This is in agreement with the Liehr–Ballhausen diagram, which shows that the energy of ν_2 is much more sensitive to changes in Δ in the region under consideration than is the energy of ν_3.[16] This shift of the ν_2 band also provides evidence that, in the cases where Ni$(ClO_4)_2 \cdot 6H_2O$ was used as the source of nickel for the acetonitrile solutions, the solvent molecule coordinated in the tribromo complex is acetonitrile rather than water.

The tri- and tetrabromo complexes are apparently the only tetrahedral species present at appreciable concentrations in the solvents investigated. The absorption bands of tetrahedral nickel(II) complexes are characterized by being about 100 times more intense than those of the octahedral complexes,[4] and only the two species characterized here are needed to explain the intense bands observed in nickel(II)–bromide solutions in the different solvents. Numerous solid tetrahedral dibromo complexes of the type NiL_2Br_2 have been prepared and their solid and solution spectra have been measured[4,17,19]; no corresponding spectra were observed for the nickel(II)–bromide solutions investigated here. This does not completely rule out the presence of a tetrahedral dibromo complex, but does indicate that if such a complex exists it incorporates such a small fraction of the total nickel that its absorption bands are completely obscured by those of the tri- and tetrabromo complexes. The tetrahedral structure apparently does not become the favored structure until the coordination of the third bromide. Similar behavior has been observed for the nickel(II)–chloride[9] and the copper(II)–chloride and bromide systems.[20] The cobalt(II)–chloride system shows similar behavior in dimethylformamide,[21] but in other solvents such as alcohols and acetone the tetrahedral structure is stabilized upon coordination of the second halide.[22]

[19] F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960); D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964), and references therein.

[20] W. Schneider and A. v. Zelewsky, *Helv. Chim. Acta*, **46**, 1848 (1963).

[21] S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961).

[22] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950); D. A. Fine, *ibid.*, **84**, 1139 (1962).

Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1, England

The Far-Infrared Spectra of Metal–Halide Complexes of Pyridine and Related Ligands

By ROBIN J. H. CLARK and CHARLES S. WILLIAMS

Received August 24, 1964

Metal–halide complexes of pyridine and certain other nitrogen-donor ligands have been extensively investigated in the 200–700 cm.$^{-1}$ region and assignments of metal–halogen ν(M–X) and metal–ligand ν(M–L) stretching vibrations are made. The relationship of the numbers of ν(M–X) and ν(M–L) vibrations and their frequencies to the stereochemistries of the complexes (MX_mL_n) is outlined. In particular, it is shown that complexes with tetrahedral and octahedral stereochemistries may be clearly distinguished by their infrared patterns. Nujol mull spectra and solution spectra are essentially the same.

Introduction

Relatively few systematic studies of the far-infrared spectra of metal–halide complexes have been carried out. However, with the appearance of commercial double-beam spectrometers capable of reaching down to at least 200 cm.$^{-1}$, data are beginning to accumulate on metal–chlorine ν(M–Cl), metal–bromine ν(M–Br), and in some cases on metal–iodine ν(M–I) stretching vibrations. The assignments were placed on a firm basis by the initial studies on the t_2 stretching vibrations of the MX_4^{n-} series of anions (M = Mn, Fe, Co, Ni, Cu, Zn) by Clark and Dunn,[1] Adams, *et al.*,[2] and later by Sabatini and Sacconi.[3]

As a natural extension to this work, we have for several years been studying the far-infrared spectra of complexes of the type MX_mL_n, where L is a neutral electron-donor ligand. Metal–pyridine complexes are among the most extensive series known, and furthermore they include examples of complexes with the following stereochemistries: tetrahedral ($MX_2 \cdot 2py$) octahedral ($MX_2 \cdot 4py$, $MX_3 \cdot 3py$, and $MX_4 \cdot 2py$, for all of which *cis* and *trans* isomers are known), polymeric octahedral and distorted polymeric octahedral ($MX_2 \cdot 2py$, both of which contain halogen bridges), and *cis*- and *trans*-planar ($MX_2 \cdot 2py$). A summary of the relevant X-ray information on metal–pyridine complexes is given in Table I.

All the above types of complexes have been included in the present study, and the relationship between ν(M–X) vibrations and stereochemistry is outlined and shown to have potential application to the diagnosis of the stereochemistry and coordination number of new metal–halide complexes. This will be particularly important where the metal atom has a closed shell of valence electrons and hence the techniques of electronic absorption spectroscopy and magnetism may yield no unambiguous information on stereochemistry.[4]

The new stretching vibrations expected in complexes of the type MX_mL_n over those found in MX_4^{n-} anions

---

[1] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

[2] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *ibid.*, 2189 (1963).

[3] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[4] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

TABLE I

INTERATOMIC DISTANCES IN NITROGEN-DONOR COMPLEXES

Compound	Structure	r(M–X), Å.	r(M–N), Å.	Ref.
$CuCl_2 \cdot 2py$	Distorted polymeric octahedral	2.28, 3.05	2.02	*a*
$CuBr_2 \cdot 2py$	Distorted polymeric octahedral	2.46, 3.19	1.99	*b*
$HgCl_2 \cdot 2py$	Distorted polymeric octahedral	2.34, 3.25	2.60	*c*
$CdCl_2 \cdot 2py$	Distorted polymeric octahedral	2.35, 3.04	2.46	*d*
$CdBr_2 \cdot 2py$	Polymeric octahedral	2.76	2.12	*e*
$ZnCl_2 \cdot 2py$	Tetrahedral	2.15, 2.25	. . .	*f*
$CoCl_2 \cdot 2p$-tol	Tetrahedral	2.26	1.95	*g*
$CoCl_2 \cdot 2py$	Polymeric octahedral	2.49	2.14	*a*
$CoCl_2 \cdot 4py$	*trans*-Octahedral	2.32	1.99	*h*
$NiCl_2 \cdot 4py$	*trans*-Octahedral	2.387	2.00	*h*
$NiBr_2 \cdot 4py$	*trans*-Octahedral	2.58	2.00	*i*

[a] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957). [b] V. Kupčik and S. Durovič, *Czechoslov. J. Phys.*, **10**, 182 (1960). [c] Reference 19. [d] R. Zanetti, *Gazz. chim. ital.*, **90**, 1428 (1960). [e] T. I. Malinovskiĭ and Y. A. Simonov, *Dokl. Akad. Nauk SSSR*, **147**, 96 (1962). [f] M. A. Poraĭ-Koshits, L. O. Atovmyan, and G. N. Tishchenko, *Zh. Strukt. Khim.*, **1**, 337 (1960). [g] T. I. Malinovskiĭ, *Soviet Phys.-Cryst.*, **2**, 723 (1957). [h] M. A. Poraĭ-Koshits, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **10**, 117 (1954). [i] Reference 23.

