lower energy in the order NCS > $SnCl_3$ > Cl > Br > I. All of the visible absorptions are extremely intense, indicative of a large amount of "borrowing" of charge-transfer intensity.[5] While the expected Cl > Br > I order suggests that these visible bands are d-d transitions and hence are indicative of a spectrochemical series in which the ligand field strength of $SnCl_3^-$ is only slightly greater than that of chloride, in view of the high intensities of these bands it is unwise to speculate too freely on their origin.

We observed a broad band at 2090 cm^{-1} in the Nujol mull infrared spectrum of $[Rh(SbPh_3)_3Cl_2(NCS)]$, which is evidence of the Rh-NCS linkage. This complex did not isomerize on heating, as does $[Rh(PMe_2Ph)_3(NCS)_3]$.[2]

Registry No. $[Rh(SbPh_3)_3Cl_3]$, 51261-83-7; $[Rh(SbPh_3)_3Cl_2Br]$, 51157-43-8; $[Rh(SbPh_3)_3Cl_2I]$, 51157-44-9; $[Rh(SbPh_3)_3Cl_2(NCS)]$, 51157-45-0; $[Rh(SbPh_3)_3Cl_2(SnCl_3)]$, 51157-46-1.

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Metal Ion Induced Pyrrole Ionization in 2-(2′-Pyridyl)imidazole[1]

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Pyrrole hydrogen ionizations in imidazole and derivatives coordinated to the metal ions of metmyoglobin, methemoglobin, and vitamin B_{12} derivatives have been invoked to account for features of potentiometric titrations and changes in absorption spectra in these systems. Transition metal ion induced pyrrole ionization takes place across the imidazole ring from the site of metal ion coordination at the pyridine nitrogen. Substitution of the pyrrole hydrogen by the metal ion is not thought to be occurring in these systems.[2] Due to their complexity, comparative studies are not practical on the macromolecules, and there is a need for greater knowledge of the extent of transition metal ion induced pyrrole ionizations in small well-defined complexes of imidazole and derivatives. Pyrrole ionization occurs from the 2:1 L-histidine complexes of Cu(II) and Co(II) with pK_a values of 11.7 and 12.5, respectively,[3] compared to 14.4 for the free ligand.[4] However, due to the high-pH region, it is uncertain how many bound ligand molecules undergo metal ion induced pyrrole ionization in these and similar complexes.[3]

The ligand 2-(2′-pyridyl)imidazole, PH, promised to be capable of metal ion induced pyrrole ionization across the imidazole ring after chelation at two pyridine nitrogens, one on the pyridine and the other on the imidazole ring, to form a chelate ring system similar to that of 2,2′-bipyridine. Also similar to bipyridine, the ligand PH is known to form tris complexes with Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) and the stability constants have been determined.[5] Neutral complexes of several transition metal ions and ligands that have undergone pyrrole ionization have been prepared in the solid state.[6] However, no solution studies characterizing the pH region in which pyrrole ionization occurs in metal complexes have been reported. This paper describes the promotion of pyrrole hydrogen ionization in solutions induced by transition metal ions coordinated across the imidazole ring.

Experimental Section

The ligand 2-(2′-pyridyl)imidazole was synthesized according to a published procedure,[5,6] mp 137–138° (uncor). $Pd(en)PH^{2+}$ was prepared by a method previously described.[7] Potentiometric titrations confirmed the purity of the preparations. Titrations were performed under nitrogen with a Radiometer TTT1-SBR2 titrimeter–titrigraph equipped with a Sargent combination electrode that was standardized with National Bureau of Standards aqueous buffer solutions at pH 4.00 and 7.00. In order to obtain a measure of the hydrogen ion activity referred to the standard state in the mixed 50% by volume ethanol solutions, 0.15 log unit was subtracted from each pH meter reading before reporting values in this paper.[8] Overlapping acidity constants involving two deprotonations were evaluated objectively,[9] and those with three deprotonations were estimated from the titration curves. Solution magnetic susceptibilities were determined by an nmr method.[10] Circular dichroism spectra were recorded on a Jasco J-10B instrument and visible spectra on a Cary 14R spectrophotometer. All solutions were 0.20 *M* in KCl and all measurements were made at room temperature, near 23°.

Results

Titrations with standard base conducted in water solutions containing 2:1 or greater molar ratios of 2-(2′-pyridyl)imidazole and added acid (PH_2^+) to transition metal ion indicated formation of complexes, but after complex formation is complete, precipitation occurs in the pH region of pyrrole hydrogen ionization. To avoid precipitation in the pH region of interest, a solvent system of 50% by volume ethanol in water was employed, and unless stated otherwise all experiments refer to this mixed-solvent medium.

