tral and structural evidence in nickel(II)[1a, 15] and cobalt(II)[1c] complexes, mentioned above, indicates some distortion of the regular structure. The high values of the extinction coefficients at the peaks in the spectra of the vanadyl compounds may also be attributed to such distortions.

Conclusions

The electronic characteristics of the substituents R, R′ seem to be the main factor which governs the stereochemistry of the complexes. Even when only one of the substituents is an aryl group, the electron-withdrawing effect on the β nitrogen prevents the coordination of this atom to the central vanadium and complexes with the same ligand are the result. When the R, R′ groups have an electron-releasing effect, the β nitrogen becomes a strong donor, the Schiff base therefore functions tridentately, and hexacoordinate complexes are formed. While in five-coordinate nickel(II) complexes with X–SALen–$N(C_2H_5)_2$ the bidentate ligand is a Schiff base, it is remarkable that with vanadyl the bidentate ligand is a salicylaldehydo group. This occurs even if the reaction is carried out using stoichiometric amounts of preformed Schiff bases and a vanadyl salt dissolved in aqueous ethanol. Part of the Schiff base is hydrolyzed and the salicylaldehyde, thus liberated, links itself to the vanadyl unit. The low solubility of the mixed-ligand chelates in aqueous ethanol is probably an important factor in directing the reaction toward the formation of complexes of this type. The nature of the ring substituent X does not seem to have any influence, in contrast to the behavior of cobalt(II) and nickel(II) complexes with these Schiff bases.

The Schiff bases with the terminal amino group $-NR_2 = -N(CH_2)_4$, $-N(CH_2)_5$, $-N(C_2H_5)_2$ deserve further consideration. Among these, only the last does not act tridentately but forms complexes with the same ligand, in which the β nitrogen is not linked to the central atom. If we arrange the various groups according to increasing steric hindrance, the following order is obtained: $-N(CH_2)_4 < -N(C_2H_5)_2 < -N(CH_2)_5$. The series of increasing donor power of the nitrogen atom, estimated on the basis of the pK values of the corresponding amines HNR_2 in equilibria with the reference acceptor NiDBH,[16] is: $HN(C_2H_5)_2 < HN(CH_2)_4 < HN(CH_2)_5$. It can be deduced that in the competition between the bulkiness and the electronic characteristics of the substituents R, the latter predominates, enabling the nitrogen to coordinate in pyrrolidino and piperidino derivatives. In the case of a terminal diethylamino group, on the contrary, the donor power does not succeed in compensating for the bulkiness of the two ethyl groups.

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Addition Compounds of Bis(dibenzoylmethano)oxovanadium with Pyridine

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The formation of mono- and diaddition compounds of pyridine with bis(dibenzoylmethano)oxovanadium was shown by measuring the amount of pyridine adsorbed with a silica balance and by visible and infrared spectroscopy. While coordination of the first molecule of pyridine causes the V=O stretching band to shift to lower frequency, further addition of the second molecule of pyridine was found to cause a shift in the reverse direction. An equilibrium constant for the monoadduct of bis(dibenzoylmethano)oxovanadium with pyridine in chloroform solution was estimated from the visible spectra and was compared with that for the acetylacetone chelate.

Introduction

Bis(acetylacetonato)oxovanadium and bis(benzoylacetonato)oxovanadium have been established from chemical and X-ray determinations to have a pentacoordinated structure with a V=O bond and two chelate rings.[2-4] Pyridine coordinates to the vanadium atom, and the monoaddition compound of bis(acetylacetonato)oxovanadium with pyridine has been known and studied spectroscopically.[5-7]

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(2) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

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Table I

Elementary Analysis of VO(dbm)$_2$ and Its Mono and Di Addition Compounds with Pyridine

Samples[a]	Formula	V, % Found	V, % Calcd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	N, % Found	N, % Calcd
a	$VO(C_6H_5COCH{=}COC_6H_5)_2$	10.20	9.94	70.85	70.18	4.77	4.29	...	...
b	$VO(C_6H_5COCH{=}COC_6H_5)_2 \cdot 2C_5H_5N$	...	...	70.48	71.53	4.86	4.80	3.88	4.17
c	$VO(C_6H_5COCH{=}COC_6H_5)_2 \cdot C_5H_5N$	...	...	69.88	70.94	4.56	4.59	2.62	2.36
d	$VO(C_6H_5COCH{=}COC_6H_5)_2$	10.05	9.94	71.16	70.18	4.48	4.29	...	...