py, pyridine; *p*-tol, *p*-toluidine.

are, of course, the ν(M–L) vibrations on which very little information is available at present. In pyridine complexes, these vibrations may loosely be termed "metal–pyridine" or "metal–nitrogen" vibrations. The highest frequency at which to expect metal–nitrogen stretching vibrations could clearly be inferred from metal–ammonia complexes, and Nakamoto[5] has assigned the triad of bands in the 419–500 cm.$^{-1}$ region in the spectra of $[Co(NH_3)_6]Cl_3$, $[Co(ND_3)_6]Cl_3$, and $[Cr(NH_3)_6]Cl_3$ to the t_{1u} ν(M–N) vibration, split in the solid state due to the low site symmetry of the metal atom in the crystal. On the other hand, no evidence for ν(M–L) stretching vibrations above 200 cm.$^{-1}$ has been found in complexes of heavy bidentate nitrogen-donor ligands such as α,α'-dipyridyl and *o*-phenanthroline.[6]

The ν(M–N) stretching vibrations of pyridine, a ligand of intermediate mass, might be expected to lie between these limits, and, indeed, a preliminary investigation of the infrared spectra of pyridine complexes in the 200–270 cm.$^{-1}$ region located bands which were assigned to ν(M–py) vibrations.[7] Halogen–metal–halogen bending vibrations in general lie below 200 cm.$^{-1}$ and are not considered in the present publication.

Wherever possible, band shapes and positions have been confirmed by solution as well as by mull measurements, and some confirmatory data on *p*-toluidine, quinoline, and α- and β-picoline complexes are also presented.

Experimental

The compounds were prepared by methods described in the literature (see Table II) and analyzed satisfactorily.

The infrared spectra of the solid compounds were recorded as Nujol mulls using Grubb-Parsons double-beam grating spectrophotometers, Type DM2 (200–455 cm.$^{-1}$) and Type GS2A (400 cm.$^{-1}$ and upward). The mulls were supported between plates which are transparent in the spectral region under study, *e.g.*, polythene or potassium bromide. Low-frequency spectra in solution were recorded by sealing the solution in thin (0.011-cm.) polythene bags. In order to avoid unwanted interference effects, it is essential to eliminate any air bubbles in the bag from the path of the infrared radiation. The low-frequency instrument was calibrated by reference to part of the rotational spectrum of water vapor.[8] The correction to the chart-read frequencies was within ±1 cm.$^{-1}$ over the whole range. The frequencies quoted should be accurate to ±2 cm.$^{-1}$.

Results

The results are given in Table II, where the classification is according to the stereochemistry of the complex. The assignments will be discussed in the following section.

It is clearly desirable to obtain solution spectra where possible in order to be certain that lattice vibrations and other solid-state effects are not responsible for any of the absorption bands or for their shapes and frequencies. The polymeric compounds have negligible solubility in all solvents, but even the monomeric compounds have only limited solubility in solvents which do not displace pyridine from them. Furthermore, it is obviously essential that the solvent should not absorb infrared radiation in the spectral region under study. Pyridine and chloroform were found to satisfy the above requirements in certain cases, and the comparison between mull and solution spectra is given in Table III.

The frequency of a given band in solution above 250 cm.$^{-1}$ is only slightly (up to 10 cm.$^{-1}$) higher than in the solid state, and the band shapes are virtually unchanged. Hence mull spectra of solids above 250 cm.$^{-1}$ seem to reproduce faithfully the vibrational frequencies of individual molecules as obtained from solution measurements. Below *ca.* 250 cm.$^{-1}$ the background absorption arising from the solution tends to obscure any absorption bands.

Discussion

Ring Vibrations of Pyridine.—The vibrational spectrum of pyridine has been extensively studied, and two of the lowest ring vibrations[9] are readily located in the

---

(5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 150.

(6) R. J. H. Clark, *J. Chem. Soc.*, 1377 (1962).

(7) R. J. H. Clark and C. S. Williams, *Chem. Ind.* (London), 1317 (1964).

(8) L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Natl. Bur. Std.*, **66A**, 223 (1962).

(9) C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944); L. Corrsin, B. J. Fax, and R. C. Lord, *ibid.*, **21**, 1170 (1953); G. Zerbi, J. Overend, and B. Crawford, *ibid.*, **38**, 122 (1963).

TABLE II

ABSORPTION FREQUENCIES (CM.$^{-1}$) OF COMPLEXES OF METAL–HALIDES WITH PYRIDINE AND RELATED LIGANDS (700–200 CM.$^{-1}$ RANGE)