For the deprotonation reaction $PH_2^+ \rightleftarrows PH + H^+$, potentiometric titration gave pK_a = 5.09 in 50% ethanol and 5.54 in water. Spectrophotometric titrations monitored at 325 nm were used to evaluate the acidity constant for ionization of the pyrrole hydrogen in the free ligand ($PH \rightleftarrows P^- + H^+$). In 50% ethanol p$K_a$ = 14.2 ± 0.2 and in water a lesser value of 13.4 ± 0.1 was obtained consistent with relative stabilization of oppositely charged ions in the higher dielectric constant medium.

In the presence of Fe(II), Co(II), Ni(II), Cu(II), or Zn(II) the deprotonation occurring with pK_a = 5.09 is depressed on the pH axis. In a solution containing a 3:1 ligand to transition metal ion ratio, complex formation is complete by pH 7 and in no case does any ligand titrate as if unbound. Thus all of the above transition metal ions form relatively stable 3:1 complexes with PH as with bipyridyl. These results are consistent with the stability constants that have already been reported for 3:1 complexes of PH with transition metal ions.[5] Addition of excess ligand so that the ratio is

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greater than 3:1 indicates ligand titrating freely with pK_a = 5.1. In all of these cases complex formation and deprotonation of PH_2^+ to give PH are complete by about pH 7 before the onset of pyrrole hydrogen ionization in the complexes.

Titration curves obtained under nitrogen after tris complex formation are shown in Figure 1. The additional equivalents titrated at pH >7 are due to transition metal ion induced pyrrole hydrogen ionization. For most of the metal ions competition with hydroxo complex formation occurs at the highest pH values in 3:1 mixtures. In order to suppress hydroxo complex formation, the titration curves in Figure 1 are obtained in the presence of excess ligand with ratios of at least 5:1. Acidity constants for metal ion induced pyrrole hydrogen ionizations in 3:1 complexes of first-row transition metal ions are listed in Table I. The two pK_3 = 11.3 values may contain a large component from hydroxo complex formation. The table assumes that the first five complexes remain 3:1 after pyrrole hydrogen ionization as before, but it is possible that the Cu(II) and Zn(II) complexes become 2:1.[6] Also included in Table I is the pK_a value for the mixed Pd(II) complex of diaminoethane and PH determined by both potentiometric and spectrophotometric titration.

Changes in visible and near-infrared absorption spectra due to pyrrole hydrogen ionization provide additional information about the structures of complexes in solutions containing at least a 3:1 ratio of PH to metal ion. Positions of the absorption maxima in the pink Ni(II) complexes at 970 nm (ϵ 9), 880 (ϵ 10), and 545 (ϵ 12) are unchanged by raising the pH from 7 to 11. A similar increase in pH results in a slight decrease in the absorption maximum of the Co(II) complex from 975 nm (ϵ 13) to 970 (ϵ 10). Bands in the visible region of the Co(II) complexes appear as shoulders on a strong charge-transfer band at 345 nm. Only metal to ligand charge-transfer bands are apparent in the red Fe(II) complex and pyrrole ionization results in their shift from 485 and 396 nm to 523 and 415 nm with the stronger band at the longer wavelength in each case. The low-spin tris complex of bipyridyl and Fe(II) yields an absorption maximum at 522 nm.[11]

Upon passing through the pH region for pyrrole hydrogen ionization of two PH ligands chelated to Cu(II), the visible absorption maxima of the green complexes undergo a shift to shorter wavelengths. As shown in Figure 2 (curves A and B) introduction of a third neutral ligand in a 2:1 Cu(II) complex decreases the intensity by about 50%. On the other hand the higher pH complexes exhibit less dependence on the Cu(II) to ligand molar ratio (curves C and D). Steric hindrance precludes formation of an undistorted 2:1 tetragonal complex. Prior to pyrrole ionization the spectra of the Cu(II) complexes of PH bear similarities to the tris and bis complexes of bipyridyl,[12] the latter of which is thought to be cis distorted octahedral with two water ligands.[12,13] The shape of the spectra of both higher pH complexes more closely resembles that of the bis-bipyridyl complex. This result suggests that after pyrrole ionization of two ligands to form a neutral complex, the third ligand may be expelled and the two cis positions occupied by water.