[a] Samples a–d refer to the state shown in Figure 2.

In contrast to the vanadyl acetylacetone chelate, coordination of pyridine to bis(dibenzoylmethano)-oxovanadium [abbreviated as VO(dbm)$_2$] causes remarkable changes of the visible and infrared spectra. Spectral as well as gravimetric studies of the VO(dbm)$_2$–pyridine complex revealed unexpectedly the formation of two types of addition compounds, evidence for which will be presented in this paper.

Experimental Section

Materials.—Bis(acetylacetonato)oxovanadium was prepared according to the method described in *Inorganic Syntheses*.[8]

Bis(dibenzoylmethano)oxovanadium was prepared from dibenzoylmethane and vanadyl sulfate which was prepared by reduction of vanadium pentoxide with hydrogen sulfide. A warm alkaline ethanol solution of dibenzoylmethane was mixed with a warm ethanol solution of vanadyl sulfate with stirring. Green crystals formed; they were filtered, washed with ethanol and water, and recrystallized from chloroform–ether solution.

Apparatus and Procedure. Adsorption Experiment.—A silica balance with a sensitivity of 0.97 mm/mg was used to determine the amount of pyridine adsorbed by the crystals of bis(dibenzoylmethano)oxovanadium in a vacuum system. Pyridine was dried over barium oxide and freed from air by a reported freeze-and-thaw method in the vacuum system at 1 × 10^{-3} mm.

The weight change of the sample (30–50 mg) due to the sorption of pyridine vapor was followed by reading the elongation and contraction of the silica helix with a cathetometer. The sample preheated at 150° and 1 × 10^{-3} mm was used for the experiment. A typical experiment is shown in Figure 2. Stage I shows the adsorption curve of pyridine vapor at room temperature, stage II the desorption curve by heating the sample. The temperature was raised at the rate of 1°/2 min. Stages III and IV repeat the adsorption and desorption experiment; stage IV indicates the second desorption follows a different course from the first. Further adsorption and desorption follow the same pattern as III and IV.

Microanalysis of the samples marked a, b, c, and d in Figure 2 was carried out, and the results are shown in Table I. The vanadium content was determined by a spectrophotometric method after the decomposition of the sample.

Infrared spectra were recorded with a Shimadzu IR 27 spectrometer equipped with a rock-salt prism. Figure 4 shows the spectra in the $CHCl_3$ solution containing pyridine and Figure 3 shows the spectra in KBr disks. Visible and ultraviolet spectra were measured with a Shimadzu SV-50A self-recording spectrometer.

Results and Discussion

In Figure 1 is shown the effect of solvents on the visible spectra of VO(dbm)$_2$ and VO(acac)$_2$. The acetylacetone chelate in chloroform solution has two maxima at 595 and 670 mμ which shift in pyridine to shorter and longer wavelengths at 575 and 760 mμ. VO(dbm)$_2$ in chloroform shows two similar maxima at 610 and 670 mμ, but the spectrum in pyridine is quite different. Whereas a new band is observed at 750 mμ as in VO(acac)$_2$ in pyridine, a shorter wavelength band is observed only as a shoulder at 493 mμ on the slope of a big ligand band at 350 mμ (not shown in Figure 1). The result appeared to indicate a different effect of pyridine coordination to VO(dbm)$_2$ from that to VO(acac)$_2$ and prompted us to investigate the amount and the mode of pyridine coordination to VO(dbm)$_2$.

