described for pyrazinepentaammineruthenium(II) in which the basicity of the pyrazine is increased by conjugation with the divalent ruthenium.[17] The decrease in acidity of C-[1,3](II) and C-[1,3,7](II) relative to C-[1,3,7](III) and C-[1,3,7](III) correlates well with the intense metal to ligand charge transfer band and the stabilization of ruthenium(II) relative to ruthenium(III) evident in the electrochemical measurements.

Electrochemistry. The more positive reduction potentials relative to that for the hexaammineruthenium(III-II) couple for all the neutral ligand nitrogen-bound complexes indicate that the xanthine ligand stabilizes ruthenium(II) relative to ruthenium(III). This is apparently caused by transfer of πd electron density to the ligand in the ruthenium(II) state and has been discussed by Lim[22] for a number of pentaammineruthenium complexes involving heterocyclic ligands. Deprotonation of the xanthine destabilizes ruthenium(II) somewhat since the presence of a negative charge on the ligand decreases its ability to accept electron density from the metal. The degree of this effect is dependent upon the proximity and conjugation of the deprotonation site with regard to the metal binding site. Less positive reduction potentials caused by the deprotonation of the xanthine ligand are also consistent with stabilization of the Ru(III) state by a negatively charged ligand. The effects of back-donation and charge stabilization cannot be separated.

Binding at the C_8 site appears to stabilize ruthenium(II) relative to ruthenium(III) much more than does coordination at N_7. The π orbital of a carbene is expected to be electron deficient and should be a good acceptor of electron density from the metal.[11,12] This property may account for the apparent thermodynamic stability of the C_8 isomer over the N_7 isomer when bound to ruthenium(II).

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A Reexamination of the Metal–Nitrogen Bond in Certain Imidazole and Pyrazole Complexes

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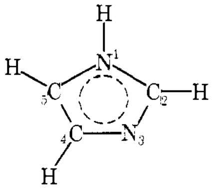
Abstract: The previously reported experimental data, which had been interpreted as evidence of ambidentate metal coordination of the aromatic bases imidazole or pyrazole through either of their nitrogen atoms, has been carefully reexamined. In direct contradiction to the previous report, the true paramagnetic proton magnetic resonance (pmr) shift of the N-1 proton of imidazole is shown to be downfield when this base is coordinated to either Ni(saloph) or Co(saloph) (saloph = *N,N′*-bis(salicylidene)-*o*-phenylenediamino). Pmr and electronic spectral data purported to indicate the existence of two different 1:1 adducts between Co(saloph) and either imidazole or pyrazole are shown to be either erroneous or misinterpreted. Electronic spectral data indicate that pyrrole does not form adducts with either Ni(saloph) or Co(saloph). It is concluded that N-1 of imidazole, N-1 of pyrazole, and the nitrogen of pyrrole do not coordinate Ni(saloph) or Co(saloph).

Imidazole, **1**, and its derivatives frequently occur as the metal binding sites of biologically important macromolecules. Consequently the mode of bonding between metals and imidazole is of considerable importance. Some recent experiments have been interpreted to indicate that imidazole may coordinate metals not only in the well-recognized manner through N-3 but also *via* N-1.[1] Similarly it has been suggested that pyrazole, **2**, may coordinate metals through either N-2 or N-1.



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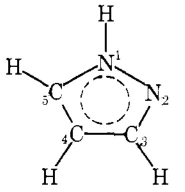

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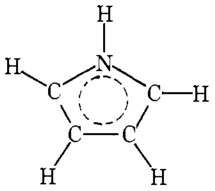

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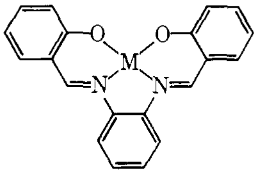
On the basis of simple theoretical arguments the coordination of imidazole through N-1 or pyrazole through N-1 appeared to us unlikely. Both pyrazole and imidazole exhibit aromatic character. Estimates of the resonance energy of imidazole range from 12 to 32 kcal/mol.[2-4] For pyrazole the resonance energy has been estimated to be between 26 and 42 kcal/mol.[2-4] Coordination of imidazole or pyrazole through their respective N-1 positions would result in the interruption of their aromatic π systems. Consequently it appears unlikely that these bases would coordinate metal ions in this fashion when each molecule possesses a basic site which is not a part of any conjugated π system. Rather we anticipate that the N-1 positions of **1** and **2** should resemble the nitrogen of pyrrole, **3**, in their reactions with metals and other acids. The feeble basicity of pyrrole is a recognized consequence of its aromatic character.[5]