Compound	Color	Pyridine ring vibrations		ν(M–X)	ν(M–L)	Unassigned bands	Ref.
			Tetrahedral Compounds				
$ZnCl_2\cdot2p$-tol	White	...	...	309 s, 295 s	...	...	*a*
$ZnCl_2\cdot$phen	White	...	...	323 vs	...	...	*b*
$ZnCl_2\cdot$dipy	White	...	...	327 vs, 322 s	...	...	*b*
$ZnCl_2\cdot2$py	White	639	422	329 s, 296 s	220 m	...	*c*
$ZnBr_2\cdot2$py	White	639	422	254 s, (220 m)	(220 m)	...	*d*
$ZnI_2\cdot2$py	White	637	425, 417	(∼220 s, br)	(∼220 s, br)	...	*e*
$CoCl_2\cdot2p$-tol	Blue	...	...	324 s, 295 m	...	...	*f*
$CoCl_2\cdot2$py	Blue	642	422	344 s, 304 s	252 m	...	*g*
$CoBr_2\cdot2p$-tol	Blue	...	...	248 s	...	...	*f*
$CoBr_2\cdot2$py	Blue	642	422, 416	274 s, 242 m	250 sh	...	*h*
$CoI_2\cdot2p$-tol	Green-blue	...	...	217 s	...	...	*f*
$CoI_2\cdot2$py	Green-blue	641	424, 417	237 s	246 s	...	*i*
$NiCl_2\cdot2\alpha$-pic	Dark blue	...	...	327 s, 297 s	239 m, 227 m	...	*j*
$NiBr_2\cdot2\alpha$-pic	Dark blue	...	...	256 s	239 m	...	*j*
$NiBr_2\cdot2$quin	Dark blue	...	...	263 s, 252 sh	212 m	...	*k*
$NiI_2\cdot2\beta$-pic	Dark green	...	...	231 s	243 m	...	*j*
$NiI_2\cdot2$py	Dark green	643	428	229 s	240 s	...	*j*
			Distorted Polymeric Octahedral Compounds				
$CrCl_2\cdot2$py	Green	640	440	328 m, 303 s	219 m	...	*h*
$CuCl_2\cdot2$py	Blue	644	441	294 s, 235 m	268 m	...	*c*
$CuBr_2\cdot2$py	Green	644	441	255 s, 202 m	269 m	...	*l*
$HgCl_2\cdot2$py	White	641	420	292 m	<200	...	*m*
$HgBr_2\cdot2$py	White	625	411	215 m	<200	...	*m*
$CdCl_2\cdot2$py	White	629	418	<200	<200	...	*c*
			Polymeric Octahedral Compounds				
$MnCl_2\cdot2$py	Pink	627	419	233 s	212 s, br	...	*o*
$MnBr_2\cdot2$py	Pink	628	422	<200	212 s, br	...	*h*
$FeCl_2\cdot2$py	Yellow	629	424	...	...	238 s, 227 sh, 219 s	*h*
$CoCl_2\cdot2$py	Violet	631	429	...	...	242 sh, 233 s, 224 s	*p*
$NiCl_2\cdot2p$-tol	Blue-green	...	...	238 s, br	<200	...	*q*
$NiCl_2\cdot2$py	Yellow-green	634	439	246 m	...	263 m, 239 m	*p*
$NiCl_2\cdot2$quin	Yellow	...	...	...	...	258 m, 216 s, br	*k*
$NiBr_2\cdot2p$-tol	Blue-green	...	...	<200	<200	...	*q*
$NiBr_2\cdot2$py	Yellow-green	634	442	<200	...	255 m, 237 s	*p*
$PbCl_2\cdot2$py	White	627	417	<200	<200	...	*r*
$CaCl_2\cdot2$py	White	621	411	267 s	...	236 s, br, 217 br	*s*
$CaBr_2\cdot2$py	White	621	410	∼200 s, br	...	233 sh, 222 s, br	*s*
$CdBr_2\cdot2$py	White	628	421	<200	<200	...	*n*
$CdI_2\cdot2$py	White	629	418, 410	<200	<200	...	*n*
			Monomeric Octahedral Compounds				
trans-$NiCl_2\cdot4$py	Blue	626	426	246 sh	236 s	...	*o*
trans-$NiBr_2\cdot4$py	Green	625	429	<200	235 s	...	*t*
trans-$NiI_2\cdot4$py	Light green	627	430	<200	240 s, 228 s	...	*j*
trans-$NiI_2\cdot4\beta$-pic	Light green	...	...	<200	225 s, 210 s	...	*j*
trans-$CoCl_2\cdot4$py	Pink	625	422	230 s	217 s	...	*p*
trans-$CoBr_2\cdot4$py	Pink	625	425	<200	214 s	...	*t*
trans-[$RhCl_2py_4$]Cl	Yellow	648	465	364 s	246 s	314 w	*u*
trans-[$IrCl_2py_4$]Cl	Light yellow	650	469	335 s	260 s, 255 sh	...	*v*

TABLE II (*Continued*)

Compound	Color	Pyridine ring vibrations		ν(M–X)	ν(M–L)	Unassigned bands	Ref.
			Monomeric Octahedral Compounds				
cis-$[IrCl_2py_4]Cl$	Light yellow	656	468	333 sh, 327 s	287 w, 273 m	221 w	*v*
trans-$[IrCl_4py_2]pyH$	Red	650	480	331 s, 305 vs	265 s	. . .	*w*
cis-$[IrCl_4py_2]pyH$	Orange	655	466	315 s, 304 sh, 299 s	262 m, 255 sh	. . .	*w*
$CrCl_3 \cdot 3py$	Green	640	444	364 s, 341 s, 307 m	221 m	. . .	*x*
trans-$RhCl_3 \cdot 3py$	Yellow	650	468	355 s, 332 s, 295 m	265 m, 245 s, 230 m	. . .	*y*, *u*
cis-$RhCl_3 \cdot 3py$	Light yellow	643	464	341 s, 325 m	266 m, 245 w	. . .	*y*, *u*
trans-$IrCl_3 \cdot 3py$	Yellow-orange	648	479, 469	329 s, 318 s, 307 sh	272 m, 264 s, 255 sh	. . .	*z*
cis-$IrCl_3 \cdot 3py$	Light yellow	645	466	325 s, 317 s, 303 sh	270 m, 266 sh	. . .	*z*
			Planar Compounds				
trans-$PdCl_2 \cdot 2py$	Yellow	655	465	350 s	. . .	279 w, 265 s, 219 m	*aa*
trans-$PdBr_2 \cdot 2py$	Yellow	654	462	. . .	. . .	307 s, 274 m, 254 s	*bb*
trans-$PtCl_2 \cdot 2py$	Yellow	656	479	341 vs	(282 s)	233 w	*cc*
trans-$PtBr_2 \cdot 2py$	Yellow	656	476	249 s	(297 w)	214 s	*cc*
cis-$PtBr_2 \cdot 2py$	Yellow	659, 644	448	218 s, 209 s	(260 s), (234 s)	. . .	*cc*
$PtCl_4(pyH)_2$	Red-orange	609	388	315 s	. . .	. . .	*cc*
$PtBr_4(pyH)_2$	Yellow	611	389	230 s	. . .	. . .	*cc*
$NiI_2 \cdot 2quin$	Dark green	. . .	. . .	218 s	. . .	299 s	*k*

