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Infrared and Reactivity Studies of Dinitrogen Complexes of Ruthenium and Osmium in Y-Type Zeolites

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Stability, reactivity, and infrared studies were carried out on the dinitrogen complexes $[Ru(NH_3)_5N_2]^{2+}$, $[Ru(H_2NCH_2CH_2NH_2)_2(H_2O)N_2]^{2+}$, and $[Os(NH_3)_5N_2]^{2+}$ formed in or following cation exchange into Na–Y zeolite. Isolation in the zeolite framework provided some change in the comparative stabilities of the complexes, and samples were maintained for reasonable periods in the absence of moisture and oxygen. Mass spectral analysis of the gaseous products following ^{15}N substitution of the dinitrogen ligand in $[Ru(NH_3)_5N_2]^{2+}$–Y has shown that the apparent ammonia production originated from the decomposition and/or reduction of hydrazine impurities.

Introduction

In almost a decade since Allen and Senoff[1] reported the first stable complex containing molecular nitrogen, a large number of such complexes[2] have been synthesized and investigated without realizing the ideal of providing a synthetic model, which emulates the low-temperature fixation of nitrogen and its subsequent reduction to ammonia[3] exhibited by nitrogenase. Although dinitrogen complexes have been produced using a variety of reagents, the Allen and Senoff ion[1,4] $[Ru(NH_3)_5N_2]^{2+}$ is the most widely studied[5-13] and the main subject of this investigation. Allen and Senoff originally reported that the dinitrogen ligand could be partially reduced to ammonia by treatment with sodium borohydride, but it has subsequently been shown,[14] and confirmed by Allen,[15] that the formation of ammonia may be attributed to hydrazine impurities in the complex. No stable dinitrogen complex has yet been isolated which provides an effective template for the reduction of N_2 to NH_3; however partial hydrogenation has been observed.[16]

This research was undertaken to study the effect that the zeolite "solvent" would have on the stability and reactivity of various dinitrogen complexes. Noting the fact that zeolite cages have approximately the same dimensions as the cavities in enzymes, it was hoped that the zeolite might provide a unique environment for the catalytic reduction of molecular nitrogen. We also explored the possibility of coexchanging another metal ion (e.g., Fe^{2+}), which could then act as an electron-transfer agent and thus parallel the situation believed to exist in nitrogenase.

Experimental Section

Na–Y zeolite was provided by the Linde Co. (lot no. 13544-76). $RuCl_3 \cdot xH_2O$ (~40%) and OsO_4 were purchased from Engelhard Industries. Nitric oxide was obtained from Matheson Gas Co. and was repeatedly distilled at the melting point of acetone (−95°) until free from N_2O and NO_2. Molecular nitrogen enriched with 95% ^{15}N was purchased from Bio-Rad Laboratories. All other chemicals used were reagent grade. $[Ru(NH_3)_6]Cl_2$,[17] $[Ru(NH_3)_5NO]Cl_3H_2O$,[18] $[Ru(NH_3)_5N_2]Br_2$,[4] $[Ru(H_2NCH_2CH_2NH_2)_3]Br_2$,[19] $[Ru(H_2NCH_2CH_2NH_2)_3]I_3$,[20] $(NH_4)_2OsCl_6$,[21] and $[Os(NH_3)_5N_2]Cl_2$[22] were prepared by standard literature methods.

The $[Ru(NH_3)_5N_2]^{2+}$ cation was exchanged into the zeolite in deoxygenated water under nitrogen. No attempt was made to control the pH of the exchange solution. The sample was filtered and subsequently degassed at room temperature in an effort to remove part of the zeolitic water.

Cation exchange of the other complexes into the zeolite were performed in the following manner. Na–Y zeolite (2.5 g) was added to water (50 ml), and the pH of the solution was adjusted to 4.5 by the addition of dilute hydrochloric acid (2 *M*). An appropriate amount of the complex (0.2–0.3 g) was then added and the exchange allowed to proceed for 3 hr. The zeolite was then filtered (the colorless filtrate indicating that complete exchange had taken place), washed thoroughly with water and then with ethanol, and dried over silica gel in a vacuum desiccator. The following exchange levels (based on the percent of sodium ions displaced) were determined: $[Ru(NH_3)_5N_2]^{2+}$, 16.0%; $[Ru(NH_3)_5NO]^{3+}$, 21.0%; $[Ru(H_2NCH_2CH_2NH_2)_3]^{2+}$, 14.5%; $[Ru(H_2NCH_2CH_2NH_2)_3]^{3+}$, 19.0%; $[Os(NH_3)_5N_2]^{2+}$, 14.5%.