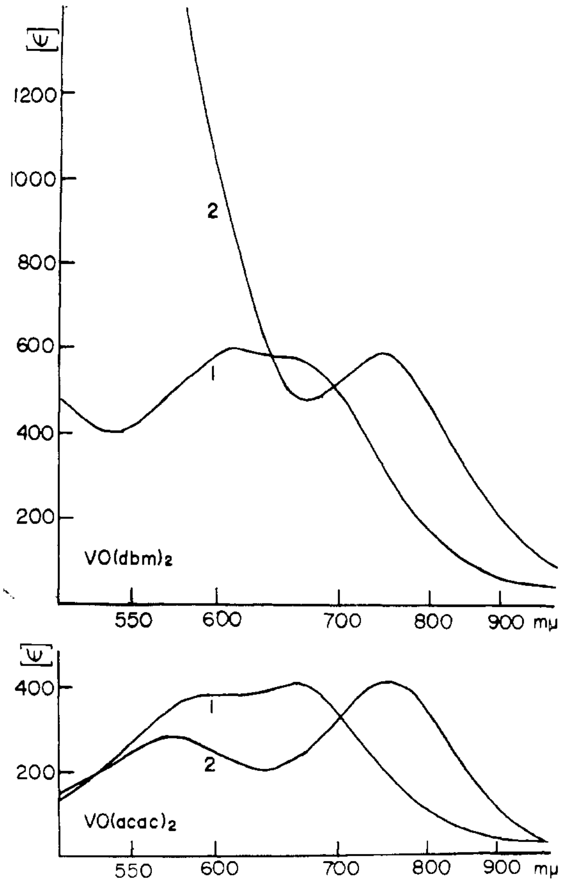

Figure 1.—Visible spectra of VO(acac)$_2$ and VO(dbm)$_2$ in chloroform (curve 1) and in pyridine (curve 2).

Figure 2 indicates the result of a determination of the amount of pyridine adsorbed by VO(dbm)$_2$. VO(dbm)$_2$ absorbs pyridine vapor rapidly as shown in stage I in the figure. When pyridine vapor is pumped off at room temperature the sample loses physically absorbed pyridine and reaches an equilibrium weight corresponding to the adsorption of two moles of pyridine per mole of VO(dbm)$_2$. When the sample is heated (stage II) it releases pyridine showing the desorption curve in two steps and resumes the original weight of VO(dbm)$_2$ at 140°. The intermediary step roughly corresponds to the adsorption of one mole of pyridine per mole of VO(dbm)$_2$. When pyridine vapor is intro-

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(8) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 114 (1959).

