diverge at higher concentration of pyridine. In VO(dbm)$_2$ the original two peaks at 610 and 670 mμ become flat by addition of smaller ratios of pyridine and isosbestic points are observed at 605 and 725 mμ (Figure 6). Further addition of pyridine causes the appearance of a 750 mμ band and the tremendous increase of the shorter wavelength band with a shoulder at 495 mμ. Deviation from the isosbestic point is significant in this case, indicating the formation of the second adduct.

These spectral studies in the pyridine–chloroform solution suggest the equilibria

$$\mathrm{VO(dbm)_2 + py \underset{}{\overset{K_1}{\rightleftarrows}} VO(dbm)_2{\cdot}py} \quad (1)$$

$$\mathrm{VO(dbm)_2{\cdot}py + py \underset{}{\overset{K_2}{\rightleftarrows}} VO(dbm)_2{\cdot}2py} \quad (2)$$

In the range where isosbestic points are observed equilibrium 1 is assumed to hold. Since pyridine has no absorption in the visible region, one can calculate K_1 from the measurement of molar extinction coefficients at a wavelength knowing the concentration of pyridine and vanadyl complex.[9] The equilibrium constant thus estimated for the dibenzoylmethane chelate was 47 ± 4 M^{-1} and was three times as big as the equilibrium constant[10,11] 17 ± 2 M^{-1} for the acetylacetone chelate.

We have presented the spectral and gravimetric evidence for the existence of two types of pyridine adducts with bis(dibenzoylmethano)oxovanadium. The first pyridine molecule may most probably coordinate to the central vanadium atom but the mode of addition of the second pyridine molecule is yet to be solved. From the infrared shift of the V=O stretching frequency it seems reasonable to assume the second may interact with the vanadyl oxygen atom from the other side of the molecular plane.

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[10] Since we have completed our work an equilibrium constant for the system VO(acac)$_2$–pyridine in benzene solution was reported.[11] The value reported is considerably higher compared with our result in chloroform; the difference may be ascribed to the effect of the solvent employed.

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Infrared Spectral Study of Metal–Pyridine, –Substituted Pyridine, and –Quinoline Complexes in the 667–150 Cm^{-1} Region

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Infrared absorption has been used to study metal–ligand bonding in a systematic series of coordination compounds containing pyridine, substituted pyridines, and quinoline as ligands; Cu, Ni, Co, Mn, and Zn as divalent ions; and Cl$^-$, NO$_3^-$, and NCS$^-$ as anions. Also, extensive series of copper chloride complexes with 4-substituted pyridines, monosubstituted methylpyridines (picolines), and disubstituted methylpyridines (lutidines) have been examined. Both metal–anion and metal–nitrogen (of the pyridine or quinoline ligand) stretching vibrations have been tentatively assigned. The metal stretching vibrational bands usually changed in a systematic way with metal complex stability in aqueous solution, metal electronegativity, and ligand base strength. When anomalous trends were found, steric factors related to the methyl group(s) probably influenced band positions in a consistent manner.

Introduction

Infrared spectroscopy has become increasingly important as a technique for studying metal–ligand bonding in inorganic and coordination compounds. New instrumentation and sampling cells have made it relatively easy to investigate frequencies beyond the sodium chloride range of 4000–667 cm^{-1}. Metal stretching vibrations are now being observed directly in the 500–200 cm^{-1} region by workers interested in studying stabilities of species containing metal–oxygen, metal–halogen, and metal–nitrogen bonds.

In the present study, the region of most interest was from 667 to 150 cm^{-1} because absorption bands associated with metal–ligand bond-stretching vibrations are generally in this range. The compounds selected for study crystallize in the form ML_aX_b, where $a = 2$ or 4 and $b = 2$; M was a divalent transition metal ion (Cu, Ni, Co, Mn, or Zn); L was pyridine, a monosubstituted methylpyridine, a dimethylpyridine, a 4-substituted pyridine (NH$_2$, i-C$_3$H$_7$, Cl, CN, NO$_2$ derivative), or quinoline; X$^-$ was Cl$^-$, NO$_3^-$, or NCS$^-$.

Therefore, many combinations existed for investigating relative bond strengths and stabilities of complexes by observing shifts of the metal stretching absorption bands. Metal–ligand bonding in the above cases involved the M–N (of the ligand ring), M–Cl, M–O (in nitrate), and M–N (in thiocyanate). A trend conforming to the classic Irving–Williams stability series was found in most cases.[2] Irving and Williams reported that the stability of high-spin complexes formed by a ligand and divalent ions of the first transition

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[1] Address correspondence to this author.

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metal series from Mn to Zn conformed to the order Mn < Fe < Co < Ni < Cu > Zn.

The present work includes correlations of metal stretching band positions with stability constants of metal–pyridine complexes in aqueous solution and with the electronegativity of the metal atom. Also, some data show possible steric and ligand base-strength effects on the band position. Until 1964, pyridine complexes of the first-row divalent transition metals had been investigated to only 400 cm^{-1}.[3-5] Early in 1964, assignments were reported for metal–halogen stretching vibrations in pyridine complexes of Zn, Hg, and Cd.[6] No study of other metal–pyridine complexes was attempted and no M–N stretching frequency was mentioned.

During the latter stages of our experimental work, which was delayed owing to instrumental difficulties, a paper was published showing results on some metal(II) halide–pyridine complexes in the 650–220 cm^{-1} region.[7] Tentative assignments were made for M–Cl, M–Br, and M–N (pyridine) stretching vibrations of Mn, Co, Cu, Zn, and Hg.