Zeolite wafers suitable for use in an infrared cell, which has been described previously,[23] were prepared by spreading the zeolite powder (100 mg) between polished stainless steel plates (~20 cm² in area) and compressing at 15 tons/in.². Wafers of density 4–6 mg/cm² were cut to size and inserted in a glass frame. Infrared spectra were recorded on a Beckman IR 12 or IR 9 grating spectrophotometer. Slit widths were set to maintain a minimum resolution of 3 cm⁻¹. Except for a small window between 800 and 900 cm⁻¹, zeolites are infrared opaque below 1200 cm⁻¹; hence, spectra are displayed on a linear transmission scale for the region 1200–2200 cm⁻¹. The recorded frequencies are accurate to ±3 cm⁻¹ below 2000 cm⁻¹ and ±5 cm⁻¹ above.

Mass spectra of gaseous products were determined using a CEC-214 residual gas analyzer.

Preparation of $[Ru(NH_3)_5N_2]^{2+}$–Y from $[Ru(NH_3)_5NO]^{3+}$–Y. (a) A wafer of $[Ru(NH_3)_5NO]^{3+}$–Y in the ir cell was degassed for 12 hr at room temperature (all subsequent degassings described were at room temperature unless otherwise stated). Aqueous hydrazine (65–95%, previously freeze-pumped to remove N_2 and O_2, 7.5 Torr) was allowed to equilibrate with the zeolite for 2 min. The color of the sample changed rapidly to a bright yellow-orange and then faded. The sample was then degassed for 45 min.

(b) $[Ru(NH_3)_5NO]^{3+}$–Y zeolite (0.5 g) was placed in water (2 ml), and following the addition of a few drops of aqueous hydrazine, the zeolite turned yellow-orange. This color faded over a period of 15–20 min. The zeolite was then filtered, washed with water and then with ethanol, and vacuum-dried over silica gel.

Addition of NO and N_2H_4 to $[Ru(H_2NCH_2CH_2NH_2)_3]^{2+ \text{ or } 3+}$–Y. A wafer of $[Ru(en)_3]^{2+ \text{ or } 3+}$–Y was degassed for 1 hr, and upon addition of NO gas (30 Torr) the sample changed to a deeper yellow color. After equilibrating for 5 min the sample was degassed for 15 min. Aqueous hydrazine (7.5 Torr) was subsequently added for 3 min (the wafer developed a brown color) and then the sample was degassed for 45 min.

Determination of NH_3 Formation and Its Origin. A gas mixture containing H_2 (200 Torr) and N_2 (200 Torr) was admitted to the infrared cell which contained approximately 0.2 g of exchanged zeolite. The mixture was allowed to react at 23° for periods up to 15 days.

For a period of 1 hr the residual gases and those molecules which desorbed from the zeolite were pumped through a trap maintained at liquid nitrogen temperature. The trap was then allowed to warm and the products were transferred to a receiver containing a measured amount of dilute sulfuric acid and Bromothymol Blue indicator. A purple color developed in the solution, and this indicated excess NH_3. This was back-titrated with acid to determine the exact amount of NH_3. Samples that were thermally decomposed were heated to 400°, in 50° increments of 15 min each, and the products were trapped and analyzed as described above.