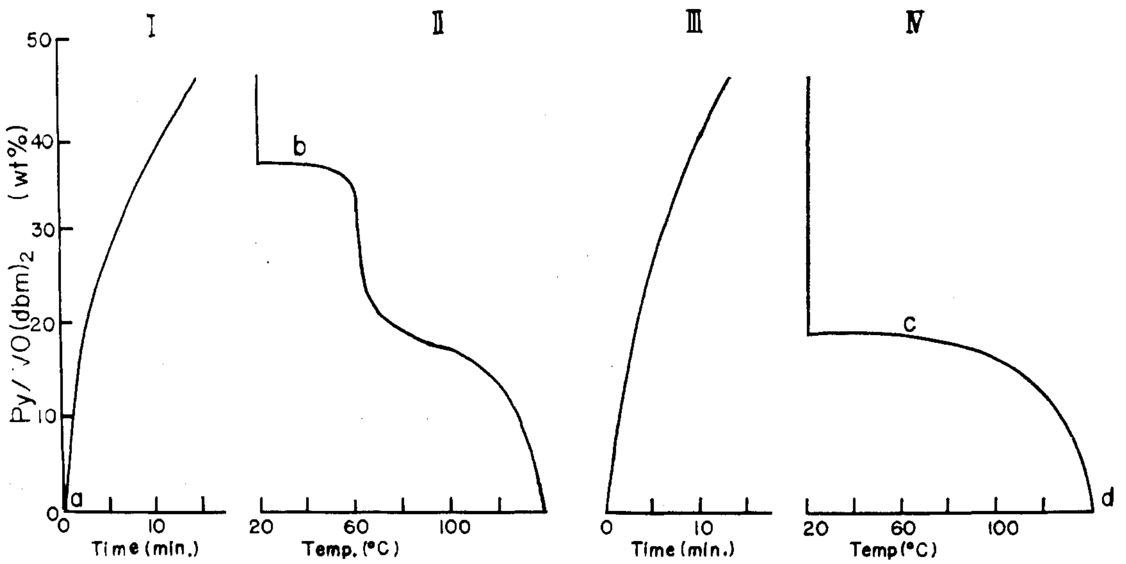

Figure 2.—Thermogravimetric measurement of the amount of pyridine adsorbed on VO(dbm)$_2$: I, absorption; II, desorption; III, second absorption; IV, second desorption.

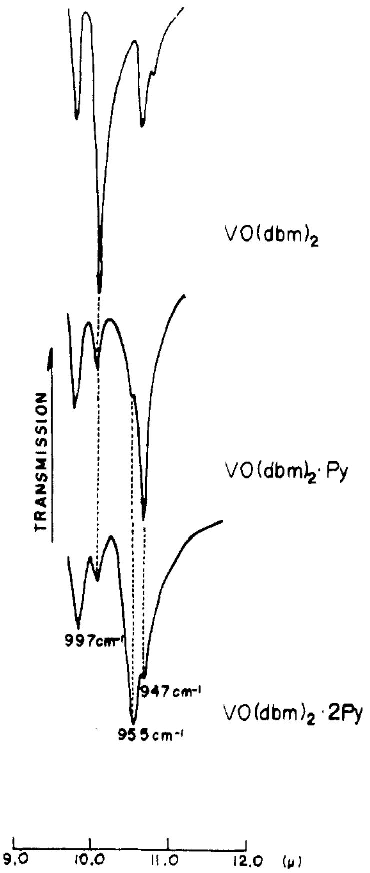

Figure 3.—Infrared spectra of VO(dbm)$_2$ and its pyridine adducts in KBr disks.

duced again (stage III), the sample absorbs pyridine in the same manner as in the first absorption, but loses pyridine differently. It loses more pyridine by evacuation at room temperature compared with stage II and reaches a weight corresponding to the adsorption of one pyridine per VO(dbm)$_2$ and then loses the remaining pyridine on heating.

This experiment suggests the existence of two types of

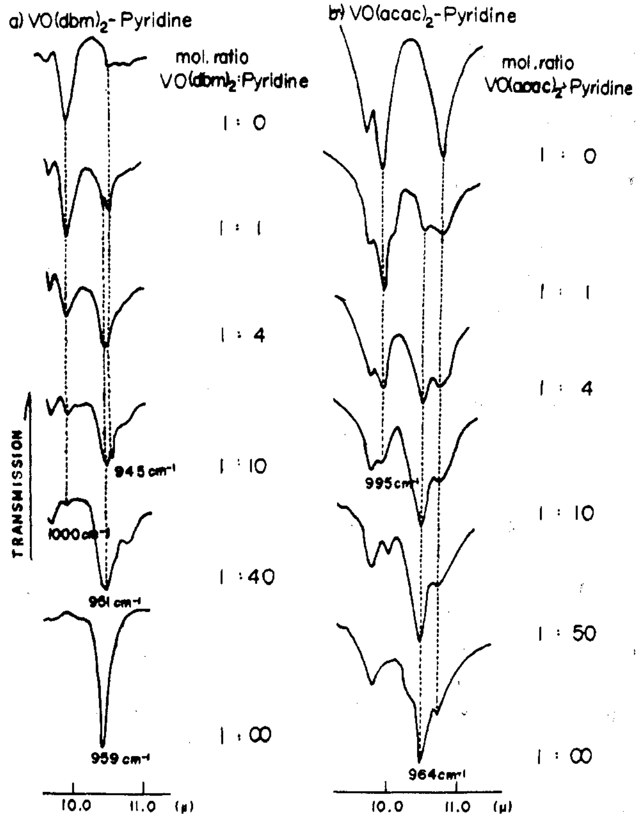

Figure 4.—Change of the infrared spectra of VO(dbm)$_2$ (a) and VO(acac)$_2$ (b) with addition of pyridine in chloroform.

