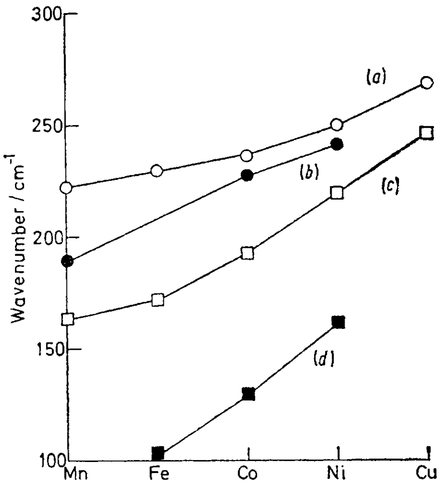
TABLE

Total shift values (cm^{-1}) for the pyridine complexes

	$[MX_2(py)_4]$				$[MX_2(py)_2]$				$[MX_2(py)]$			
X	Cl		Br		Cl		Br		Cl		Br	
M	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman
Mn					163	172	172	179				
Fe	103				172	177						
Co	129		121		217 [a]		206		221			
Ni	161	167	151	143	219	212	228	228				
Cu					246	246	259		251			
Zn					219	227	210	210				
Cd					163	160	147	158	168	176	155	178
Hg					146	148	86	104	192	197	102	117
Hg [b]									205	207	102	99

[a] The complex α-$[CoCl_2(py)_2]$, which has a polymeric octahedral structure, has an i.r. shift value of 193 cm^{-1}. [b] The $[Hg_3X_6(py)_2]$ complexes.

In most cases the difference between the total shift value of the chloro- and bromo-complexes of the same metal is small, the largest difference being 17 cm^{-1} in the Raman spectra of the zinc(II) complexes. For the mercury(II) complexes, however, there is a difference of 60 cm^{-1} for the i.r. values, and 44 cm^{-1} for the Raman values. This large difference seems to support the recent conclusion [7] from far-i.r. studies that $[HgBr_2(py)_2]$ has a monomeric tetrahedral structure in contrast to the known distorted polymeric octahedral structure of $[HgCl_2(py)_2]$.



Plots of the metal dependency of (*a*) ν(M–N) modes of polymeric octahedral $[MCl_2(py)_2]$ complexes, values from refs. 9 and 10, (*b*) ν(M–N) modes of monomeric octahedral $[MCl_2(py)_4]$ complexes, values from ref. 3, no value for $[FeCl_2(py)_4]$, (*c*) the i.r. shift values of polymeric octahedral $[MCl_2(py)_2]$ complexes, and (*d*) the i.r. shift values of monomeric octahedral $[MCl_2(py)_4]$ complexes

There are distinct structure–spectra correlations for the dipyridine complexes. The general trend is for the tetrahedral complexes to have a far greater number of split bands (in both the i.r. and Raman spectra) than the polymeric octahedral complexes. The distorted polymeric octahedral complexes $\{[CuCl_2(py)_2]$, $[CuBr_2(py)_2]$,

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and $[HgCl_2(py)_2]\}$ have a greater number of split i.r. bands than the non-distorted complexes, although there seems to be no regular pattern as to which bands split. In a previous publication [9] $[CdCl_2(py)_2]$ was described as having a distorted polymeric structure, but our spectra support the conclusion of a recent crystallographic study [14] that this complex has a non-distorted structure.

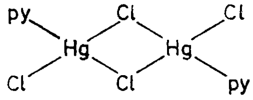
The Monopyridine Complexes.—The existence of monopyridine complexes has been discussed previously on the basis of thermogravimetric studies.[15] As far as we are aware, ours is the first report of spectra of such complexes apart from the low-wavenumber spectra of $[HgCl_2(py)]$ reported by Barr *et al.*[7]

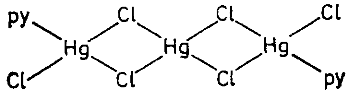
The crystal structures of these complexes have not been reported, but there are certain clear trends apparent in their vibrational spectra. The i.r. and Raman spectra of the monopyridine complexes are much simpler than those of the corresponding dipyridine complexes showing very few split bands. The total shift values (see Table) are greater for the mono- than for the corresponding dipyridine complexes which may indicate a greater metal–nitrogen bond strength in the mono complexes.