Samples for mass spectral analysis[24] were trapped in the same way and then transferred to a freshly prepared solution of NaOBr, which had been freeze-pumped four times to remove N_2 and O_2. The mass spectrum of the oxidation products from the trapped material was then recorded. A blank of $^{30}N_2$ (10 Torr) and $^{14}NH_3$ (10 Torr) put

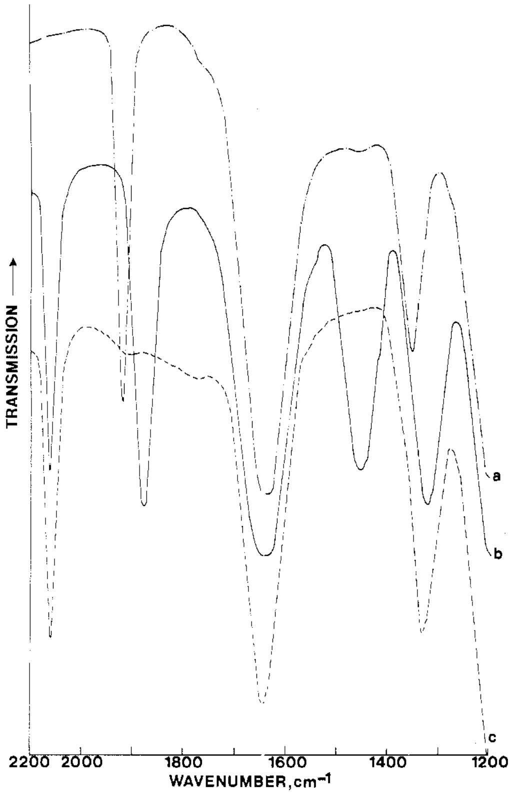

Figure 1. Infrared spectrum of $[Ru(NH_3)_5NO]^{3+}$-Y zeolite (a) after degassing overnight, (b) after the addition of N_2H_4 (7.5 Torr), and (c) after degassing for 45 min.

through the same procedure yielded only $^{28}N_2$, confirming a successful separation technique.

Results and Discussion

Ruthenium–Pentaamine Complexes. Formation. Bottomley and Crawford[12] have shown that the complex $[Ru(NH_3)_5NO]^{3+}$ could react with hydrazine to yield the analogous dinitrogen complex. This nitrosyl complex was therefore exchanged into the zeolite and an infrared wafer was degassed overnight to remove more than 90% of the zeolitic water. The infrared spectrum of this complex (Figure 1a) also showed three significant bands assigned as follows: 1927 cm^{-1} (very strong, $\nu(NO)$), 1640 cm^{-1} (very strong, broad, $\delta(NH_3$, degen)), and 1365 cm^{-1} (medium, $\delta(NH_3$, sym)). Aqueous hydrazine has a vapor pressure of $\sim$7.5 Torr at room temperature, which is sufficient for reaction with the $[Ru(NH_3)_5NO]^{3+}$–Y zeolite wafer.

After the addition of hydrazine, either from the vapor phase or via the aqueous slurry, the ir spectrum as depicted in Figure 1b was recorded. The strong absorption at 2132 cm^{-1} was assigned to $\nu(NN)$, the very strong, broad absorption at 1640 cm^{-1} to $\delta(NH_3$, degen), in conjunction with absorbed water, which has a bending vibration in this region,[25] and the medium absorption at 1335 cm^{-1} to $\delta(NH_3$, sym), somewhat higher than in the free ion. The band at 1885 cm^{-1} might be attributed to nitric oxide, liberated in the reaction, which is weakly adsorbed in the interior of the zeolite. (Gas-phase NO absorbs at 1876 cm^{-1}, but experiments with NO adsorbed on Y-type zeolites[26] have shown only disproportionation products and no NO species.) This assignment, however, would be in contrast to the reaction believed to occur in aqueous solution. It was shown[12d] that the reaction of $[Ru(NH_3)_5{}^{15}NO]^{3+}$ with $^{28}N_2H_4$ gave $[Ru(NH_3)_5{}^{29}N_2]^{2+}$, indicating that the nitrogen of the nitrosyl ligand remained bound to the ruthenium. The band at 1885 cm^{-1} may arise from a species such as $[Ru(NH_3)_5N(=O)NHNH_2]^{2+}$, which has been proposed as an intermediate[12d] in the above process. The band at 1460 cm^{-1} was ascribed to NH_4^+ from the decomposition of hydrazine, but this band and the one at 1885 cm^{-1} disappeared during the degassing procedure (Figure 1c). Uytterhoeven[25] found that it was necessary to degas an NH_4^+–Y zeolite to 500° to remove all the NH_4^+; hence the NH_4^+ produced in the reaction with hydrazine must not be so strongly coordinated to the zeolite, since it can be quickly degassed at room temperature.