pyridine adsorbed: one molecule of pyridine is firmly bound to VO(dbm)$_2$ and the other is loosely bound. The reason for the difference of desorption curves II and IV is not clear. A possible explanation is the change of the crystalline structure after the first adsorption experiment although we have not been able to get conclusive evidence for this. Elementary analysis of the samples labeled a, b, c, and d in Figure 2 shows that samples b and c correspond to di- and monopyridine adducts as well as that the composition of the samples

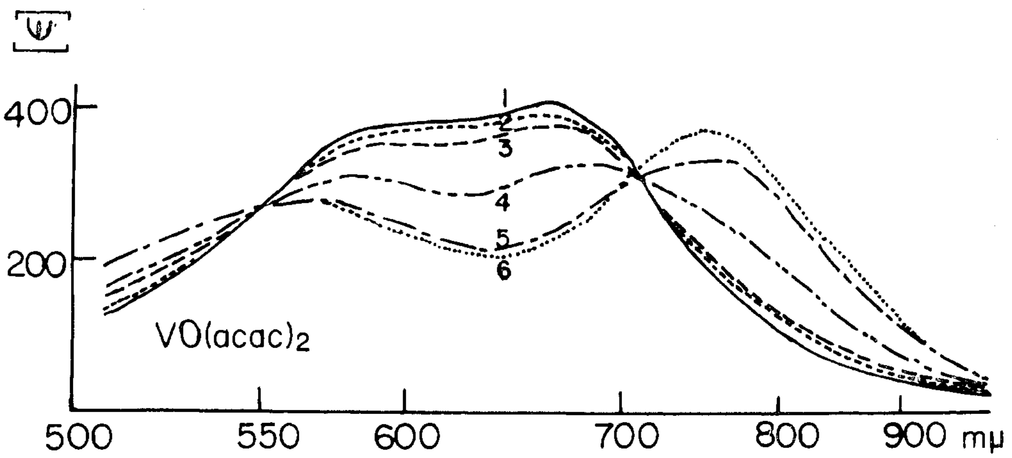

Figure 5.—Change of the visible spectrum of $VO(acac)_2$ with addition of pyridine in chloroform. Molar ratio of $Py/VO(acac)_2$: Curve 1, 0; 2, 1:1; 3, 2:1; 4, 10:1; 5, 50:1; 6, 100:1.

(a and d) is identical before and after the adsorption experiment. Samples a and d showed identical visible spectra. Similar experiment with the vanadyl acetylacetonate was not performed, since the acetylacetonate sublimes on heating *in vacuo*.

The comparison of the infrared spectra of solid samples a, b, and c revealed interesting shifts on the V=O stretching band as shown in Figure 3. The parent compound $VO(dbm)_2$ (sample a) has a strong absorption band at 997 cm^{-1} which is ascribed to the V=O stretching frequency. In the spectrum of sample b with the composition of $VO(dbm)_2 \cdot py$ the band at 997 cm^{-1} decreases whereas a new strong band appears at 947 cm^{-1} with a small shoulder at 955 cm^{-1}. Although a weak band exists at 944 cm^{-1} in the parent compound $VO(dbm)_2$, the new band at 947 cm^{-1} is much stronger and can be assigned to the V=O stretching band shifted by the coordination of pyridine. The similar shift arising from addition of pyridine is observed in many vanadyl complexes and is interpreted as a coordination of a pyridine molecule to a vanadium atom and the resulting loosening of the V=O bond. In the sample b, $VO(dbm)_2 \cdot 2py$, a new absorption band is observed at 955 cm^{-1}, the V=O band being shifted in the reverse direction by the addition of one more molecule of pyridine to the chelate. The band at 997 cm^{-1} persisting in the addition products is considered to be caused by the evacuation during the preparation of KBr disks.