Briefly the primary data reported in ref 1 which is pertinent to the mode of aromatic base coordination involves the behavior of the proton magnetic resonance (pmr) spectra of the two heterocycles **1** and **2** in the presence of the metal complexes Ni(saloph), **4**, and Co(saloph), **5**. The effect of adding either of the metal complexes to solutions of imidazole is reported to result in a broadening and an upfield shift of the N-H resonance while the resonances of the carbon-bound protons remain unaffected both in chemical shift as well as in line width. Similar observations were made for solutions of pyrazole in the presence of **5**. The shift of the N-H resonances of imidazole and pyrazole in the presence of **4** or **5** has been attributed to a paramagnetic shift resulting from coordination of the base to the metal of the complexes. Since the pmr resonance of the N-1 proton was the only resonance shifted and since that shift was upfield, the same direction observed for ammonia[6] and other saturated amines[7,8] when coordinated by nickel, it was argued that the metal was coordinated through N-1.



4, M = Ni
5, M = Co

It appeared to us that the shift of the N-H resonance might have originated with other causes. It is well documented that hydrogen bonding and chemical exchange may cause broadening and shifting of N-H resonances. Consequently a reinvestigation of the interaction of aromatic bases with the complexes **4** and **5** was undertaken. Results which are at variance with those reported in ref 1 are reported here.

Experimental Section

Compounds. Commercial samples of imidazole (Matheson Coleman and Bell) and pyrazole (Aldrich) were purified by vacuum sublimation. Pyrrole (Aldrich) was purified by fractional distillation. Minute quantities of basic impurities which remained were removed by stirring the pyrrole with anhydrous cobalt chloride followed by a bulb to bulb distillation under vacuum. The metal complexes Co(saloph) and Ni(saloph) were prepared by the method described previously for Co(saloph).[9,10] *Anal.* Calcd for $CoC_{20}H_{14}O_2N_2$: C, 64.35; H, 3.78; N, 7.51. Found: C, 64.30; H, 3.90; N, 7.45. Calcd for $NiC_{20}H_{14}O_2N_2$: C, 64.39; H, 3.78; N, 7.51. Found: C, 64.25; H, 3.88; N, 7.41.