More recently, during the writing of the present paper, another study reported spectra in the 4000–20 cm^{-1} region on copper(II) halide complexes of the type CuL_2X_2, where L was pyridine, 2-methylpyridine, 2-ethylpyridine, 2,6-dimethylpyridine, or quinoline, and X was Cl or Br.[8] Assignments of Cu–X and Cu–N stretching vibrations were made. In general, our assignments agree with those reported; however, our study includes more ligands and, for the first time, pyridine complexes containing thiocyanate and nitrate. In addition, correlations with variations in metal atom, possible ligand steric factors, and ligand base strengths have been attempted. Although a continuation of earlier work on metal–halide complexes of pyridine was recently published[9] in which relationships between the number and frequencies of metal–ligand vibrations and the stereochemistry were pointed out, no systematic study with variations in metal atom, ligand base strength, and ligand steric factors was reported. However, mention was made of a forthcoming publication on metal–thiocyanate complexes of pyridine.

Finally, infrared spectra in a higher frequency region from 4000 to 650 cm^{-1} have been reported for some picoline and lutidine complexes, but no metal stretching frequencies were assigned.[10,11] Ligand spectra have been run for pyridine and the picolines,[12-14] the lutidines,[15] and other substituted pyridines,[16] mainly in the 4000–667 cm^{-1} region. The limited work in the far-infrared did not assign the ligand bands.[13]

In the present work, the band assignments for the metal stretching vibrations (M–NCS, 324–256 cm^{-1}; M–ONO_2, 324–220 cm^{-1}; M–Cl, 333–231 cm^{-1}; and M–N (ligand), 281–195 cm^{-1}) are tentative in some cases. However, trends established using these assignments seem to be valid. Probably these metal stretching vibrations are not pure in nature. Therefore, the assignments and conclusions given here should be qualified to include mixing with other vibrations. If the degree of mixing or coupling is approximately constant, our assignments and observed systematic trends can be explained.

Experimental Section

Starting Materials.—The picolines and lutidines were purchased from Aldrich Chemical Co. and Reilly Tar and Chemical Corp. Pyridine and quinoline were obtained from Koppers Chemical Co. and Fisher Scientific Co., respectively. Each of these ligands was checked for purity by gas chromatographic analysis and gave a single peak.

Most of the 4-substituted pyridines were obtained from Aldrich Chemical Co. and K and K Laboratories; however, the 4-NO_2 derivative had to be synthesized from pyridine N-oxide by deoxygenation with PCl_3 in CHCl_3.[17] Microanalyses for carbon, hydrogen, and nitrogen corresponded closely to the theoretical values in all cases.

All of the inorganic salts were reagent quality and were used without further purification.

Preparation of Metal–Pyridine Complexes.—Various $\text{M(py)}_2\text{Cl}_2$, $\text{M(py)}_4\text{Cl}_2$, and $\text{M(py)}_2(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ complexes were prepared using, at most, slight variations of existing methods.[18-22] Complexes of the form $\text{M(py)}_2(\text{NCS})_2$ and $\text{M(py)}_4(\text{NCS})_2$ were prepared according to standard quantitative methods.[23] The products were usually washed with ethanol and ether and then dried in a vacuum oven. However, the $\text{M(py)}_2(\text{NCS})_2$ complexes of Co and Mn were prepared by heating the tetraligand complex.[24,25]

Preparation of Copper–Picoline and –Lutidine Complexes.—Complexes of the form CuL_2Cl_2 were prepared by using variations of the pyridine complex syntheses. In these cases, L was 2-picoline, 3-picoline, 4-picoline, 2,3-lutidine, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, 3,4-lutidine, and 3,5-lutidine. Again, these compounds were washed with ethanol and ether and then dried in a vacuum oven.

Preparation of Copper Complexes with 4-Substituted Pyridines.—CuCl_2 complexes of the form CuL_2Cl_2 were prepared with the 4-NH_2, 4-*i*-C_3H_7, 4-CN, 4-Cl, and 4-NO_2 pyridine derivatives. Except for the 4-NH_2 complex, all syntheses were performed according to the copper–pyridine, –picoline, and –lutidine specifications. The 4-NH_2 complex was obtained by heating the purple tetraligand complex at 110° until the desired light green product resulted.

Preparation of Metal–Quinoline Complexes.—Using synthe-

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ses of metal–quinoline complexes similar to those reported in the literature,[26,27] complexes of the form M(quinoline)$_2$Cl$_2$ were isolated. The products were washed and dried as before.

Analyses.—Microanalyses for carbon, hydrogen, and nitrogen corresponded closely to theoretical values in all but a few cases. Some loss of ligand was found in Co(py)$_4$Cl$_2$ and MnQ$_2$Cl$_2$. Also, Mn(py)$_2$(NCS)$_2$ probably contained a small amount of Mn(py)$_3$(NCS)$_2$.

Metal content was determined by an EDTA titration method in which a small sample (0.1 g or less) of each complex was usually decomposed by boiling down a HNO$_3$–HClO$_4$ or a HNO$_3$–H$_2$SO$_4$ mixture so as to release free metal ion.[28] The moist residue was dissolved in deionized water, and the necessary pH adjustments were made using a Beckman Zeromatic pH meter. An appropriate indicator was added and the solution was titrated with 0.01 or 0.02 *M* EDTA solution.

Instrumentation.—To scan the wavenumber range of 909–286 cm^{-1}, a Beckman IR-5A instrument, with CsBr optics, was used. Sample preparation included grinding the solid complex with a mortar and pestle before dropwise addition of Nujol oil. The subsequent mull was placed between two CsBr disks and then inserted into the cell holder.

A Beckman IR-11 multiple-grating spectrophotometer was used for the 350–150 cm^{-1} range. The 350 cm^{-1} upper limit overlapped the 286 cm^{-1} lower limit of the IR-5A scan; bands occurring at frequencies less than 350 cm^{-1} were taken from the IR-11 spectrum.