[a] V. G. Sonalkar and M. G. Datar, *Current Sci.* (India), **29**, 468 (1960). [b] Reference 13. [c] W. Lang, *Ber.*, **21**, 1578 (1888). [d] L. Varet, *Compt. rend.*, **112**, 622 (1891). [e] J. V. Dubsky and J. Reitmayer, *Chem. Listy*, **40**, 207 (1946). [f] T. I. Malinovskiĭ, *Soviet Phys.-Cryst.*, **2**, 723 (1957). [g] E. G. Cox, A. J. Shorter, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937). [h] Reference 4. [i] A. Hantzsch, *Z. anorg. allgem. Chem.*, **159**, 273 (1927), [j] M. D. Glonek, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **84**, 2014 (1962). [k] Reference 28. [l] P. Pfeiffer, *Z. anorg. Chem.*, **48**, 108 (1906). [m] A. Pesci, *Gazz. chim. ital.*, **25**, 429 (1895). [n] S. Prasad, K. S. R. Krishnaiah, and T. Ranganathachar, *J. Indian Chem. Soc.*, **37**, 344 (1960). [o] F. Reitzenstein, *Z. anorg. Chem.*, **18**, 253 (1899). [p] F. Reitzenstein, *Ann.*, **282**, 273 (1894). [q] Synthesized here for the first time. [r] G. W. Heise, *J. Phys. Chem.*, **16**, 373 (1912). [s] R. Zanetti and R. Serra, *Gazz. chim. ital.*, **90**, 328, (1960). [t] H. Grossman, *Ber. Deut. Chem. Ges.*, **37**, 1256 (1904). [u] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1224 (1964), and references therein. [v] M. Delépine and F. Lareze, *Compt. rend.*, **257**, 3772 (1963). [w] M. Delépine, *ibid.*, **175**, 1075 (1922). [x] J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960). [y] Reference 24. [z] Reference 24. [aa] F. Krauss and F. Brodkorb, *Z. anorg. allgem. Chem.*, **165**, 73 (1927). [bb] Gmelin, "Handbuch der Anorganischen Chemie. Palladium," Berlin, Vol. 65, 1942. [cc] Gmelin, "Handbuch der Anorganischen Chemie. Platin," Weinheim/Bergstrasse, Vol. 68, Teil D, 1957.

py, pyridine; *p*-tol, *p*-toluidine; pic, picoline; quin, quinoline; dipy, α,α′-dipyridyl; phen, 1,10-phenanthroline; pyH, pyridinium ion; s, strong; m, medium; w, weak; br, broad; sh, shoulder; vs, very strong.

liquid; they are at 405 cm.$^{-1}$ (vibration 16b, of b_2 symmetry in the point group C_{2v} of the molecule, an out-of-plane ring deformation) and at 604 cm.$^{-1}$ (vibration 6a, of symmetry a_1, an in-plane ring deformation).

As Gill, *et al.*, initially indicated,[10] both of these bands suffer significant shifts toward higher frequencies on coordination of pyridine to a metal. It is clear from Table II that the magnitudes of the shifts depend on the stereochemistries of the complexes and on the metal atoms, but are virtually independent of the halogen. The 604 cm.$^{-1}$ band appears to be the more sensitive to the stereochemistry of the complexes, for a given metal, *e.g.*, $CoCl_2 \cdot 2py$ (tetrahedral) 642, 422 cm.$^{-1}$; $CoCl_2 \cdot 2py$ (polymeric octahedral) 631, 422 cm.$^{-1}$; $CoCl_2 \cdot 4py$ (octahedral) 625, 422 cm.$^{-1}$; but, as noted previously,[10] both bands seem to be functions either directly or indirectly of the metallic radius, *e.g.*, in the polymeric octahedral chloro compounds, both bands increase in the order Mn^{2+} (419, 627), Fe^{2+} (424, 629), Co^{2+} (429, 631), Ni^{2+} (439, 634), Cu^{2+} (441, 644), which is the order of decreasing ionic radii.

TABLE III

COMPARISON OF ν(M–X) VIBRATIONS (CM.$^{-1}$) IN METAL–PYRIDINE COMPLEXES AS DETERMINED IN THE SOLID STATE AND IN SOLUTION

Complex	Nujol mull	Pyridine soln.	Chloroform soln.
$ZnCl_2 \cdot 2py$	329,296	335,300	334,302
$ZnBr_2 \cdot 2py$	254,221	262 asym.	263
$CoCl_2 \cdot 2py$	344,304	*a*	354,308
$CrCl_3 \cdot 3py$	364,341,307	365,347,304	*b*

[a] Compound dissolves to form $CoCl_2 \cdot 4py$. [b] Compound is insufficiently soluble for infrared measurements in solution.

Both bands shift rather more (50–80 cm.$^{-1}$) and are weaker in transition metal complexes of the second and third rows than they are for those of the first row, *viz.*, the *cis*- and *trans*-planar derivatives of palladium

---

(10) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

TABLE IV

DISTRIBUTION OF NORMAL MODES OF VIBRATION IN COMPOUNDS OF STOICHIOMETRY MX_mL_n[a]

Type	Stereochemistry	Symmetry group	ν(MX)	Number infrared active	ν(ML)	Number infrared active
MX_4	Tetrahedral	T_d	$a_1 + t_2$	1	...	...
MX_3L	Tetrahedral	C_{3v}	$a_1 + e$	2	a_1	1
MX_2L_2	Tetrahedral	C_{2v}	$a_1 + b_1$	2	$a_1 + b_2$	2
MX_4	Planar	D_{4h}	$a_{1g} + b_{1g} + e_u$	1	...	...
MX_3L	Planar	C_{2v}	$2a_1 + b_1$	3	a_1	1
MX_2L_2	*trans*-Planar	D_{2h}	$a_g + b_{3u}$	1	$a_g + b_{2u}$	1
MX_2L_2	*cis*-Planar	C_{2v}	$a_1 + b_1$	2	$a_1 + b_1$	2
MX_2L_4	*trans*-Octahedral	D_{4h}	$a_{1g} + a_{2u}$	1	$a_{1g} + b_{1g} + e_u$	1
MX_2L_4	*cis*-Octahedral	C_{2v}	$a_1 + b_1$	2	$2a_1 + b_1 + b_2$	4
MX_3L_3	*trans*-Octahedral	C_{2v}	$2a_1 + b_1$	3	$2a_1 + b_2$	3
MX_3L_3	*cis*-Octahedral	C_{3v}	$a_1 + e$	2	$a_1 + e$	2
MX_2L_2	Polymeric octahedral	C_i	$2a_g + 2a_u$	2	$a_g + a_u$	1

[a] Calculated by the methods described by E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

and platinum and the octahedral derivatives of rhodium and iridium.

In six cases, a doubling of the 405 cm.$^{-1}$ band takes place, and in one case there is a doubling of the 604 cm.$^{-1}$ band. As these vibrations are nondegenerate it appears that some interaction between different pyridine molecules exists, either within a single molecule or between different molecules of the unit cell.

The position of the ring frequencies (643, 428 cm.$^{-1}$) of $NiI_2 \cdot 2py$ suggests a tetrahedral arrangement of ligands and this conclusion is substantiated by the study of the ν(M–X) vibrations (presented below).