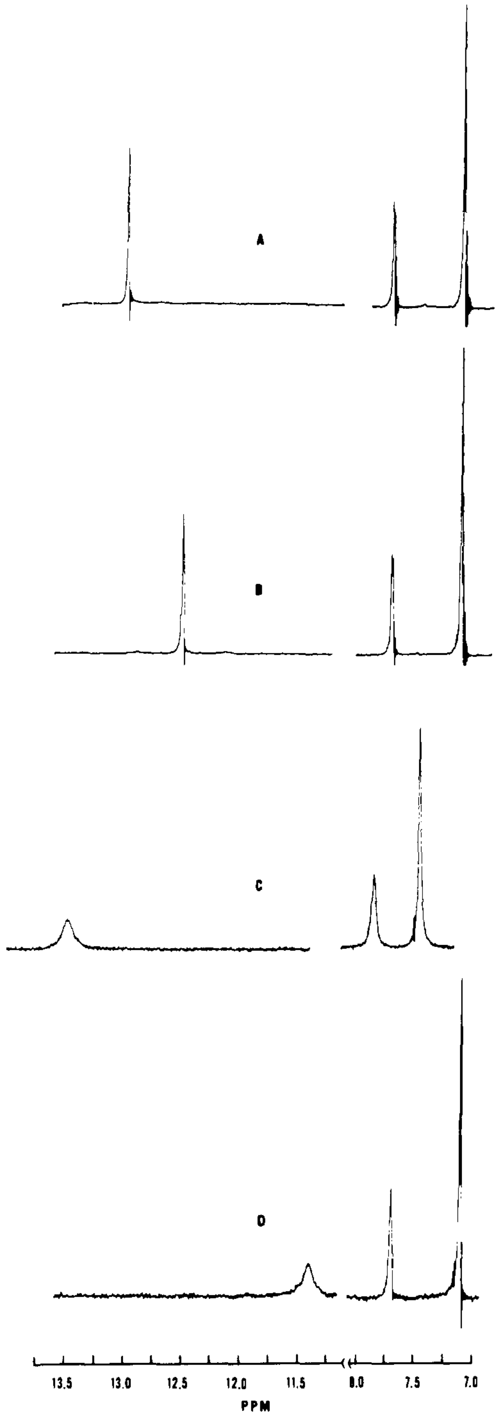


Figure 1. Pmr spectra of imidazole in dichloromethane at 35°: (A) 1.04 *M* imidazole, (B) 0.52 *M* imidazole, (C) 0.52 *M* imidazole containing 8.05×10^{-3} *M* Co(saloph), (D) 0.26 *M* imidazole.

Pmr Measurements. Pmr spectra were run on a JEOL JNM-MH-100 spectrometer operating at 100 MHz. All chemical shifts were measured relative to internal tetramethylsilane. A JES-VT-3 temperature controller was used to maintain the temperature for all of the spectra reported. Temperatures were monitored by the use of a methanol sample and calibration chart supplied by JEOL. Dichloromethane was fractionally distilled from phosphorus pentoxide. Solutions were prepared under a dry nitrogen atmosphere.

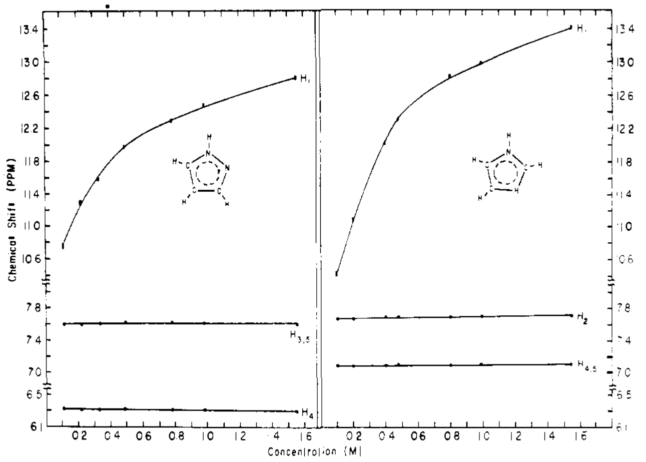


Figure 2. Concentration dependence of the pmr chemical shifts for dichloromethane solutions of imidazole and pyrazole at 35°.

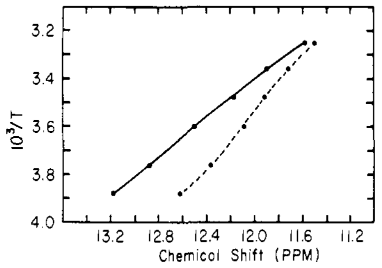


Figure 3. Chemical shift of the H_1 proton *vs.* $1/T$ for 0.26 M imidazole (- - - -) and 0.32 M pyrazole (——) in dichloromethane.

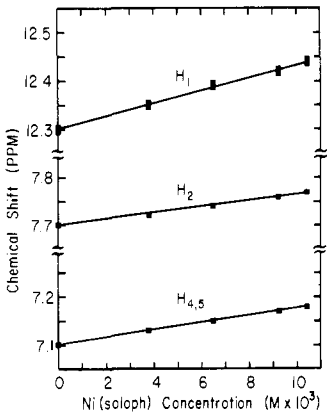


Figure 4. Effect of Ni(saloph) concentration on the chemical shifts of 0.49 M imidazole in dichloromethane at 35°.

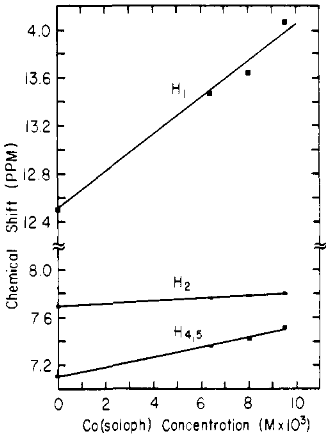


Figure 5. Effect of Co(saloph) concentration on the chemical shifts of 0.52 M imidazole in dichloromethane at 35°.