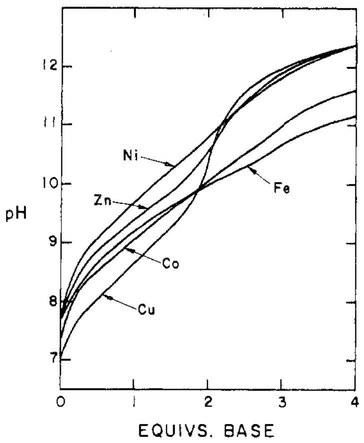

Figure 1. Titration curves of 2-(2′-pyridyl)imidazole, PH, in the presence of transition metal ions. The abscissa represents the equivalents of base added per mole of metal ion. The ligand to metal ion molar ratios are 5:1 except for Ni(II) which is 6:1 and Fe(II) which is 10:1. Solvent is 50% ethanol-water.

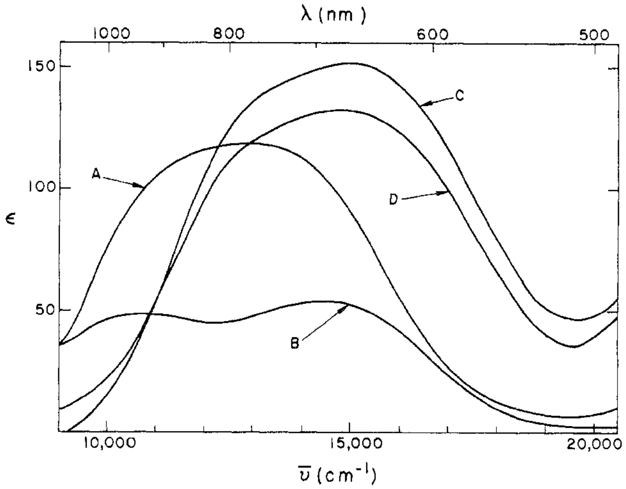

Figure 2. Visible absorption spectra of Cu(II) complexes of PH. Curves A and B refer to 2:1 and 3:1, respectively, molar ratios of ligand to Cu(II) at pH 6.3, and curves C and D to 2:1 and 3:1 molar ratios at pH 11.

Table I. Logarithms of Acidity Constants for Pyrrole Hydrogen Ionization in Complexes of 2-(2′-Pyridyl)imidazole (PH)[a]

Complex	pK_1	pK_2	pK_3
$Fe(PH)_3^{2+}$	8.6	9.4	10.0
$Co(PH)_3^{2+}$	8.5	9.4	10.3
$Ni(PH)_3^{2+}$	9.0	10.1	11.2
$Cu(PH)_3^{2+}$	7.9	9.0	11.3
$Zn(PH)_3^{2+}$	8.8	9.8	11.3
$Pd(en)PH^{2+}$	6.3		

[a] With excess ligand in 50% ethanol. For free ligand pK_a = 14.2. All values are ±0.1

In 50% ethanol the ligand PH absorbs at 295 nm (ϵ 15,200) with a well-developed shoulder at 275 nm (ϵ 10,600) while in 1 *N* NaOH a single absorption band appears at 305 nm (ϵ 12,550). Most of the tris complexes of PH show ultraviolet ligand absorption bands near 298 and 265 nm. Upon pyrrole hydrogen ionization the ligand bands in the complexes appear near 295 nm with an additional peak or shoulder near 330 nm.

The properties of mixed-ligand complexes of PH and L-alanine were studied on solutions containing equimolar amounts of each ligand and Cu(II). As with bipyridyl, it is anticipated that little disproportionation of mixed complex to 2:1 complexes of one ligand occurs in this

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system with an aromatic amine.[14] In 50% ethanol, pyrrole hydrogen ionization in the mixed 1+ complex occurs with $pK_a = 8.2$, slightly lower than the statistically adjusted value (see Discussion) from Table I for a nontetragonal complex. The visible absorption spectrum of the mixed complex is that of a tetragonal Cu(II) complex with the wavelength of maximum absorption shifting from 625 nm before pyrrole hydrogen ionization to 608 nm afterward. Spectra in the ultraviolet region are comparable to the 2:1 complexes presented above.

As for many mixed complexes of L-alaninate and Cu(II),[15] the visible circular dichroism (CD) of Cu(PH)(L-Ala)$^+$ exhibits a net negative sign. In water the CD extrema show $\Delta\epsilon = -0.03$ and $+0.01$ at 568 and 695 nm, respectively. Transfer to 50% ethanol and pyrrole hydrogen ionization result in increases in CD magnitudes within the same sign pattern. The mixed complexes of Cu(II), L-alaninate, and either bis(imdazolyl)methane[16] or bipyridyl in 50% ethanol yield a similar sign pattern. However, the mixed complex of Cu(II), L-alaninate, and bipyridyl in water yields a visible CD spectrum with two positive maxima[15] in contrast to the net negative CD for the mixed PH complex. These solvent effects which alter the sign of the CD deserve further investigation.