In the pyridinium salts of platinum, $(pyH)_2PtX_4$, the 604 cm.$^{-1}$ band is raised very slightly, but the 405 cm.$^{-1}$ band is depressed $\sim$16 cm.$^{-1}$ and appears with lower intensity.

Metal–Halogen and Metal–Ligand Vibrations.—The ν(M–L) vibrations are assigned on the assumption that for a series of compounds, $MX_2 \cdot n$py, of the same stereochemistry, the ν(M–L) vibrations will occur at approximately the same frequencies in the chloro, bromo, and iodo analogs of a given metal, in the absence of significant coupling with ν(M–X) vibrations. However, the ν(M–X) vibrations will clearly depend on X, and as a guide to the magnitude of this dependence for first row transition metals, the following data are cited: $\nu(M\text{–}Br)/\nu(M\text{–}Cl) \approx 0.77$ and $\nu(M\text{–}I)/\nu(M\text{–}Cl) \approx 0.65$ in tetrahedral anions MX_4^{-n},[1,3] $\nu(M\text{–}Br)/\nu(M\text{–}Cl) \approx 0.74$ in the octahedral metal carbonyl halides $M(CO)_5X$ and $M(CO)_4X_2$.[11] A certain degree of coupling between vibrations of the same symmetry may occur, and in order to facilitate later discussion, the symmetries of all ν(M–X) and ν(M–L) vibrations in the complexes studied are listed in Table IV. The vibrations are strictly only primarily stretchings, for some coupling with bending vibrations will also occur; this should be small, however, as bending[3] vibrations in these systems appear to be only $\sim$100 cm.$^{-1}$.

Tetrahedral Compounds.—For molecules of the type $MX_2 \cdot 2py$, two ν(M–X) vibrations and two ν(M–L) vibrations are expected to be infrared-active (Table IV). The spectra of the tetrahedral chloro compounds are characterized by two strong bands and one medium band in the 200–400 cm.$^{-1}$ region. The former two bands are clearly ν(M–X) vibrations, because they shift down to $\sim$0.77 of their values in the analogous bromo derivatives and lower still in iodo derivatives, where they may be confused with ν(M–L) vibrations. The frequency of the third band is almost independent of halogen and is accordingly assigned as a ν(M–L) vibration ($\sim$250 cm.$^{-1}$ in the series $CoX_2 \cdot 2py$, $\sim$220 cm.$^{-1}$ in the series $ZnX_2 \cdot 2py$, and 227 cm.$^{-1}$ in $Zn(NCS)_2 \cdot 2py$[12]).

The second ν(M–L) vibration must either be too weak to locate or else below 200 cm.$^{-1}$. For the *o*-phenanthroline, α,α'-dipyridyl (recorded previously, and confirmed herein),[13] *p*-toluidine, and picoline complexes, the two ν(M–X) vibrations are assigned similarly. Furthermore, the ν(M–X) and ν(M–L) vibrations of cobalt complexes (Table II) lie 10–30 cm.$^{-1}$ above those of comparable zinc complexes, as indeed is the case for the ν(M–X) vibrations of MX_4^{2-} anions.[1]

A further point of interest is the increase in ν(M–X) vibrations on passing from MX_4^{2-} to $MX_2 \cdot 2L$ (Table V). This point is illustrated for the series $CoX_2 \cdot 2py$ and CoX_4^{2-} in Figure 1.

Nickel complexes of all three halogens are known with the stoichiometry $NiX_2 \cdot 2py$, but only the iodide appears to be tetrahedral, the chloride and bromide being halogen-bridged polymers. The ν(Ni–I) and ν(Ni–py) vibrations are assigned on the assumption that both vibrational frequencies will occur slightly lower than the analogous vibrations of the corresponding cobalt compound $CoI_2 \cdot 2py$ (*cf.* the vibrational frequencies of CoX_4^{2-} and NiX_4^{2-}).[1,3]

Distorted Polymeric Octahedral Complexes.—The compounds designated in this paper as distorted poly-

---

(11) M. A. Bennett and R. J. H. Clark, *Chem. Ind.* (London), 861 (1963); M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, in press.

(12) R. J. H. Clark and C. S. Williams; a far-infrared study of metal thiocyanate complexes with pyridine and related ligands will be published shortly.

(13) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).

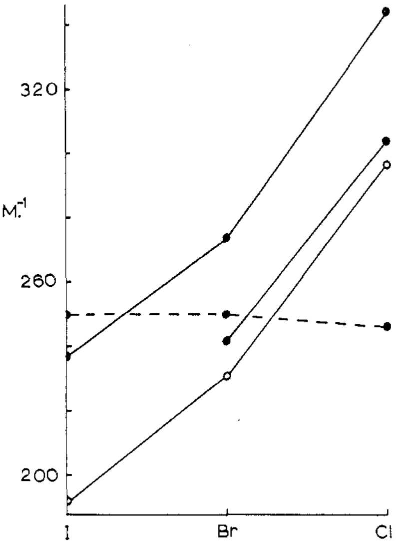

Figure 1.—Metal–halogen stretching frequencies (full lines) in $CoX_2\cdot 2py$ complexes (full circles) and in CoX_4^{2-} (open circles), X = Cl, Br, I. Metal–pyridine stretching frequencies (broken line) in $CoX_2\cdot 2py$ complexes.

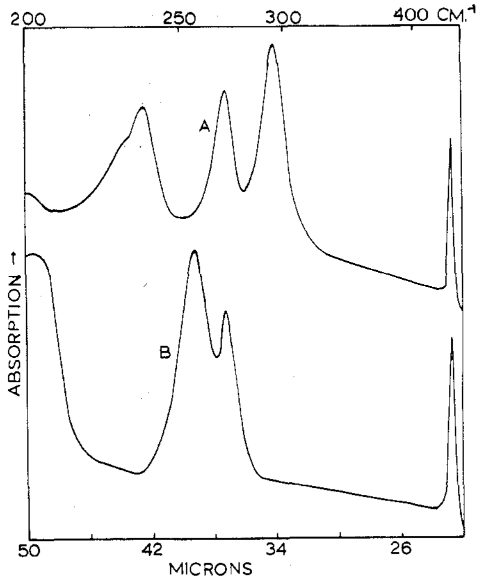

Figure 2.—Far-infrared spectra of (A) $CuCl_2\cdot 2py$ and (B) $CuBr_2\cdot 2py$.