Due to the extreme sensitivity of Co(saloph) to oxygen in the presence of the bases under study, all solutions containing Co(saloph) were prepared on a vacuum line, and tubes for nmr studies were sealed under vacuum. All solution molarities refer to the solution at 25°.

Results

The pmr spectrum of imidazole is strongly dependent on the imidazole concentration and on the temperature. Figure 1 reproduces the pmr spectra of imidazole at three different concentrations in dichloromethane solutions. As the imidazole concentration decreases the N-H resonance broadens and moves upfield, while the C-H resonances show only very minor shifts. Figure 2 shows a plot of the chemical shifts of imidazole as a function of concentration. Similar observations have been made for the pmr spectrum of imidazole in acetone and in benzene solutions.[11] These changes have been ascribed to the formation of strongly hydrogen-bonded agregates of imidazole in solution.[11] The pmr spectrum of pyrazole in dichloromethane displays a similar concentration dependence as shown in Figure 2. Similar observations have been made previously for pyrazole in carbon tetrachloride.[12] Figure 3 shows the temperature dependence of the chemical shifts of imidazole and of pyrazole. For both bases the N-H resonance undergoes a pronounced downfield shift as the temperature is lowered. The chemical shifts of the C-H resonances of both bases exhibit only slight downfield displacements (*ca.* 0.04 ppm) over the temperature range indicated.

Because of the sensitivity of the N-H resonances of imidazole and pyrazole to both concentration and temperature, the effect of the metal complexes **4** and **5** on the pmr spectra of these bases has been investigated under conditions where both of these factors were carefully controlled. The effect of adding Co(saloph) to a dichloromethane solution of imidazole may be seen by comparing traces B and C of Figure 1. All resonances, C-H as well as N-H, are shifted to lower field and are broadened. A similar, although smaller, downfield shift and broadening is observed when Ni(saloph) is added to a solution of imidazole. In Figure 4 the chemical shifts for a solution of imidazole in dichloromethane are plotted as a function of the concentration of Ni(saloph) present. Analogous data for imidazole solutions containing Co(saloph) are presented in Figure 5. In both cases a linear dependence of the paramagnetic shift on the metal complex concentration was observed. This behavior is that anticipated for a system involving rapid exchange at equilibrium of base between free and coordinated sites (*vide infra*).

Similar experiments were performed to determine the effect of the metal complexes on the pmr spectrum of pyrazole. An 0.8 M solution of pyrazole in dichloromethane containing up to 6.5×10^{-3} M Ni(saloph) shows no effect on either the position or the line widths of the pyrazole resonances. Attempts to measure the pmr spectrum of pyrazole with Co(saloph) present were thwarted by our inability to dissolve Co(saloph) in a 0.5 M solution of pyrazole in dichloromethane.[13] Finally, addition of Ni(saloph) up to a concentration of 5×10^{-3} M does not result in any change in the pmr spectrum of an 0.8 M solution of pyrrole in dichloromethane.

In order to further examine the ability of pyrrole to coordinate Ni(saloph) or Co(saloph) the electronic spctra of these complexes were obtained in the presence of pyrrole. The spectrum of a 1.05×10^{-4} M solution of Ni(saloph) in dichloromethane was unaffected by the addition of up to 0.13 M pyrrole. Similarily addition of up to 0.56 M pyrrole to a 1.4×10^{-4} solution of Co(saloph) produced no spectral changes. We conclude that pyrrole does not form adducts with either metal complex.

Discussion

We find no evidence that indicates that either imidazole or pyrazole bind Ni(saloph) or Co(saloph) through their N-1 atoms. The discussion supporting this conclusion will consider the differences in the experimental data reported here and those described in ref 1 and then will evaluate the arguments presented in favor of unconventional coordination of these bases in the context of the corrected experimental data.