The magnetic susceptibility of the Fe(PH)$_3^{2+}$ complex in D_2O at pH ~7 is 3.4 BM at 34°. This value is within the range observed for solid complexes at Fe(PH)$_3^{2+}$ and a variety of anions which show a temperature-dependent susceptibility with a predominance of the low-spin form at room temperature.[17]

Discussion

Marked promotion of pyrrole hydrogen ionization in 2-(2′-pyridyl)imidazole, PH, upon chelation to transition metal ions is revealed by inspection of Table I. Saturation of metal ion coordination sites in tris complexes of the bidentate ligand indicates that pyrrole ionization is promoted by coordination of the metal ion across the imidazole ring and not by substitution of the pyrrole hydrogen by the metal ion. Pyrrole ionization in complexes of glycylhistidine is promoted by metal ion substitution and the system exhibits behavior different from that described in this paper.[18] Since there are three ligand molecules in the tris complexes of Table I, the successive intrinsic acidity constants are indicated by $pK_1 + \log 3 = pK_1 + 0.5$, pK_2, and $pK_3 - 0.5$. Chelation of the ligand PH in a dipositively charged transition metal ion complex results in promotion of the first pyrrole ionization by 5.1, 5.2, 4.7, 5.8, and 4.9 log units for the five tris complexes of first-row transition metal ions of Table I, respectively, and 7.9 log units for the Pd(II) complex. This last value is markedly greater than the promotion of 3.6 log units found for the pyrrole hydrogen ionization in Pd(en)(L-His)$^+$.[19] Though the pK_a of the unbound ligand is unknown, promotion of the pyrrole ionization in 2-(2′-pyridyl)benzimidazole by first-row transition metal ions in 50% dioxane follows the same order as above for PH.[20]

The ability of the metal ions to promote ionization of the pyrrole hydrogen shows marked differences from the stability constant order. Though its stability constant has not been determined, the Pd(II) complex of Table I is almost certainly the most stable, and it is also the one with the lowest pK_a. For the first-row divalent transition metal ions the stability order as given by the first stability constant or as the product of the first two stability constants is Cu > Ni > Co > Zn > Fe.[5] If all three stability constants are considered, the positions of Cu and Ni are reversed. On the other hand the acidity of the complexes (Table I) as measured by pK_1 or $pK_1 + pK_2$ is given by Cu > Co > Fe > Zn > Ni. If all three ionizations are considered, the order becomes Fe > Cu = Co > Zn > Ni. Considering its high position in the stability series and its bottom position in the acidity series, Ni(II) appears relatively ineffective in promoting pyrrole hydrogen ionization compared to the other metal ions. Co(II) and especially Fe(II) are markedly more effective in promoting pyrrole ionization than the stability series predicts. The Fe(II) complexes are at the bottom of the stability series, in the middle of the first acidity series, and at the top of the final acidity series. The near equality of the three successive stability constants[5] suggests a tendency for a low-spin complex in solutions of Fe(PH)$_3^{2+}$. This conclusion is confirmed by the susceptibility determination with an intermediate result of 3.4 BM corresponding to about 57% low-spin Fe(II).[17] The marked promotion of Fe(II) from the bottom of the stability series to the top of the final acidity series suggests a mutal promotion of pyrrole hydrogen ionization and further stabilization of a low-spin form.

The results reported here for the complexes of 2-(2′-pyridyl)imidazole indicate that metal ion induced pyrrole hydrogen ionization may be a feature of many systems containing imidazole and derivatives as ligands.

Registry No. Fe(PH)$_3^{2+}$, 18745-06-7; Co(PH)$_3^{2+}$, 18973-12-1; Ni(PH)$_3^{2+}$, 18745-07-8; Cu(PH)$_3^{2+}$, 20219-48-1; Zn(PH)$_3^{2+}$, 18745-08-9; Pd(en)PH^{2+}, 51052-18-7; PH, 18653-75-3; Cu(PH)(L-Ala)$^+$, 51108-14-6.

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Application of Magnetic Measurements to Complex Formation in Fused Salts

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Magnetic susceptibility measurements on transition metal complexes are routine for the investigation of structure and are complementary to ligand field spectral studies. In investigating transition metal ions in fused-salt solutions, spectroscopy has been widely used, but only a handful of reports of magnetic work have appeared in this area.[1-5] The

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