TABLE V

COMPARISON OF ν(M–X) VALUES FOR TETRAHEDRAL COMPOUNDS OF THE TYPES MX_4^{2-} [a] AND $MX_2\cdot$2LIGAND

Compound [b]	ν(M–X)	Compound [b]	ν(M–X)
$ZnCl_4^{2-}$	277	$CoBr_2\cdot 2p$-tol	248
$ZnCl_2\cdot 2p$-tol	309,295	$CoBr_2\cdot 2py$	274,242
$ZnCl_2\cdot 2py$	329,296	CoI_4^{2-}	192
$ZnCl_2\cdot$dipy	327,322	$CoI_2\cdot 2p$-tol	217
$ZnCl_2\cdot$phen	323	$CoI_2\cdot 2py$	246,237
$ZnBr_4^{2-}$	205	$NiCl_4^{2-}$	285
$ZnBr_2\cdot 2py$	254,220	$NiCl_2\cdot 2\alpha$-pic	327,297
ZnI_4^{2-}	165	$NiBr_4^{2-}$	224
$ZnI_2\cdot 2py$	229	$NiBr_2\cdot 2\alpha$-pic	256
$CoCl_4^{2-}$	300	$NiBr_2\cdot 2$quin	263,252 sh
$CoCl_2\cdot 2p$-tol	324,295	NiI_4^{2-}	189
$CoCl_2\cdot 2py$	344,304	$NiI_2\cdot 2py$	229
$CoBr_4^{2-}$	227	$NiI_2\cdot 2\beta$-pic	231

[a] References 1 and 3. [b] py, pyridine; *p*-tol, *p*-toluidine; dipy, α,α'-dipyridyl; pic, picoline; quin, quinoline.

meric octahedral compounds consist of halogen-bridged polymers with two short and two long metal–halogen bonds and the pyridine molecules in *trans* positions perpendicular to the chain. At least three compounds of the type $MCl_2\cdot 2py$ (M = Cu, Cd, Hg) are isomorphous (see Table I), but their far-infrared spectra are significantly different. The site symmetry of the metal atom is only C_i, although each repeat unit approximates to D_{2h} symmetry. On either basis, two ν(M–X) and one ν(M–L) vibration are infrared-active (Table IV). Indeed three bands are seen in the 200–400 cm.$^{-1}$ region (Figure 2), for two of which the ν(M–Br)/ν(M–Cl) ratio is ~0.86, suggesting that they are ν(M–X) vibrations, while the third (at 268 cm.$^{-1}$) is independent of halogen and is thus the ν(M–L) vibration. The ν(M–X) vibrations of $CuCl_2\cdot$2py (294, 235 cm.$^{-1}$) and $CuBr_2\cdot$2py (255, 202 cm.$^{-1}$) are comparable but lower than those[14] found for $CuCl_2$ (329, 277 cm.$^{-1}$) and $CuBr_2$ (254, 223 cm.$^{-1}$), which also consist of halogen-bridged octahedral polymers.[15] While it seems surprising that Cu–Cl bond lengths differing by as much as 0.77 Å. should give rise to stretching frequencies differing only by 59 cm.$^{-1}$, no more satisfactory explanation can be advanced at present.

Contrary to a report by Coates and Ridley,[13] one ν(M–X) vibration occurs above 200 cm.$^{-1}$ in both $HgCl_2\cdot$2py (292 cm.$^{-1}$) and $HgBr_2\cdot$2py (215 cm.$^{-1}$). This result is in accord with the presence of one pair of short Hg–X bonds in the compounds, as X-ray work has already indicated (Table I). The ν(Hg–Cl) vibration falls well in line with other data on mercury compounds: compare, for instance, the following Hg–Cl bond lengths (in each case the shortest in the compound by at least 0.5 Å.) with the highest ν(Hg–Cl) vibration (in each case the only vibration above 200 cm.$^{-1}$); in $HgCl_2$,[16] r(Hg–Cl) = 2.25 Å., ν(Hg–Cl) = 375 cm.$^{-1}$; in $CsHgCl_3$,[17] r(Hg–Cl) = 2.29 Å., ν(Hg–Cl) = 320 cm.$^{-1}$; in NH_4HgCl_3,[18] r(Hg–Cl) = 2.34 Å., ν(Hg–Cl) = 309 cm.$^{-1}$; in $HgCl_2\cdot$2py,[19] r(Hg–Cl) = 2.34 Å., ν(Hg–Cl) = 292 cm.$^{-1}$. When $HgCl_2\cdot$2py is dissolved in pyridine, the 292 cm.$^{-1}$ band disappears, presumably due to the formation of an octahedral species such as $HgCl_2\cdot$4py. The solid material isolated from this solution showed the same infrared spectrum as the solution itself, but on exposure to air it rapidly reverted to the original $HgCl_2\cdot$2py complex with an absorption band at 292 cm.$^{-1}$.

None of the series $CdX_2\cdot$2py shows any absorption above 200 cm.$^{-1}$ which might be attributed to ν(Cd–X) or ν(Cd–py) vibrations. This is more surprising for the chloride, which has bond lengths comparable with the mercury analog, than it is for the bromide, which is

---

(14) D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, **59**, 2228 (1963).

(15) A. F. Wells, *J. Chem. Soc.*, 1670 (1947).

(16) D. Grdenić, *Arhiv Kem.*, **22**, 14 (1950).

(17) Z. V. Zvonkova, V. V. Samodurova, and L. G. Vorontsova, *Dokl. Akad. Nauk SSSR*, **102**, 1115 (1955).

(18) E. J. Harmsen, *Z. Krist.*, **100**, 208 (1938).

(19) D. Grdenić and I. Krstanović, *Arhiv Kem.*, **27**, 143 (1955).

polymeric octahedral, and the iodide, which is clearly polymeric but has not been subjected to a detailed X-ray analysis. However it is clear from previous work on ν(Cd–Cl) vibrations[18] that these are invariably below 200 cm.$^{-1}$ in octahedral complexes and only slightly above 200 cm.$^{-1}$ in tetrahedral complexes.

Polymeric Octahedral Complexes.—The polymeric halogen-bridged octahedral complexes consist in part of isomorphous series, *e.g.*, $MCl_2\cdot 2py$ (M = Mn, Fe, Co, Ni) and their far-infrared spectra consist of badly resolved bands in the 200–260 cm.$^{-1}$ region. Unfortunately the corresponding bromo complex of iron is not known, while that of the cobalt complex exists only as the tetrahedral isomer. Hence interpretations of the spectra of these complexes are not in general possible and must await a study below 200 cm.$^{-1}$.