For measurements with the IR-11, compounds were dispersed in Nujol oil medium as before and pressed between polyethylene strips, since both Nujol and polyethylene have a "window" in the 350–150 cm^{-1} region. In order to obtain intense absorption bands of liquid ligands, polyethylene liquid cells, purchased from Barnes Engineering, were used.

All scans used double-beam operation and instruments were continually purged with dry air. A single-beam water vapor spectrum was run for calibration purposes.[29]

Limited use was made of a Perkin-Elmer 221 infrared spectrophotometer to scan frequencies of 4000–667 cm^{-1}. Samples were run as Nujol or Fluorolube mulls and as KBr pellets. This instrument was used to differentiate between ionic and coordinated nitrate bands and between water of crystallization and coordinated water bands. In addition, it was used to observe ligand vibrations in some of the 4-substituted pyridine complexes.

Results

Metal–Pyridine and –Quinoline Complexes.—In most cases, the metal stretching vibrations were located by comparing the spectrum of the coordinated ligand in the metal complex and the spectrum of the free ligand. Where small band splittings were found, the average frequency was used for the assignments. The splittings can usually be attributed to: (a) deviations from perfect octahedral or tetrahedral symmetry to remove degeneracy; (b) nearest and next-nearest neighbor interactions in the solid state; (c) isotope effects (since Cl^{37} has an abundance of 24.6%); (d) slight rotation of coordinated pyridine about the M–N bond to relieve steric strain in some cases; and (e) Fermi resonance effects.[30]

Table I, in addition to data for complexes, shows bands of pyridine at 602 and 404 cm^{-1}, due to ring vibrations (C–C in-plane bend and C–C out-of-plane bend, respectively), and spectra of free and coordinated thiocyanate. For KSCN, the band at 746 cm^{-1} is the C–S stretching vibration; the split band at 485, 473 cm^{-1} is the NCS bending mode. In the next two compounds, the Cr–N and Cu–N stretching vibrations are found at 362 and 342 cm^{-1}, respectively.[31] The Cr compound was used for supporting purposes only, indicating metal stretching vibrations of the coordinated NCS group.

To facilitate comparisons, Table II contains only the metal stretching bands for all complexes. Bands assigned previously by Clark and Williams[9] and by Goldstein, *et al.*,[8] are included for comparison. Representative spectra have not been included in the present work; however, peak shapes, relative intensities, and resolution compared favorably with spectra and tabular data recently published.[8,9] Small differences will be cited in a later section.

The metal–pyridine complexes containing coordinated thiocyanate are said to be octahedral in nature, except for the zinc complex which is tetrahedral. The bis-pyridine complexes contain bridging NCS groups to form a hexacoordinated species in the solid state, while the tetrapyridine compound forms an octahedron without bridging.[32,33]

The 324–256 cm^{-1} band has been asigned to a metal–nitrogen stretching mode involving the nitrogen of the thiocyanate anion. Using the interpretation that the most stable bis-pyridine complex has its M–N band at the highest frequency (cm^{-1}), the ranking follows the Irving–Williams stability series of Zn $<$ Cu $>$ Ni $>$ Co $>$ Mn. The band in the lower frequency range of 268–195 cm^{-1} also showed the same trend, except for the zinc complex. This band has been tentatively assigned to the metal–nitrogen stretching vibration of the pyridine ring. Only three tetra-pyridine complexes of Ni, Co, and Mn are shown because both the Cu and Zn analogs were extremely unstable. Even so, the three available compounds followed the same trend. These data appear to provide evidence that relative stabilities of metal complexes can be estimated from the metal–ligand stretching vibrations.

The metal stretching vibrations for the M(py)$_2$(NO$_3$)$_2$·2H$_2$O complexes as well as the Cu(py)$_2$(NO$_3$)$_2$, Cu(py)$_3$(NO$_3$)$_2$, Cu(py)$_4$(NO$_3$)$_2$, and the Zn(py)$_3$(NO$_3$)$_2$ species are shown in Table II. The 324–220 cm^{-1} band has been assigned to a M–O stretching vibration of the coordinated nitrate group, and the 281–204 cm^{-1} band tentatively assigned to a M–N (ligand) stretching vibration. Several points of interest should be noted. First, a strong absorption band in the 324–220 cm^{-1} region is missing for Cu(py)$_4$(NO$_3$)$_2$, signifying no strong M–O bonding involving the nitrate groups. This omission, along with the occurrence of bands at 1404, 1062, and 822 cm^{-1}, indicates noncoordinated nitrate groups

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TABLE I

INFRARED ABSORPTION BANDS OF METAL–PYRIDINE, –SUBSTITUTED PYRIDINE, AND –QUINOLINE COMPLEXES IN THE 667–150 CM^{-1} REGION[a,b]