In some preparations, a band at 1560 cm^{-1} appeared as a shoulder on the broad absorption centered on 1640 cm^{-1}. This is assigned to the presence of some impurity containing NH_2^-. The presence of the amide ligand in an intermediate in the formation of $[Ru(NH_3)_5N_2]^{2+}$ has frequently been postulated.[11b,c,12c]

Direct exchange of the $[Ru(NH_3)_5N_2]^{2+}$ complex into the zeolite resulted in a complex which was relatively unstable. After the zeolite has been isolated and an infrared wafer prepared, the zeolite turned faintly purple. The ir spectrum was the same as that shown in Figure 1c; however, after one scan the 2132-cm^{-1} band was no longer observed and a strong absorption appeared at 1460 cm^{-1}. Furthermore, the zeolite turned purple. $[Ru(NH_3)_5OH]^{2+}$ is reported to be wine red or purple,[27] and the band at 1460 cm^{-1} indicates the formation of NH_4^+ ions. The decrease in stability may be attributed to the greater pH of the zeolite in the direct-exchange procedure. Two possible reactions may have taken place

$$[Ru^{II}(NH_3)_5N_2]^{2+}\text{-Y} + H_2O \rightarrow [Ru^{III}(NH_3)_4(H_2O)OH]^{2+}\text{-Y} + N_2 + NH_4^+ + \text{other products} \quad (1)$$

$$[Ru^{II}(NH_3)_5N_2]^{2+}\text{-Y} + H_2O \rightarrow [Ru^{III}(NH_3)_5OH]^{2+}\text{-Y} + NH_4^+ + \text{other products} \quad (2)$$

the second of which implies the reduction of coordinated nitrogen. This idea has been proposed before by Sigwart and Spence,[28] who studied the photochemical oxidation of $[Ru(NH_3)_5N_2]^{2+}$ and found that following exposure to uv light from a mercury lamp, $[Ru(NH_3)_5OH]^{2+}$ was formed in neutral solution. Although certain Ru(II) species[29] can reduce H_2O, no H_2 was observed in the mass spectral analysis of the gases above the solution. They speculated that the reduction product might be NH_3 and suggested analyzing the products from a similar reaction with $[Ru(NH_3)_5{}^{30}N_2]^{2+}$, but to date no further publication has appeared.

Little information about the strength of the N–N bond can be inferred from the absolute value of the nitrogen stretching frequency, since it varies in $[Ru(NH_3)_5N_2]^{2+}$ complexes from almost 2100 to 2170 cm^{-1}, depending upon the anion. This has been interpreted[30] in terms of the amount of charge transfer caused by the other ligands, the counterion, and the solvent. In this case, the zeolite can be considered to be both the counterion and the solvent.

Stability. In the absence of moisture and oxidizing agents, the $[Ru(NH_3)_5N_2]^{2+}$–Y zeolite is stable for several months, and even when exposed to the atmosphere, it is stable for up to 2 weeks. Several samples still retained 50–60% of their nitrogen (as estimated from the intensity of $\nu(NN)$) following 12–24 hr of degassing at room temperature. (Decomposition involving irreversible loss of the N_2 occurs on heating the zeolite sample above 35–40°). Other samples, particularly those prepared external to the ir cell, could have all the N_2 removed in 3–4 hr of degassing and up to 90% of it restored by exposing the wafer to N_2 (200 Torr). In this manner it was possible to prepare the labeled complex $[Ru(NH_3)_5{}^{30}N_2]^{2+}$–Y. This is characterized by a nitrogen stretching frequency at 2067 cm^{-1} and this decrease in frequency is in excellent agreement with the theoretical 68 cm^{-1}.