Nevertheless, as a group, the distinction between octahedral and tetrahedral complexes of the same stoichiometry is compelling,[20] *e.g.*, in the case of $CoCl_2\cdot 2py$ (Figure 3).

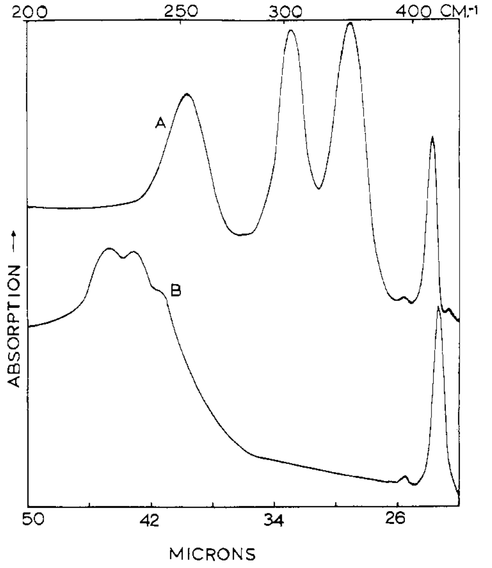

Figure 3.—Far-infrared spectra of (A) tetrahedral form and (B) polymeric octahedral form of $CoCl_2\cdot 2py$.

Monomeric Octahedral Complexes.—As a class, these complexes give much better defined spectra than the polymeric octahedral derivatives and convincing evidence for ν(M–py) vibrations in the 200–287 cm.$^{-1}$ range is obtained, *e.g.*, ν(M–py) is at ~236 cm.$^{-1}$ in $NiCl_2\cdot 4py$, $NiBr_2\cdot 4py$, and $Ni(NCS)_2\cdot 4py$,[12] and at ~216 cm.$^{-1}$ in $CoCl_2\cdot 4py$, $CoBr_2\cdot 4py$, and $Co(NCS)_2\cdot 4py$. Furthermore, the distinction between *cis* and *trans* isomers is usually clear-cut.

The complexes of the type $MX_2\cdot 4py$ are known to be *trans*-octahedral from X-ray structural investigations (Table I). In fact $CoCl_2\cdot 4py$ is isomorphous with $NiCl_2\cdot 4py$[21] and $CoBr_2\cdot 4py$ is isomorphous with $NiBr_2\cdot 4py$.[22] Consistent with these X-ray results, only one ν(M–X) vibration (a_{2u} in D_{4h} symmetry) is observed, and only one ν(M–py) vibration (e_u) is seen in the chlorides and bromides, although in the iodides the e_u vibration is split, presumably due to solid state effects and/or distortion from octahedral symmetry. Both ν(Ni–X) and ν(Ni–py) vibrational frequencies in these complexes are higher than the analogous vibrational frequencies of the corresponding cobalt complexes, as also was found for the polymeric octahedral complexes $MX_2\cdot 2py$ (note the reverse situation for tetrahedral complexes).[1]

In the spectra of trivalent complexes of rhodium and iridium, the ν(M–X) and ν(M–py) vibrations are well separated; ν(Rh–Cl) lies between 364 and 295 cm.$^{-1}$, ν(Rh–py) between 266 and 230 cm.$^{-1}$, ν(Ir–Cl) between 335 and 299 cm.$^{-1}$, and ν(Ir–py) between 287 and 255 cm.$^{-1}$. In general, the *trans* complexes of the types $[MX_2\cdot 4py]^+$ and $[MX_4\cdot 2py]^-$ give simpler spectra than the *cis*, as expected from Table IV, except that there is a tendency for the e_u vibration (which is ν(M–py) in the former and ν(M–X) in the latter) of the *trans* isomers to split in mull spectra. For the neutral complexes[23] $MCl_3\cdot 3py$, Table IV indicates that in the *cis* isomers, with C_{3v} symmetry, two ν(M–X) and two ν(M–L) vibrations are infrared-active, whereas in the *trans* isomers, with C_{2v} symmetry, three of each type of vibration are infrared-active. The infrared spectra of the *cis* and *trans* rhodium complexes are in accord with these simple predictions (see Figure 4) and thus substantiate the stereochemical assignments by Jørgensen,[24] based on electronic absorption spectral measurements. The confirmation of the infrared assignments must await the unambiguous characteriza-

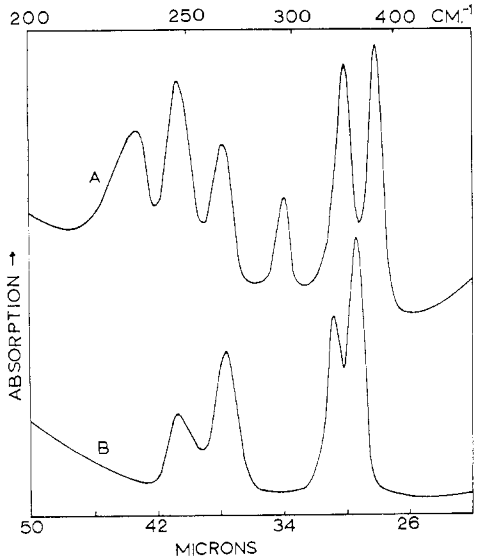

Figure 4.—Far-infrared spectra of (A) *trans*- and (B) *cis*-$RhCl_3\cdot 3py$.

---

(20) R. J. H. Clark, Symposium on the Structure and Properties of Coordination compounds, Bratislava, 1964.

(21) M. A. Poraĭ-Koshits and A. S. Antsishkina, *Izv. Sektora Platiny i Drug. Blagorodn. Metal. Inst. Obshch. i. Neorgan. Khim. Akad. Nauk, SSSR*, **29**, 19 (1955).

(22) A. S. Antsishkina and M. A. Poraĭ-Koshits, *Soviet Phys.-Cryst.*, **3**, 684 (1958).

(23) M. Delépine, *Ann. Chim.*, **19**,145 (1923); *Bull. soc. chim. France*, **45**, 235 (1929); H. H. Schmidtke, *Z. physik. Chem.*, **34**, 295 (1962).

(24) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 151 (1957).

tion of the analogous bromo complexes. The iridium complexes are less clear-cut, for it appears that the ν(M–X) vibration of e symmetry is split in the solid state.