COMPOUND	ABSORPTION BANDS (cm.$^{-1}$)									
Pyridine		602			404					
KSCN	746			485,473						
$K_3Cr(NCS)_6$	724			481		362s				
$Cu(NCS)_2$	796			466,437		342s				
$Cu(py)_2(NCS)_2$		641		478,468	435	324s	256s	218m		197w
$Zn(py)_2(NCS)_2$		645		486	427,414,391	313s	268s	231s		166s
$Ni(py)_2(NCS)_2$		629		477,469	432	283s	230s			158s
$Co(py)_2(NCS)_2$		627		473	425	270s	211s			165w
$Mn(py)_2(NCS)_2$		623		475,468	417	256s	201s			168,155s
$Ni(py)_4(NCS)_2$		628		482	438,432,402	287s	232s			174,164w
$Co(py)_4(NCS)_2$		627		483	433,423,400	272s	220,204s			170w
$Mn(py)_4(NCS)_2$		624		482	422,415,395	259s	195s			178s
$Cu(py)_2(Cl)_2$		645			444	294s	269s	237s,204m		178s
$Zn(py)_2(Cl)_2$		639			423	331,298s	222s	205m		
$Ni(py)_2(Cl)_2$		632			441	264m	247,240m	194s		181s
$Co(py)_2(Cl)_2$		632			433	234s	227s			176s
$Mn(py)_2(Cl)_2$		628			421	231s	213s			174s,155s
$Ni(py)_4(Cl)_2$		627			430,394		242s			177w,158s
$Co(py)_4(Cl)_2$		623			424,391		225s			167m
$Cu(py)_2(Br)_2$		645			443	269s	260s	204s		
$Cu(py)_2(NO_3)_2 \cdot 2H_2O$		641			439	265s	232s	193s		
$Ni(py)_2(NO_3)_2 \cdot 2H_2O$		635			436	263s	247,233s	211,189m		166m
$Co(py)_2(NO_3)_2 \cdot 2H_2O$		631			420	255s	231s	191m		171m
$Mn(py)_2(NO_3)_2 \cdot 2H_2O$		627			417	246s	214s			172s
$Cu(py)_4(NO_3)_2$		640			438,418		266s,249m	192m		
$Cu(py)_2(NO_3)_2$		642			443,428	324s	281s	218m		173w
$Cu(py)_3(NO_3)_2$		641			435,428	272s	226m			156m
$Zn(py)_3(NC_3)_2$		632			423,392		220s	204s		
Quinoline		628,613	523	480	392,377					184s
$Cu(Q)_2(Cl)_2$		637	532	501,468	406,400	332s	259s			188m
$Zn(Q)_2(Cl)_2$		635,623	528,519	490,467	395	316,300s	205s			187w
$Ni(Q)_2(Cl)_2$		631,621	523	490,473	406,397	263m-s	223s			199s
$Co(Q)_2(Cl)_2$		635	528	489,467	396	333,312s	226s AVG			191w
$Mn(Q)_2(Cl)_2$		621	525	483,468	397,390,379	246s	196s			164s
$CuCl_2$						327s	288s			
$Cu(py)_2(Cl)_2$		645			444	294s	269s	237s	204m	178s
2-Picoline		630	547	472	405 360				210m	
$Cu(2\text{-}pic)_2(Cl)_2$		649	559	481	439 383	309s	261s		206w	164s
3-Picoline		631	537	487	456 402 340				220w	
$Cu(3\text{-}pic)_2(Cl)_2$		657	540	497	485 413 357	294s	267s		212w	192s
4-Picoline		724	517	587					213w	167w
$Cu(4\text{-}pic)_2(Cl)_2$		667	549	494		299s	266s		209m	170m
2,3-Lutidine		588	521,510	437	416		267m			168w
$Cu(2,3\text{-}lut)_2(Cl)_2$		610	525,515	472	441	323s	288w	270s	205w	
2,4-Lutidine		557,536,518		438	410		284m		225m	198m
$Cu(2,4\text{-}lut)_2(Cl)_2$		549,542		446	431	320s	300s	254s	214w	196w
2,5-Lutidine		647	485	435	410,392		295w			198w
$Cu(2,5\text{-}lut)_2(Cl)_2$		668	501	443	417	318s		257s		198m
2,6-Lutidine		557,539			420		298w		215m	
$Cu(2,6\text{-}lut)_2(Cl)_2$		576,541			443	315s	285w	242s	203w	
3,4-Lutidine		602	526,508		423			257m		
$Cu(3,4\text{-}lut)_2(Cl)_2$		613	538		428	295s	259s		192s	165m
3,5-Lutidine			534	438	397			273w	207m	
$Cu(3,5\text{-}lut)_2(Cl)_2$			541	480	421	295s	250m	225w	181m	169w
$4\text{-}NH_2 \cdot$Pyridine			538		437,408			230m		
$Cu(4\text{-}NH_2 \cdot py)_2(Cl)_2$			573,523		413	278s	264s			174w
$4\text{-}iC_3H_7 \cdot$Pyridine		664	568		456	312w				
$Cu(4\text{-}iC_3H_7 \cdot py)_2(Cl)_2$		664	583,561		475	333w	287s	275s	237s	187w,164w
$4\text{-}Cl \cdot$Pyridine$\cdot HCl$			491		424,403	307m		229w	191s	
$Cu(4\text{-}Cl \cdot py)_2(Cl)_2$			502			330s	295s	244s	194s	166m
$4\text{-}CN \cdot$Pyridine			560		370					172s
$Cu(4\text{-}CN \cdot py)_2(Cl)_2$			560		493,401	307s	242s		217s	171s
$4\text{-}NO_2 \cdot$Pyridine		645	540,517		464		254m-s			180s
$Cu(4\text{-}NO_2 \cdot py)_2(Cl)_2$			532		457	313s	277s	235s		188s,168m

[a] py = pyridine, pic = picoline, lut = lutidine [b] s = strong, m = medium, w = weak, br = broad

Q = quinoline AVG = average frequency of split bond

TABLE II

METAL STRETCHING FREQUENCIES OF METAL(II)–PYRIDINE, –SUBSTITUTED PYRIDINE, AND –QUINOLINE COMPLEXES IN THE 350–150 CM^{-1} REGION[a,b]