The $^{30}N_2$ complex was also prepared by direct exchange between $[Ru(NH_3)_5{}^{28}N_2]^{2+}$–Y and $^{30}N_2$ (150 Torr), but the exchange was slow and significant loss of total N_2 was observed. After 10–15 days of equilibration, the extent of

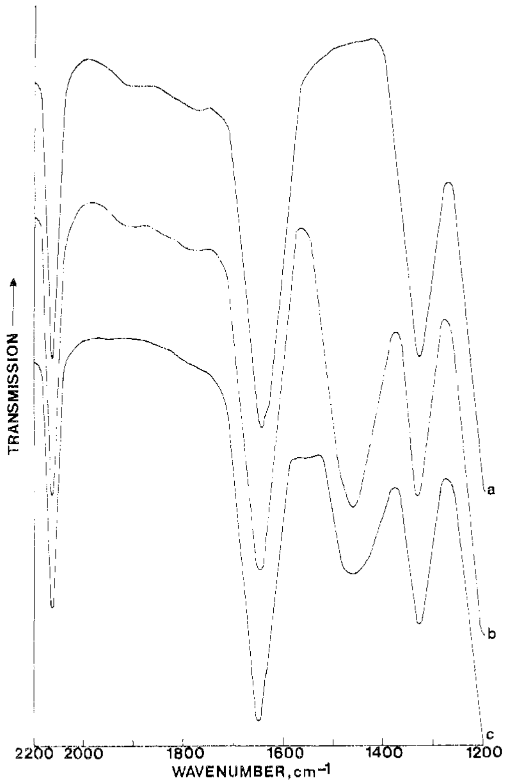

Figure 2. Infrared spectrum of $[Ru(NH_3)_5N_2]^{2+}$-Y zeolite (a) after degassing, (b) at 24 hr after the addition of N_2 (200 Torr) and H_2 (200 Torr), and (c) after degassing for 1 hr.

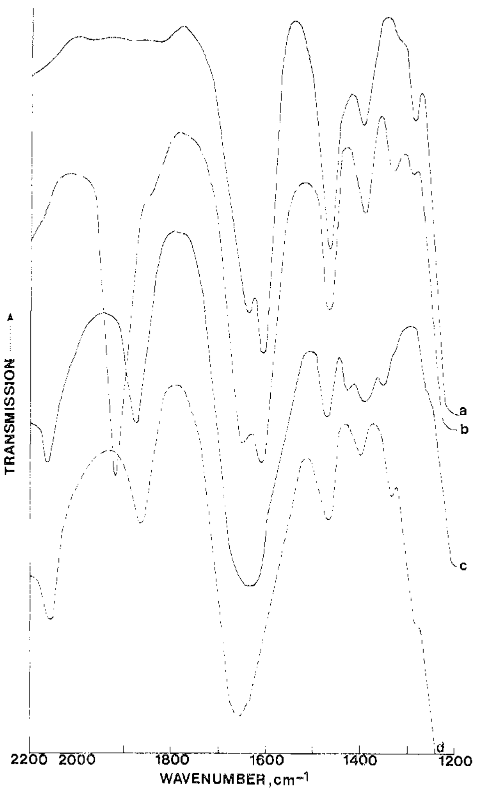

Figure 3. Infrared spectrum of $[Ru(en)_3]^{2+}$-Y zeolite (a) after degassing for 1 hr, (b) after the addition of NO (50 Torr) and degassing for 15 min, (c) after the addition of N_2H_4 (7.5 Torr), and (d) after degassing for 45 min.

exchange was 70–90%, as estimated from the relative intensities of the respective nitrogen stretching frequencies. The rate of exchange of $[Ru(NH_3)_5{}^{29}N_2]^{2+}$ with $^{28}N_2$ has been reported[11a] to be very slow and was thought to involve substitution by water to give $[Ru(NH_3)_5H_2O]^{2+}$ followed by reentry by $^{28}N_2$. The same aquo complex is considered to be present in the above two substitution processes, and the rapidity with which $^{28}N_2$ or $^{30}N_2$ is taken up by samples which have had N_2 removed would indicate that the rate-determining step in the exchange reaction is substitution by H_2O.