A similar trend is observed in the solution spectra of $VO(dbm)_2$ in chloroform containing various molar ratios of pyridine to the vanadyl complex (Figure 4). The original V=O stretching band at 1000 cm^{-1} decreases with addition of pyridine and shifts first to 945 cm^{-1} and then back to the higher frequency 951 cm^{-1} with further addition of pyridine. In the pure pyridine solution no band is observed at 1000 cm^{-1} and a single strong band is observed at 959 cm^{-1}.

In the case of acetylacetone complex the V=O band shifts from 995 to 964 cm^{-1} by the coordination of pyridine to vanadium but no further shift of 964 cm^{-1} band was observed.

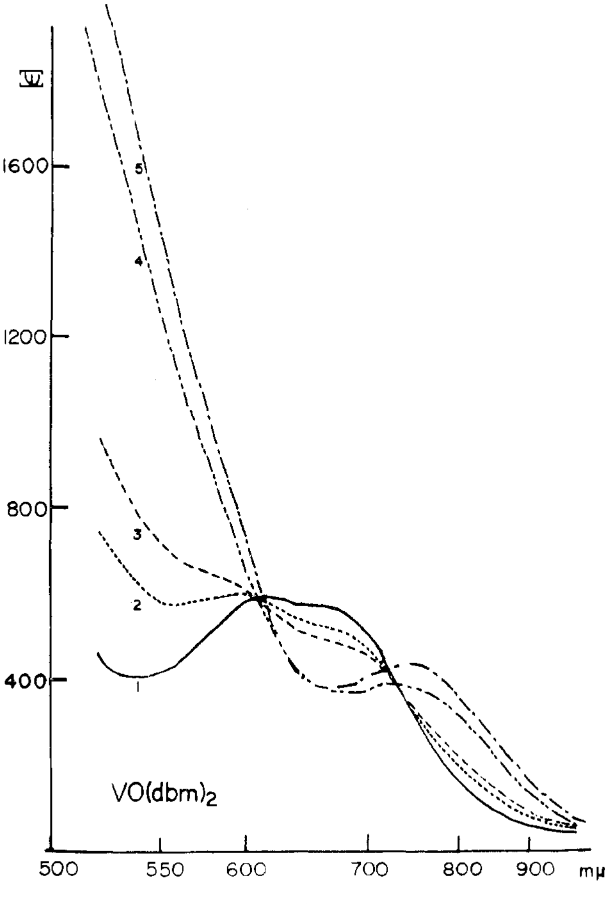

Figure 6.—Change of the visible spectrum of $VO(dbm)_2$ with addition of pyridine in chloroform. Molar ratio of $Py/VO(dbm)_2$: Curve 1, 0; 2, 1:1; 3, 2:1; 4, 20:1; 5, 50:1.

Evidence supporting the formation of mono addition compound of pyridine with the dibenzoylmethane complex at low concentration of pyridine and the formation of the second adduct at higher concentration was also obtained from the visible spectra in Figures 5 and 6. The extinction of the two absorption maxima of $VO(acac)_2$ in chloroform at 595 and 670 mμ decreases with the addition of pyridine, and new bands appear at 565 and 750 mμ (Figure 5). Distinct isosbestic points are observed at 550 and 710 mμ which only slightly 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

$$\mathrm{VO(dbm)_2 + py \overset{K_1}{\rightleftharpoons} VO(dbm)_2{\cdot}py} \qquad (1)$$

$$\mathrm{VO(dbm)_2{\cdot}py + py \overset{K_2}{\rightleftharpoons} VO(dbm)_2{\cdot}2py} \qquad (2)$$

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.

(9) Japan Chemical Society Monograph, "Jikken Kagaku Koza" ("Techniques in Chemistry"), Vol. 3, Maruzen, Tokyo, 1957.

(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.

(11) R. L. Carlin and F. A. Walker, *J. Am. Chem. Soc.*, **87**, 2128 (1965).

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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 $\mathrm{ML}_a\mathrm{X}_b$, 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.

(2) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).