COMPOUND	BAND ASSIGNMENTS (cm.$^{-1}$)	
	(M-NCS)	(M-N)
$Cu(py)_2(NCS)_2$	324s	256s
$Ni(py)_2(NCS)_2$	283s	230s
$Co(py)_2(NCS)_2$	270s	211s
$Mn(py)_2(NCS)_2$	256s	201s
$Zn(py)_2(NCS)_2$	313s	268s
$Ni(py)_4(NCS)_2$	287s	232s
$Co(py)_4(NCS)_2$	272s	212s AVG
$Mn(py)_4(NCS)_2$	259s	195s
	(M-Cl)	(M-N)
$Cu(py)_2(Cl)_2$	294s,237 [294s,235m]^{c}	269s [268m]^{c}
$Ni(py)_2(Cl)_2$	264m [un]^{c}	244m AVG [un]^{c}
$Co(py)_2(Cl)_2$	234s [un]^{c}	227s [un]^{c}
$Mn(py)_2(Cl)_2$	231s [233s]^{c}	213s [212s,br]^{c}
$Zn(py)_2(Cl)_2$	331s,298s [329s,296s]^{c}	222s [220m]^{c}
$Ni(py)_4(Cl)_2$	[246s]^{c}	242s [236s]^{c}
$Co(py)_4(Cl)_2$	[230s]^{c}	225s [217s]^{c}
$Cu(Q)_2(Cl)_2$	332s [un]^{c}	259s [un]^{c}
$Ni(Q)_2(Cl)_2$	263s	223s
$Co(Q)_2(Cl)_2$	333s,312s	226s AVG
$Mn(Q)_2(Cl)_2$	246s	196s
$Zn(Q)_2(Cl)_2$	316s,300s	205s
	(M-Br)	(M-N)
$Cu(py)_2(Br)_2$	260s,204s [255s,202m]^{c}	269s [269m]^{c}

COMPOUND	BAND ASSIGNMENTS (cm.$^{-1}$)	
	($M-ONO_2$)	(M-N)
$Cu(py)_2(NO_3)_2\cdot 2H_2O$	265s	232s
$Ni(py)_2(NO_3)_2\cdot 2H_2O$	263s	240s AVG
$Co(py)_2(NO_3)_2\cdot 2H_2O$	255s	231s
$Mn(py)_2(NO_3)_2\cdot 2H_2O$	246s	214s
$Cu(py)_4(NO_3)_2$		258s AVG
$Cu(py)_2(NO_3)_2$	324s	281s
$Cu(py)_3(NO_3)_2$	272s	226s
$Zn(py)_3(NO_3)_2$	220s	204s
	(Cu-Cl)	(Cu-N of L)
$Cu(py)_2(Cl)_2$	294s,237s[287,229]^{d}	269s [266]^{d}
$Cu(2\text{-}pic)_2(Cl)_2$	309s [308]^{d}	261s [259]^{d}
$Cu(3\text{-}pic)_2(Cl)_2$	294s	267
$Cu(4\text{-}pic)_2(Cl)_2$	299s	266
$Cu(2,3\text{-}lut)_2(Cl)_2$	323s	270
$Cu(2,4\text{-}lut)_2(Cl)_2$	320s	254
$Cu(2,5\text{-}lut)_2(Cl)_2$	318s	257
$Cu(2,6\text{-}lut)_2(Cl)_2$	315s [314]^{d}	242s [241]^{d}
$Cu(3,4\text{-}lut)_2(Cl)_2$	295s	259s
$Cu(3,5\text{-}lut)_2(Cl)_2$	295s	250m
$Cu(4\text{-}NH_2\cdot py)_2(Cl)_2$	278s^{e}	264s^{e}
$Cu(4\text{-}iC_3H_7\cdot py)_2(Cl)_2$	287s	275s
$Cu(4\text{-}Cl\cdot py)_2(Cl)_2$	295s	244s
$Cu(4\text{-}CN\cdot py)_2(Cl)_2$	307s	242s
$Cu(4\text{-}NO_2\cdot py)_2(Cl)_2$	313s	235s

[a] py = pyridine, pic = picoline, lut = lutidine, Q = quinoline , un = unassigned by (9) [b] s = strong, m = medium, b = broad, AVG = average frequency of split band [c] data in brackets from (9) [d] data in brackets from (8)
[e] possibly these values should be interchanged

in the complex.[34, 35] Second, the compounds $Cu(py)_3(NO_3)_2$ and $Zn(py)_3(NO_3)_2$ obviously contain coordinated nitrate groups bonded to the metal atom. However, the exact stereochemistry is in doubt because unidentate, bidentate, and bridging nitrate groups cannot be differentiated unambiguously with present infrared information. Third, the hydrated complexes of the form $M(py)_2(NO_3)_2\cdot 2H_2O$ (where M = Cu, Ni, Co, or Mn) may contain coordinated water ($M\text{–}OH_2$ bonds) or water of crystallization. All of these complexes have strong bands in the 3600–3000 and 1670–1600 cm^{-1} regions, probably signifying the presence of lattice water. In addition, they also have bands in or near the regions of 1290–1253, 1034–970, and 800–781 cm^{-1}, in which vibrations due to coordinated nitrate groups are known to occur.[36] Therefore, on the basis of these observations, the mode of M–O bonding seems to be with the nitrate.

The expected stability trend is shown for M–O bonding ($Cu > Ni > Co > Mn$); however, the trend is not followed for the M–N stretching vibration. The copper complex should have the maximum stability, but since this compound was prepared by exposing the anhydrous form to an atmosphere of water, it may have a different structure or some lattice distortion or may not be due to simple M–N stretching.

Also listed in Table II are the metal stretching bands of $M(py)_2Cl_2$, $M(py)_4Cl_2$, and $Cu(py)_2Br_2$ complexes which show the expected stability trends ($Cu > Ni > Co > Mn$) for both sets of bands. The 331–231 cm^{-1} band has been assigned to a metal–chloride stretching mode, while the 269–213 cm^{-1} band has been tentatively assigned to a metal–nitrogen stretching vibration. Clark and Williams[9] reported bands for $Fe(py)_2Cl_2$ at 238 (s), 227 (sh), and 219 (s) cm^{-1} but did not assign them. If the 238 cm^{-1} band is tentatively assigned to Fe–Cl stretching and the 219 cm^{-1} band to Fe–N stretching, the values fall in the expected positions on curves for the Irving–Williams ranking of stabilities and for the logarithm of the first formation constant, K (not illustrated). Our assignments and data agree, usually to ±2 cm^{-1}, with those that have just been published.[9] However, in our work, bands in the ~232 cm^{-1} region for $Ni(py)_4Cl_2$ and $Co(py)_4Cl_2$ could not be resolved into the M–Cl and M–N stretching vibrations.