NH_3 Production. It was observed in most samples that, on standing, the broad absorption band at 1460 cm^{-1} slowly increased in intensity over a period of time with a concomitant diminution in the intensity of the nitrogen stretching frequency. The NH_4^+ production could be enhanced by the addition of both H_2 (200 Torr) and N_2 (200 Torr); the latter also served to maintain the nitrogen stretching frequency at its full intensity. Measurable portions of NH_3 could be pumped off at room temperature causing a reduction in the intensity of the absorption at 1460 cm^{-1}, sometimes removing it completely. This cycle (depicted in Figure 2) could be repeated up to five times (when the NH_4^+ could no longer be pumped away, unless the zeolite wafer was reactivated by brief exposure to hydrazine vapor) yielding approximately 10 mol of NH_3/mol of Ru complex. Subsequent thermal decomposition of the complex produced a further 4.8–5.4 mol/mol of complex, attributable to the ammine ligands. A sample in which a small amount of Fe^{2+} had been coexchanged produced identical results. Blank tests on a zeolite sample that had not had the ruthenium nitrosyl complex exchanged into it, but otherwise pretreated in exactly the same manner, produced none of the above observations. Thus, it appeared that the coordinated dinitrogen was being catalytically reduced to NH_3 under extremely mild conditions.

Mass spectral analysis of the ammonia produced by the system ($[Ru(NH_3)_5{}^{30}N_2]^{2+}$–Y)–$^{30}N_2$–$H_2$ yielded oxidation products $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$ in the ratios 360:2:1, thus refuting the supposition that catalytic reduction was taking place. Subsequently, a sample of $[Ru(NH_3)_5N_2]^{2+}$-Y zeolite which was prepared external to the ir cell, thoroughly washed and degassed, yielded a total of only 5.2 mol of NH_3/mol of complex.

It now appears that there are two possible sources of the ammonia which was in excess of the ammine ligands. As described before, the same complex in aqueous solution had been mistakenly interpreted as having its N_2 partially reduced, but this was later shown to be due to the decomposition of $[Ru(NH_3)_5N_2H_4]X_2$ or similar complexes.[6,14a] Such a complex could be present in the zeolite, but the opacity of the zeolite to infrared radiation below 1200 cm^{-1} precluded the observation of bands around 950 and 1130 cm^{-1} ascribed to such complexes. It was also noted that in the most active samples, the zeolite had a pink color following treatment with hydrazine, which could be due to polynuclear ammine and/or hydrazine complexes.[4,12a,31] The second possibility is that the pink coloration is due to $[Ru(NH_3)_5OH]^{2+}$, and the NH_3 stems from residual hydrazine that was trapped in the zeolite and not removed by degassing at room temperature. Its decomposition and/or reduction could have been catalyzed by the ruthenium in the zeolite.

Ethylenediamine Complexes. $[Ru(en)_3]^{2+}$ and $[Ru(en)_3]^{3+}$ were independently exchanged into Na–Y zeolite. Following degassing for 1 hr, the samples were treated with NO gas (50 Torr) for 5 min and then degassed for 15 min. The ir spectrum (Figure 3b) showed a strong band at 1915 cm^{-1} in addition to those observed in the parent ethylenediamine complexes, i.e., 1610 (strong), 1465 (medium), 1390 (weak), and 1290 cm^{-1} (weak). This spectrum is undoubtedly due to a nitrosyl complex such as $[Ru(en)_2(H_2O)NO]^{3+}$. The $[Ru(en)_3]^{3+}$ ion has been reported[32] to react with NO in an acidic medium to give an uncharacterized nitrosyl product (ν(NO) 1905 cm^{-1})

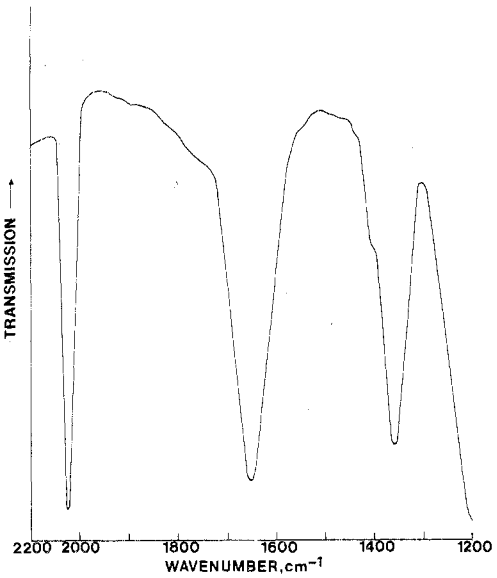

Figure 4. Infrared spectrum of $[Os(NH_3)_5N_2]^{2+}$-Y zeolite.