It appears that the effects ascribed in ref 1 to a paramagnetic shift resulting from coordination by the complexes **4** and **5** to imidazole or pyrazole were actually caused by dilution of the bases. Unfortunately the experimental conditions and procedures are not described with sufficient precision in ref 1 to allow direct confirmation of this conclusion, but the following observations are offered in support of it. (1) Comparison of Figure 1 of ref 1 with Figure 1 of this paper or Figure 1 of ref 11 demonstrates the similarity between the presumed paramagnetic shifts and the known dilution shifts. Both the shifts of resonance position and the line width alterations are similar. (2) The limited solubility of **4** and **5** require that dilution was necessary in order to span the range of "mole per cent" (actually the ratio of total complex concentration to total base concentration) reported in Figures 3-5 of ref 1.[14] (3) The effects described in ref 1 as due to Ni(saloph) and Co(saloph) are nearly identical, whereas we report that very different paramagnetic shifts are produced by the two complexes. The similarity of behavior observed in ref 1 can be explained if a common cause—dilution—was responsible for the shifts. In the case of Ni(saloph) the true paramagnetic shifts are sufficiently small so that they might be obscured by the effect of dilution. In the case of Co(saloph), however, much larger paramagnetic shifts in the opposite direction as the dilution shifts are found. The failure of the authors of ref 1 to observe components of the true shifts in this case may have been due to aerial oxidation or oxygenation of the cobalt complex. Atmospheric exposure of sealed tubes of Co(saloph) and imidazole in dichloromethane results in the complete loss of the true paramagnetic shift and restores the unaltered pmr spectrum of imidazole.[15]

We now turn to arguments concerning the mode of base coordination. The cornerstone of the arguments in favor of imidazole coordination to **4** and **5** *via* N-1 rested on the observation[1] of an exclusive upfield shift of the N-H resonance in the presence of Ni(saloph). Upfield shifts of N-H resonances are found when saturated amines coordinate nickel and the theoretical origin of this shift has been discussed.[6-8] However, as shown here, the true paramagnetic shifts experienced by imidazole in the presence of Ni(saloph) are in the opposite direction. Consequently the direction of the paramagnetic shift of the imidazole N-1 proton is not consistent with coordination by the metal at N-1. With pyrazole the argument concerning the direction of the paramagnetic N-H shift is irrelevant since no shift due to coordination by Ni(saloph) or Co(saloph) is observable.

Another group of arguments advanced in favor of imidazole or pyrazole coordination *via* N-1 concern nmr and electronic spectral data which were purported to indicate that more than two metal complexes were present in mixtures of **4** or **5** and either aromatic base in dichloromethane. Such data, where they do exist, must be viewed with caution, of course, since the data serve only at best to identify the number of species present, but in themselves offer no structural information.

In ref 1 it was noted that plots of the observed chemical shift (δ_{obsd}) for imidazole or pyrazole solutions containing **4** or **5** *vs.* the mole per cent of complex present were nonlinear. This nonlinearity was taken as evidence that more than two metal complexes were present. These data have been shown to be incorrect, but it is important to point out that the data presented here in Figures 4 and 5 *cannot* be used to determine the number of species present in equilibrium. A linear plot of δ_{obsd} *vs.* the formal complex concentration is anticipated under a variety of two and three site exchange processes. The situation which pertains for the simple equilibrium (eq 1) has been described in ref 1. For the case

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \tag{1}$$

given by eq 2 with rapid equilibrium between the three sites

$$\mathrm{A} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{AB}, \qquad \mathrm{AB} + \mathrm{B} \overset{K_2}{\rightleftharpoons} \mathrm{AB_2} \tag{2}$$

and the base in large excess, the observed chemical shift will be given by eq 3, where δ_B, δ_{AB}, and δ_{AB_2} are the chemical shifts of free B, AB, and AB_2, respectively, K_1 and K_2 are the equilibrium constants in eq 2, and $[A_0]$ and $[B_0]$ are the formal concentrations of the metal complex and aromatic base. Similarly if two isomeric five-coordinate adducts (AB and AB′) are formed (eq 4), then the observed

$$\delta_{\text{obsd}} = \delta_B + \left(\frac{[A_0]}{1 + K_1[B_0] + K_1K_2[B_0]^2}\right) \times \\ [K_1(\delta_{AB} - \delta_B) + 2K_1K_2[B_0](\delta_{AB_2} - \delta_B)] \tag{3}$$