The quinoline complexes in Table II crystallize in the form $M(quinoline)_2Cl_2$, but differences in structure exist. Brown, *et al.*,[27] concluded from visible spectra that the Mn and Ni complexes were octahedral in nature and the Co complex was tetrahedral. The visible spectra of the Cu and Zn complexes were less conclusive, and no unambiguous structures could be assigned even though comparisons with their pyridine analogs were possible. Probably the Zn complex is tetrahedral and the Cu complex a distorted octahedron. Each of the metal chlorides crystallizes in the same structure as its corresponding quinoline complex except for the $CoCl_2$ species which is octahedral.

The 333–246 cm^{-1} bands have been assigned to an M–Cl stretching vibration and the 259–196 cm^{-1} band to an M–N (quinoline) stretching mode. It was ob-

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served that the M–N frequency band did not follow the normal stability trend. It is known that high-spin tetrahedral Co(II) complexes, compared to other divalent first-row transition metals,[37] have the highest crystal field stabilization energy (CESF) for this type of structure. This may account for the higher Co–N stretching mode; however, this frequency and the accompanying higher Co–Cl frequency may result from a steric requirement in tetrahedral structures. Also, since the frequency assignment for the Co–N band was the average of multiple absorption, the band must only be tentatively assigned.

In order to illustrate further indications of systematic behavior in the observed metal stretching frequencies, the values are shown as a function of metal complex stability constants and metal electronegativity.

Figure 1 shows the metal stretching bands of the $M(py)_2(NCS)_2$ complexes plotted against the stability constants for the metal-pyridine complexes in aqueous solution using the log K_1 values.[38, 39] Despite the obvious limitations of any comparison of data for solids and solutions, a smooth curve connecting the four points resulted, thereby confirming a systematic trend.

Figure 2 is a plot of the metal electronegativity (Cu = 2.0, Ni = 1.8, Co = 1.7, Mn = 1.4)[40] against the metal stretching vibrational bands in the same $M(py)_2(NCS)_2$ complexes. Again, a smooth curve resulted for both the M–NCS and M–N (ligand) bands.

A further correlation, also shown in Figure 2, was made between the stability constants of metal–thiocyanate complexes (log K_1 of $M(NCS)^+$) and the frequencies of the M–NCS stretching vibrations in Table II.[41]

Plots of solution stability constants and metal electronegativity *vs.* peak positions of metal stretching vibrations can also be constructed for the $M(py)_2Cl_2$ and $M(py)_2(NO_3)_2 \cdot 2H_2O$ complexes. In all cases, a curved line was estimated visually and drawn through the four points. The systematic behavior for the $M(py)_2(NO_3)_2 \cdot 2H_2O$ complexes was noticeably poorer (metal(II)–N band) because the maximum M–N stretching frequency for the nickel complex broke the trend. A large increase in peak position for both bands occurred when the copper compound in the anhydrous form was substituted for the hydrated species, indicating stronger metal–ligand bonds ($M-ONO_2$ and M–N) in the anhydrous form.

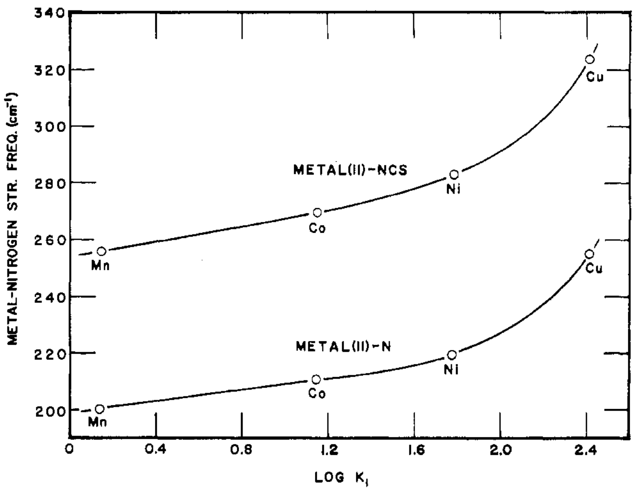

Figure 1.—Metal stretching frequencies as a function of metal(II)-pyridine stability constants in aqueous solution for $M(py)_2(NCS)_2$ complexes.

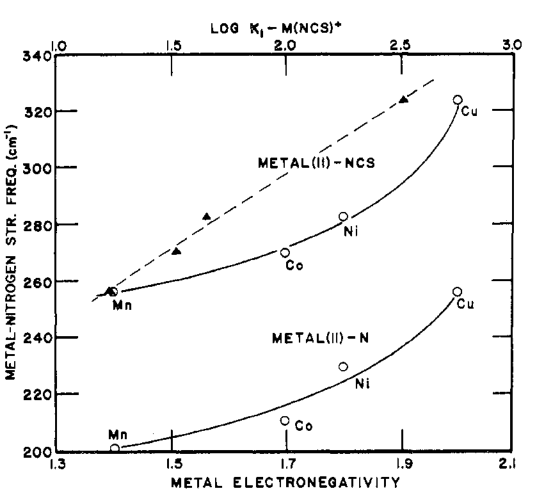

Figure 2.—Metal stretching frequencies as a function of metal electronegativity for $M(py)_2(NCS)_2$ complexes shown as O——O. Metal–NCS stretching frequencies as a function of metal(II)–NCS stability constants in aqueous solution for $M(py)_2(NCS)_2$ complexes shown as ▲– – –▲.