and in base to give the previously reported[33] $[Ru(en)_2(H_2O)N_2]^{2+}$ complex. The nitrogen stretching frequency in the latter complex has been reported at 2120 and 2130 cm^{-1}. Use of ^{15}NO has given a product with ν(NN) at 2067 cm^{-1}, which is said to provide evidence that the dinitrogen ligand ($^{29}N_2$) is derived from both the NO and an ethylenediamine ligand via scission of a C–N bond. However, due to the uncertainty in the reported position of ν(NN) in the unlabeled complex and the significant decrease in frequency (53–63 cm^{-1}) for the band, the product may involve $^{30}N_2$.

When the $Ru(en)_2(H_2O)NO]^{3+}$–Y zeolite was treated with N_2H_4, the band at 1885 cm^{-1} was again observed (Figure 3c), and although this band did not completely disappear during degassing, the dinitrogen complex $[Ru(en)_2(H_2O)N_2]^{2+}$–Y is thought to be formed. This is characterized by a weak band at 2120 cm^{-1}. Since the complex appeared to be relatively unstable, no further investigations were undertaken.

Osmium–Pentaammine–Dinitrogen Complex. Formation. $[Os(NH_3)_5N_2]Cl_2$ was prepared and exchanged into the zeolite as described in the Experimental Section. The infrared spectrum (Figure 4) of the colorless zeolite was recorded, and the complex is characterized by absorption bands at 2050 cm^{-1} (very strong, ν(NN)), 1640 cm^{-1} (very strong, broad, combination of H_2O and $\delta(NH_3$, degen)), and 1360 cm^{-1} (strong, $\delta(NH_3$, sym)). In the complex before exchange, no trace was seen of the higher frequency bands[34] due to $[Os(NH_3)_4(N_2)_2]^{2+}$, and after exchange only the one band was observed, with no evidence of the solid-state splitting[22,35] exhibited by crystalline samples. The frequency of ν(NN) has been reported from about 2010 to 2060 cm^{-1} in the various osmium salts.

Stability and Reactivity. In the absence of moisture and particularly oxidizing agents, the $[Os(NH_3)_5N_2]^{2+}$–Y zeolite was stable for several weeks, but when exposed to the atmosphere it decomposed in 24–48 hr. The decreased stability upon exposure to the atmosphere compared to the behavior of the ruthenium analog is in direct contrast to the relative stabilities of the two complexes in other media. Degassing the zeolite at room temperature, for up to 24 hr, had no appreciable effect on the intensity of the nitrogen stretching frequency, but there was some reduction in amplitude and a sharpening of the 1640-cm^{-1} absorption band, which is indicative of a decrease in the water content of the zeolite. Irreversible loss of the N_2 can be brought about by heating to 45–50°. This greater thermal stability of the osmium complex compared to the ruthenium complex parallels the behavior in the crystalline state. A mixture of N_2 (200 Torr) and H_2 (200 Torr) was added to a degassed wafer to $[Os(NH_3)_5N_2]^{2+}$–Y zeolite, but after 24 hr no significant production of NH_4^+ was noted.

Conclusion

The synthesis or exchange of dinitrogen complexes within the zeolite framework has been demonstrated. Of the three dinitrogen complexes prepared in the Y-type zeolite only the $[Ru(NH_3)_5N_2]^{2+}$ complex showed any tendency to form NH_3 and essentially all of it could be traced back to impurities. Hydrogenation of the N_2 ligand could not be conclusively established nor could any incorporation into a catalytic cycle be achieved. It was possible, however, to exchange the N_2 ligand with gas-phase nitrogen, thus demonstrating the accessibility of such complexes to gaseous reactants, within the zeolite.

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Registry No. $[Ru(NH_3)_5NO]^{3+}$, 37874-79-6; $[Ru(NH_3)_5N_2]^{2+}$, 19504-40-6; $[Ru(en)_3]^{2+}$, 21393-86-2; $[Os(NH_3)_5N_2]^{2+}$, 22840-90-0; $[Ru(en)_3]^{3+}$, 21393-87-3; $[Ru(en)_2(H_2O)NO]^{3+}$, 54714-05-5.

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