There is a marked decrease in the stability of the dipyridine complex on going down the Group from zinc to mercury. The dipyridine complex seems to be the only pyridine complex of zinc, repeated attempts to prepare the mono complex being unsuccessful. It is however possible to prepare both the di- and mono-pyridine complexes of cadmium, whilst the dipyridine complexes of mercury decompose on standing in air giving first the mono and, finally, the $HgX_2\cdot\frac{2}{3}py$, $[Hg_3X_6(py)_2]$, complexes. The complex $[HgBr_2(py)_2]$ is far more stable than its chloro-analogue, the dibromide complex being converted into $[Hg_3Br_6(py)_2]$ in 10 d, whereas the corresponding conversion for the dichloride complex takes only 48 h. The conversions are more facile if the samples are either placed *in vacuo* or heated.

The vibrational spectra of $[HgCl_2(py)]$ and $[Hg_3Cl_6(py)_2]$ are very similar, the most significant differences occurring in the low-wavenumber region. The complex $[HgCl_2(py)]$ gives strong bands at 292 (i.r.) and 287 cm^{-1} (Raman) whereas for $[Hg_3Cl_6(py)_2]$ the corresponding values are 350 and 303 cm^{-1}. In contrast, the spectra of $[HgBr_2(py)]$ and $[Hg_3Br_6(py)_2]$ are notably different particularly with respect to some of the pyridine modes.

It has been proposed [16] that $[HgCl_2(py)]$ is dimeric (I). This structure is consistent with the observed spectra which show a band characteristic of a terminal mercury–chlorine bond. The dipyridine complex shows no such band [7] since it has a polymeric octahedral structure. It is possible that $[Hg_3Cl_6(py)_2]$ has an analogous trimeric structure, (II). This is again consistent with the presence of bands in the i.r. and Raman spectra arising from terminal mercury–chlorine bonds. Since there is a marked non-coincidence between the i.r. and Raman values (350 and 303 cm^{-1} respectively), it is tempting to propose a structure with the two terminal bonds in a *trans* configuration. To the best of our knowledge, the $[Hg_3X_6(py)_2]$ complexes have not been reported previously, although similar complexes of other transition metals have been reported.[15]


(I)


(II)

The Tetrapyridine Complexes.—The tetrapyridine complexes have a monomeric *trans*-octahedral structure with four molecules in the Bravais unit cell.[17] The correlation between the C_{2v} molecular point group of pyridine, the C_1 site symmetry, and the D_{4h} factor group indicates that site-group splitting would result in 27 coincident i.r. and Raman bands while factor-group splitting would result in no coincidences between split i.r. and Raman bands.

The observation of some split bands is indicative of factor-group splitting. However, unlike the situation with the polymeric octahedral dipyridine complexes, there is no clear case of non-coincidence except for ν_{16} in the nickel(II) complexes. There are a few features in the i.r. spectra characteristic of tetrapyridine complexes. In particular, the bands arising from the ν_{17}, ν_{20}, ν_{23}, and ν_{24} modes are much more intense for the tetra- than for the di-pyridine complexes. The bands arising from the metal–halogen stretching modes are also at higher wavenumber values in the tetra- than in the polymeric octahedral di-pyridine complexes, since the latter contain bridging halogens.

The total shift values of the tetra- are less than those of the corresponding di-pyridine complexes. Both types, however, show the same trend, *viz.* that the total shift value increases on going from the iron(II) to the nickel(II) complexes, the ν(M–N) modes also showing a similar trend [4,9] (Figure and Table).

EXPERIMENTAL

The complexes were prepared using the established literature methods of either recrystallising the anhydrous metal(II) halide from dry pyridine or allowing pyridine and the metal(II) halide to react in ethanol in the appropriate molar ratio. The halide content of all the complexes, except those of Hg^{II}, was determined using Volhard's method. In the case of the mercury(II) complexes the pyridine content was determined by titration with hydrochloric acid.[16]

Spectra.—The Raman spectra of the solid samples were excited using a CRL mixed Ar$^+$–Kr$^+$ gas laser and recorded on a Cary 81 spectrometer, the choice of exciting wavelength (488.0, 520.8, 568.2, or 647.1 nm) being dependent on the colour of the sample. The spectrometer was calibrated using krypton emission lines and the wavenumber values are

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accurate to ±1 cm^{-1} for strong sharp bands, but weak and/or broad bands are accurate to ±2—3 cm^{-1}.

The i.r. spectra of discs and mulls were recorded on Perkin-Elmer 621 and 225 spectrometers, which were calibrated using polystyrene films and water rotational bands.

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