Copper(II) Chloride Complexes with Substituted Pyridines.—Absorption bands in the 667–150 cm^{-1} region for copper(II) chloride complexes with pyridine and substituted pyridines are shown in Table I. Indications of band positions of Cu–Cl stretching vibrations have come from the spectrum of $CuCl_2$ and of copper chloride inorganic complexes.[42, 43] The ligands varied in base strength and in probable steric factors related to the methyl group(s), so trends in the metal stretching frequencies have been established with these properties. As the electron density increased on the basic pyridine nitrogen, one would expect the copper complex to have stronger copper–ligand bonds. The 4-substituted pyridines had base strengths in the order. $4\text{-}NH_2 > 4\text{-}i\text{-}C_3H_7 > 4\text{-}CH_3 > 4\text{-}Cl > 4\text{-}CN > 4\text{-}NO_2$, as indicated by their respective pK_a values determined in aqueous solution at 25° of $9.12 > 6.04 > 6.03 > 3.83 > 1.86 > 1.39$.[44]

To elucidate the basic center of some of the 4-substituted pyridine complexes, especially the $4\text{-}NO_2$, 4-CN, and $4\text{-}NH_2$ complexes, spectra in the 4000–667 cm^{-1} region were taken. For both the $4\text{-}NO_2$-py and $Cu(4\text{-}NO_2\text{-}py)_2Cl_2$ species, a band was found in the

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1570–1500 cm^{-1} region due to the antisymmetric NO_2 stretching vibration, and another in the 1370–1300 cm^{-1} region for the symmetric NO_2 stretching vibration of $C–NO_2$ groups. Also, a band in the 850–750 cm^{-1} region due to the C–N stretching vibration, characteristic of all aromatic nitro compounds, was found in both spectra.[45] Hence, the pyridine nitrogen was bound, as expected, to the copper. Likewise, the presence of $C\equiv N$ groups in both 4-CN-py and the copper complex was shown by a band in the 2250–2225 cm^{-1} region due to the $C\equiv N$ stretching vibration in $R—C\equiv N$ compounds.

In contrast, positive evidence for the presence of the NH_2 group in the copper complex was lacking. Although infrared bands in the 1650–1590 cm^{-1} ($R–NH_2$ scissoring vibration) and 1340–1250 cm^{-1} (C–N stretching vibration in $R–NH_2$ compounds) regions occurred in both the ligand and the complex, the nature of the bonding is still in doubt because the N–H stretching vibration (in $-NH_2$) in the 3530–3400 cm^{-1} region was obscured by OH bands from adsorbed water in the KBr pellet and both compounds seemed to be insoluble in common solvents such as CCl_4, $CHCl_3$, and CS_2. A possible polymeric nature could account for the negligible solubility observed.

Although the exact stereochemistry of these complexes is unknown, an octahedral polymer-chain structure may be present. The substituents in the 4-position probably exert little steric influence.

The frequencies of metal stretching vibrations in copper chloride complexes with 4-substituted pyridines are shown in Table II. Recent work by Goldstein, *et al.*,[8] is also shown in Table II for comparison purposes. The 313–278 cm^{-1} band can be assigned to a Cu–Cl stretching vibration, and the 275–235 cm^{-1} band to a Cu–N (ligand) stretching frequency. The $Cu(4\text{-}NH_2\text{-}py)_2Cl_2$ complex was omitted from correlations because the mode of metal bonding has not been established.

A general decrease in the Cu–N stretching frequency followed a decrease in the ligand base strength (pk_a) in these 4-substituted pyridine complexes. This followed the expected trend. However, when copper–picoline and -lutidine complexes were examined, possible steric factors complicated the picture and caused reversals in complex stabilities.

The copper–picoline and -lutidine complexes shown in Table II have intense metal stretching vibrational bands. The band in the 323–294 cm^{-1} region has been assigned to a Cu–Cl stretching vibration and the 270–242 cm^{-1} band to the Cu–N (ligand) stretching vibration. The structures of these complexes have not been determined, except for $Cu(py)_2Cl_2$; however, most are assumed to be tetracoordinated.

Although there have been several experimental determinations of pk_a values of the picolines, lutidines, and pyridine,[46–48] in only one study were the relative base strengths for all these ligands determined under the same conditions.[46] The order of base strengths is: 2,6-L > 2,4-L > 2,3-L > 3,4-L > 2,5-L > 3,5-L > 4-pic > 2-pic > 3-pic > py as shown by the pK_a values of 6.72 > 6.63 > 6.57 > 6.46 > 6.40 > 6.15 > 5.98 > 5.96 > 5.63 > 5.22.[46] The main discrepancy between that list and two other references is with respect to the order of the pK_a values of 2,6-lutidine and 2,4-lutidine. Because the differences in the three sets of data are less than 0.1 pK_a unit, the discrepancy is understandable.

The frequencies of metal stretching vibrations for these picoline and lutidine complexes seem to be a combination of base-strength effects and steric factors related to the metal group(s). With a ΔpK_a of only 1.5, any systematic trend based upon base strength broke down within the lutidine series. However, when a pair of copper complexes at both ends of the list was examined, an explainable trend was detectable; namely, as the base strength of the ligand *decreased*, the frequency of the Cu–N stretching vibration *increased*. The fact that the observed trend was opposite to the predicted one could be attributed to a steric effect of the methyl groups, especially those α to the nitrogen. The Cu–N bond strength changes in the order 2,6-L < 2,4-L < 2-pic < py. Hence, this suggests that steric factors as well as ligand base strength may be playing a part in determining the strengths of the metal–ligand bond.