$$\mathrm{A} + \mathrm{B} \overset{K_3}{\rightleftharpoons} \mathrm{AB}, \qquad \mathrm{A} + \mathrm{B} \overset{K_4}{\rightleftharpoons} \mathrm{AB'} \tag{4}$$

chemical shift is given by eq 5 where the symbols are defined similarily. Thus in the case of either equilibria 1, 2, or 4 a linear plot of δ_{obsd} *vs.* $[A_0]$ is expected as long as the imidazole concentration is both held constant and greatly exceeds that of the complex introduced.

$$\delta_{\text{obsd}} = \delta_B + \left(\frac{[A_0]}{1 + K_3[B_0] + K_4[B_0]}\right) \times \\ [K_3(\delta_{AB} - \delta_B) + K_4(\delta_{AB'} - \delta_B)] \tag{5}$$

The inability to observe isosbestic points in the Co(saloph)-imidazole system in dichloromethane solution was quoted in ref 1 as evidence that two different five-coordinate adducts of Co(saloph) with imidazole exist. On the contrary *isosbestic points are expected* in a system described by eq 4 when increasing amounts of base B, which is transparent in the region of observation, are added to a fixed amount of metal complex. The equilibrium ratio of the two isomeric adducts is a constant and does not depend upon the base concentration. The existence of a pair of five-coordinate adducts could be detected by observation of the electronic spectra as a function of temperature but could not be detected in experiments where only the base concentration was varied. For a system governed by eq 4 the total absorbance $a(\lambda)$ at any wavelength will be given by eq 6,

$$a(\lambda) = \epsilon_A[A] + \epsilon_{AB}[AB] + \epsilon_{AB'}[AB'] \tag{6}$$

and it may be readily shown that isosbestic points are predicted by eq 7 where ϵ_A, ϵ_{AB}, and $\epsilon_{AB'}$ are the extinction coefficients at a particular wavelength of A, AB, and AB′.

$$\epsilon_A = \epsilon_{AB}\left(\frac{K_3}{K_3 + K_4}\right) + \epsilon_{AB'}\left(\frac{K_4}{K_3 + K_4}\right) \tag{7}$$

However, isosbestic points are not expected in the Co(saloph)-imidazole system if a six-coordinate adduct is formed. The arguments advanced in ref 1 against the existence of a six-coordinate bis adduct are unconvincing, and in fact experimental evidence of the formation of a bis adduct in this system has been reported.[16]

Finally we have examined the behavior of Ni(saloph) and Co(saloph) in the presence of pyrrole. Pyrrole, like imidazole and pyrazole, is an aromatic molecule but it is a much weaker base since it lacks a nitrogen lone pair which is not a part of a conjugated π-system. In fact, it is interesting to note that protonation of pyrrole preferentially occurs at a carbon atom rather than at the nitrogen.[17] The electronic spectra of Co(saloph) and Ni(saloph) are unaffected by up to a 1000-fold excess of pyrrole. We conclude then that the pyrrole nitrogen as well as N-1 of imidazole and N-1 of pyrazole are incapable of significant coordination to the acids **4** and **5.**

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(13) Sufficient Co(saloph) to give a 1×10^{-3} *M* solution would not dissolve in a 0.5 *M* solution of pyrazole in dichloromethane. However, upon exposure of this mixture to air, the cobalt complex readily dissolved.

(14) Considering Figure 3 of ref 1 and assuming a pmr probe temperature of 35° we calculate that a 1 *M* imidazole solution was utilized to obtain the data point at 0% Ni(saloph). At this imidazole concentration Ni(saloph) is insufficiently soluble to produce $[\text{Ni(saloph)}]/[\text{imidazole}] > 0.02$. Consequently in order to span the range of complex concentrations reported some dilution was required. Further speculation about the details of the procedure that led to dilution is unwarranted.