The presence of three well-separated ν(M–X) vibrations in the infrared spectrum of $CrCl_3 \cdot 3py$ points strongly toward a *trans* arrangement of ligands in the molecule. The lowest frequency ν(M–Cl) vibration of $CrCl_3 \cdot 3py$, *trans*-$RhCl_3 \cdot 3py$, and *trans*-$IrCl_3 \cdot 3py$ is weaker than the other two in each case, suggesting that this may be the symmetric (a_1) vibration of the *trans* Cl–M–Cl group.

Planar Complexes.—Planar complexes have been the subject of previous infrared investigations.[25,26] As is clear from Table IV, *cis*-planar complexes should show two ν(M–X) vibrations (a_1, b_1) and two ν(M–L) vibrations (also a_1, b_1) in the infrared, whereas *trans*-planar complexes should only show one vibration of each kind (b_{3u} and b_{2u}, respectively).

For completeness the planar complexes of platinum and palladium were also studied in this investigation with results in essential agreement with those of previous workers.[26] However, the medium-strong band at 240 cm.$^{-1}$ in *trans*-$PtBr_2 \cdot 2py$ was not present in our spectrum, and the band reported as strong at 297 cm.$^{-1}$ appeared weakly. The spectrum of the complex *trans*-$PtCl_2 \cdot 2py$ contains a very strong band at 349 cm.$^{-1}$ which is not present in that of the corresponding bromide, but is replaced by a strong band at 249 cm.$^{-1}$. This leads to a ν(Pt–Br)/ν(Pt–Cl) ratio of 0.73, a value exactly equal to that calculated from the quoted[27] ν(M–X) vibrational frequencies of the series PtX_4^{2-} (X = Cl, Br). Some uncertainty is associated with the assignment of ν(M–py) vibrations in these complexes, partly because the apparent frequency of *ca.* 290 cm.$^{-1}$ seems to be unusually high, and partly because of the considerable intensity drop on passing from chloride to bromide. In the *cis* compound, both the ν(M–X) vibrations and the ν(M–py) vibrations apparently lie at lower frequencies than in the corresponding *trans* compounds, but the spectra are complicated and cannot be assigned with certainty.

In the spectrum of the compound *trans*-$PdCl_2 \cdot 2py$, the ν(Pd–Cl) vibration clearly lies at 350 cm.$^{-1}$, but two bands are seen in the possible ν(Pd–py) region (*ca.* 270 cm.$^{-1}$). In the spectrum of the corresponding bromide, the assignment of the ν(Pd–Br) vibration is also uncertain, as it occurs in the same region as ν(Pd–py) vibrations. The band at 219 cm.$^{-1}$ in the spectrum of the chloride may be a Cl–Pd–Cl bending mode.

Important results were obtained for the pyridinium salts $(pyH)_2PtCl_4$ and $(pyH)_2PtBr_4$. In the former, the ν(M–X) vibration is at 315 cm.$^{-1}$ and in the latter at 230 cm.$^{-1}$; *cf.* the corresponding bands for the compounds K_2PtCl_4 and K_2PtBr_4 at 320 and 233 cm.$^{-1}$, respectively[27] (these are the vibrations of e_u symmetry in the D_{4h} symmetry point group). Hence, in agreement with results on other systems,[1,20] the more bulky the cation, the lower is a ν(M–X) vibration in the counterion. Furthermore, no other bands appear in the 380–200 cm.$^{-1}$ region; *i.e.*, there are no bands which might be ascribed to ν(M–py) vibrations, in agreement with the above formulation for the compounds as pyridinium salts, rather than as compounds involving platinum–pyridine bonds.

From the magnetic moments of the bis(quinoline)-nickel dihalide complexes, Goodgame and Goodgame[28] concluded that while $NiCl_2 \cdot 2quin$ (yellow) is polymeric octahedral, and $NiCl_2 \cdot 2quin$ (blue) and $NiBr_2 \cdot 2quin$ are both tetrahedral, $NiI_2 \cdot 2quin$ is *trans*-planar. The far-infrared spectra of the chloro and bromo complexes confirm these stereochemistries, while that of the iodide is consistent with its being *trans*-planar. The ν(Ni–I) vibration occurs at 218 cm.$^{-1}$, *i.e.*, in a similar region to the tetrahedral ν(Ni–I) vibrations, but the ν(Ni–quin) vibration appears to be at 299 cm.$^{-1}$, *i.e.*, 80 cm.$^{-1}$ higher than for tetrahedrally-coordinated quinoline. Thus, while we do not yet regard the conclusion as certain, it appears that ν(M–L) vibrations occur with higher frequencies in planar situations than in other stereochemistries.

Conclusion

The frequencies of pyridine ring vibrations and especially of ν(M–X) vibrations in metal–pyridine complexes are in general diagnostic of stereochemistry, *e.g.*, for nickel complexes, ν(Ni–Cl) vibrations occur at ~400 cm.$^{-1}$ in planar complexes,[25] at ~310 cm.$^{-1}$ in tetrahedral complexes, and at ~240 cm.$^{-1}$ in monomeric octahedral complexes. Different stereochemical isomers may be distinguished by their far-infrared patterns, although on occasions ambiguities may arise owing to solid-state splittings of degenerate vibrations.

Metal–pyridine vibrations have been located, although these are weaker than metal–halogen vibrations. ν(M–N) vibrations are thus strongly dependent on the ligand to which the nitrogen atom is attached, and their frequencies fall off in the order metal–ammonia[5] (420–500 cm.$^{-1}$), metal–hydrazine (306–440 cm.$^{-1}$),[29] metal–glycine (275–423 cm.$^{-1}$),[30] metal–pyridine (*ca.* 200–287 cm.$^{-1}$), metal–*p*-toluidine, metal–α,α'-dipyridyl,[6] metal–*o*-phenanthroline[6]; *i.e.*, among other factors, they are functions of the mass of the ligand.

It is perhaps surprising that group frequency arguments apply to such low-frequency vibrations, but the internal consistency of the results seems to justify the assignments.

Acknowledgments.—The authors wish to thank Professor R. S. Nyholm, F.R.S., for his interest in this work and Professor M. Delépine for samples of the iridium complexes. C. S. W. thanks the British Council for financial assistance.

---

[25] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

[26] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *ibid.*, 734 (1964).

[27] D. M. Adams, *Proc. Chem. Soc.*, 335 (1961).

[28] D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

[29] L. Sacconi and A. Sabatini, *J. Inorg. Nucl. Chem.*, **25**, 1389 (1963).

[30] T. J. Lane, J. A. Durkin, and R. J. Hooper, *Spectrochim. Acta*, **20**, 1013 (1964).