Not only is the Cu–N stretching frequency of $Cu(2,4\text{-}lutidine)_2Cl_2$ higher than $Cu(2,6\text{-}lutidine)_2Cl_2$, presumably due to a shorter Cu–N bond length in the 2,4-lutidine complex, but so also is its Cu–Cl stretching frequency. Also, the Cu–Cl stretching frequencies in the lutidine complexes showed that the Cl atom can best approach the Cu atom in the 2,3-lutidine complex.

Some scans to 33 cm^{-1} were made on the Beckman IR-11 instrument for pyridine, $CuCl_2$, $Cu(py)_2Cl_2$, and polyethylene. The only new bands observed were at 78 cm^{-1} due to a polyethylene vibration and a strong broad band at 131 cm^{-1} in the spectrum of $CuCl_2$. The latter band might be a Cu–Cl bending vibration that shifts to 178 cm^{-1} in the $Cu(py)_2Cl_2$ species.

Conclusion

The assigned metal stretching vibrational bands have been shown to vary in a systematic way with properties of the central atom and the ligand. Assignments and interpretations may be subject to revision in the future, but this work has attempted to illustrate the utility of this infrared region for investigations of metal–ligand vibrational frequencies. Indeed, further exploration in this area is necessary in order to generalize further on the systematic trends and correlations that seem to be valid for these complexes.

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in taking spectra. Some metal complex syntheses were performed by P. B. Bowman. Elemental analyses were done by C. S. Yeh.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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The Kinetics of Replacement Reactions of Complexes of the Transition Metals with 2,2′,2′′-Terpyridine

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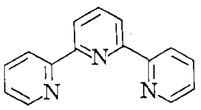
The kinetics of formation and dissociation of complexes of Mn–Zn and Cd with 2,6-bis(2′-pyridyl)pyridine (2,2′,2′′-terpyridine) have been measured by the stopped-flow method. Stability constants have been calculated from these results and the thermodynamic and kinetic data are compared with those for bipyridine and phenanthroline complexes.

Introduction

The kinetics of reactions of metal–phenanthroline and bipyridine complexes have been investigated extensively recently.[2] Many of the labile complexes of the transition metal ions were included in the study and a number of conclusions were reached regarding the mechanism of their formation and dissociation. The present work is an extension to similar complexes of the terdentate ligand 2,6-bis(2′-pyridyl)pyridine (2,2′,2′′-terpyridine, terpy, I). These have been previously much less studied than their bidentate analogs.[3,4] For our purposes, however, terpyridine is a very suitable ligand. It has the desirable properties[2] of high extinction coefficients (bands shifted in the metal complex), weak basicity (pK_1 = 4.7, pK_2 = 3.3),[5] strong chelation, and sufficient solubility in water ($\sim 10^{-3}$ M) for study in micromolar concentration. Furthermore, it has the decided advantage that it forms only two metal complex species in solution, namely, mono and bis, and this simplifies somewhat the unravelling of consecutive associative reactions. (These complexes can exist in only one stereoisomeric form because of the planarity of the ligand.) Finally, the solid complexes M(terpy)Br$_2$, M = Fe, Co, and Ni, can be prepared,[4] and dissolution of these generates M(terpy)(H$_2$O)$_n{}^{2+}$ ions, which only slowly disproportionate and can thus be allowed to react with ligand to allow unequivocal study of the formation of the bis species. A combination of formation rate data with dissociative rate constants (some obtained previously by conventional exchange methods[4]) allows the estimation of stability constants of the complexes, an added bonus from this work, since thermodynamic data for the terpyridine complexes are virtually nonexistent. A few experiments with another strongly chelating terdentate ligand 4-(2-pyridylazo)resorcinol (PAR, II) have also been performed for comparative purposes. This forms strongly colored complexes of analytical value.[6]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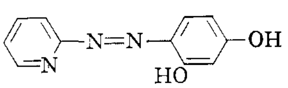
II

Experimental Section

Materials.—Terpyridine, purchased from B. Newton Maine and G. F. Smith, was purified by heating *in vacuo* at 130° for several hours. The white sublimate had mp 86°. M(terpy)Br$_2$, M = Fe, Co, and Ni, was prepared as described previously.[4] PAR and the other reagents were AR grade. Standard solutions were prepared by shaking weighed amounts of terpyridine with hot conductivity water and analyzing the cooled solutions colorimetrically with ferrous ion before runs.

Spectra.—In general two peaks between 310 and 340 mμ are observed for the metal complexes, well separated from the maximum of the free ligand base at 285 mμ.[7] For example the maxima for the bis(terpyridine) complexes in this region are (Ni) ϵ_{334} 3.2×10^4, ϵ_{320} 3.6×10^4; (Cu) ϵ_{323} 3.8×10^4; (Zn) ϵ_{333} 4.1×10^4, ϵ_{320} 3.9×10^4; and for the mono (Co) ϵ_{325} 1.9×10^4, ϵ_{315} 1.8×10^4; (Ni) ϵ_{331} 2.0×10^4, ϵ_{318} 1.8×10^4; (Cu) ϵ_{340} 1.4×10^4, ϵ_{326} 1.4×10^4; (Zn) ϵ_{330} 2.3×10^4, ϵ_{317} 2.2×10^4. For free terpyridine, maxima are at 290 mμ (ϵ 1.6×10^4) and 228 mμ (ϵ 2.0×10^4).

The bulk of the formation studies were observed at wavelengths of 320–335 mμ. The decomposition studies used the visible and near-infrared absorption characteristics of the iron(II), cobalt(II), and copper(II) complexes.[4] The experiments with PAR were observed around 500 mμ where the metal complexes have high absorption.

Kinetics Runs.—The general procedure resembled that reported previously.[2] Both the Sheffield and the Buffalo stopped-flow apparatus were used in this work. Pseudo-first-order kinetics were usually obtained in the formation studies by using rela-

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