(15) Another indication that insufficient precautions were taken by the authors of ref 1 in handling Co(saloph) solutions occurs in their claim that Co(saloph) produces changes in the pmr spectrum of pyrazole similar to the changes produced by Ni(saloph). However, we have observed that Co(saloph) will not dissolve sufficiently in a dichloromethane–pyrazole solution (in the absence of oxygen) to allow such data to be obtained.[13] Exposure of such mixtures to air causes the dissolution of the cobalt complex but this produces no alterations of the pmr spectrum of the base.

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Structure and Reactivity of Cobalt–Nitrosyl Complexes in Y-Type Zeolites

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Abstract: Nitric oxide was allowed to react with Co^{2+} ions, as well as with cobalt ammine complexes, in cobalt-exchanged zeolites. The formation of $[\text{Co}^{\text{II}}(\text{NO})_2]^{2+}$, $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$, and $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}]^{2+}$ was suggested from the infrared and adsorption data. In the latter complex n is probably equal to 5. Infrared absorption bands for N–O stretching vibrations were observed at 1830 and 1910 cm^{-1} for $[\text{Co}^{\text{II}}(\text{NO})_2]^{2+}$, at 1800 and 1880 cm^{-1} for $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$, and at 1710 cm^{-1} for the $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}]^{2+}$ complex. A bond angle of 123° was estimated for the ON–Co–NO moiety in the dinitrosyl complexes from ir band intensities. When $[\text{Co}(\text{NO})_2]^{2+}$ was thermally decomposed at 200°, N_2, N_2O, and NO were observed as products. The intramolecular reaction of $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}]^{2+}$, as well as its intermolecular reaction with gas phase NO, was followed at 23°, and the two reactions were found to yield N_2, N_2O, and $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}_2]^{2+}$. Isotope labeling proved that N_2 was produced by the reaction of the NO^- ligand with NH_3, whereas N_2O and NO_2 were produced by the disproportionation reaction of the NO^- ligand with two nitric oxide molecules. It was observed that the disproportionation reaction was favored by a greater pressure of NO over the zeolite. The production of NO_2 and its coordination with cobalt prevented further formation of the nitrosyl complex and hence destroyed the catalytic activity.

The importance of transition metal complexes in the dissociation and reduction of nitric oxide has led to a number of investigations of nitrosyl complexes in heterogeneous systems.[1-6] Nitric oxide has also been used as a probe to study the state of supported transition metal ions. It has been shown that Cu^+, Ag^+, Ni^{2+}, Fe^{2+}, and Cr^{2+} ions form complexes with NO in zeolites.[1-5] In each of these cases the data may be interpreted in terms of either covalent bonding or the donation of an electron from the nitric oxide to the metal ion. The latter tends to strengthen the N–O bond and to increase the stability of the nitric oxide molecule.

Several nitrosyl complexes of rhodium and cobalt are known to have a high electron density on the NO ligand.[7] Such complexes are characterized by an M–N–O bond angle of about 120° and an N–O stretching frequency in the range 1550–1700 cm^{-1}. By way of contrast the cationic nitrosyl ligands of these same metal ions are nearly linear with an N–O stretching frequency near 1850 cm^{-1}. The decrease in the N–O bond strength for the anionic nitrosyl is associated with the additional electron in a π^* antibonding orbital.

Recent studies on the bent Co–NO moiety have demonstrated that the nitrosyl ligand is subject to reaction with either molecular oxygen or free nitric oxide.[8,9] Alternately, the nitrosyl ligand may react with another ligand such as ammonia, forming N_2 and H_2O. One would, of course, hope to observe the direct dissociation of the nitric oxide; however, this has yet to be accomplished at moderate temperatures. The reactions of interest may be summarized as

$$\text{L}_n\text{M–NO} + 2\text{NO} \longrightarrow \text{L}_n\text{M–NO}_2 + \text{N}_2\text{O} \qquad (1)$$

$$\text{L}_n\text{M–NO} \longrightarrow \text{L}_{n-1}\text{M} + \text{N}_2 + \text{H}_2\text{O} \qquad (2)$$

$$\text{L}_n\text{M–NO} + \text{NO} \longrightarrow \text{L}_n\text{M} + \text{N}_2 + \text{O}_2 \qquad (3)$$

where in this study $\text{M} = \text{Co}^{2+}$ and $\text{L} = \text{NH}_3$.