lines are more intense than the absorption lines; Figure 1c is a time-average of 65 passes whereas Figure 1d required only 16 passes. Third, the lines in the emission spectrum are broader than the lines in the absorption spectrum. This difference in line width cannot be due to a difference in field homogeneity since the line width of the benzene line before irradiation is approximately equal to the line width during irradiation. A triplet-energy-transfer process could be responsible for this broadening.[2,13] Fourth, the nmr emission spectrum is not simply an inversion of the nmr absorption spectrum. Some of the lines in the absorption spectrum are either missing or very weak in the emission spectrum, indicating that all of the protons are not affected equally.

As mentioned earlier,[4] during irradiation anthraquinone slowly decomposes. This can be seen by comparison of Figure 1c with Figure 1e which is the spectrum obtained after the sample had been irradiated for 30 min. Both 1c and 1e were time-averaged over 65 passes. Clearly, the lines in 1c are more intense than the lines in 1e, indicating some of the anthraquinone had decomposed. Whether the mechanism for this decomposition involves a free radical or triplet anthraquinone or both species cannot be decided on the basis of the present data.

In conclusion, the results reported in this communication demonstrate that nmr spectroscopy can be used to study optically excited molecules. Because of the amount of information which can be obtained by means of nmr, this technique is a potentially powerful tool for studying excited molecules.

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[13] This possibility is currently being studied using pyrene which exhibits appreciably larger broadening than anthraquinone under these conditions.

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A Diazotization Leading to the Formation of a Dinitrogen Complex

Sir:

The formation of nitrogen complexes by the decomposition of hydrazine,[1] azide ion,[2] and NH_3,[3] by the capture of N_2 from acyl azides,[4] and by the reaction of elementary N_2 has been described.[5-8] We here report the formation of a nitrogen-containing complex by the reaction of nitrous acid with coordinated ammonia.

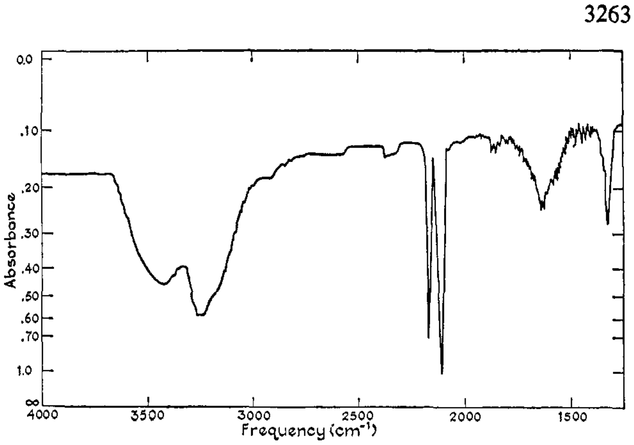

Figure 1. The infrared spectrum of $Os(NH_3)_4(N_2)_2Cl_2$ in the high-frequency range. When the wavelength scale is corrected by calibration, the two bands characteristic of N_2 appear at 2175 and 2120 cm^{-1}.

This reaction is remarkable in its own right, proceeding as it does with great rapidity at room temperature, and is significant also in that it produces the ion $(NH_3)_4Os(N_2)_2^{2+}$, which, to our knowledge, is the first complex containing two coordinated nitrogen molecules for each metal atom to have been characterized.

For the preparation, 1×10^{-3} mole each of $NaNO_2$ and $(NH_3)_5OsN_2Cl_2$, the latter prepared as described by Allen and Stevens,[9,10] was dissolved in 35 ml of water, and the solution was deaerated by using a stream of argon. After *ca.* 30 min, 4 ml of 1 *M* HCl was added slowly, while the reaction solution was stirred vigorously. Up to this point, no reaction was apparent, but when acid was added the solution at once became more deeply yellow and gas was evolved. A sample removed 1 min after the addition of HCl and appropriately diluted showed that the peak characteristic of $(NH_3)_5OsN_2^{2+}$ (208 mμ, log ϵ 4.4) had disappeared and that a new peak was present at 221 mμ (log ϵ 4.3). From the spectrophotometric measurements, a yield of *ca.* 34% was determined. Upon the addition of solid alkali halide, an osmium-containing solid is formed. The crude material contains a substantial (*ca.* 25%) admixture of a nitrosyl-containing species. On repeated recrystallization, the intensity of the peak characteristic of the nitrosyl-containing species is greatly diminished, but the characteristic structure (see below) of the nitrogen-containing component is unaltered.

Chloride, bromide, and iodide salts of the refined product were prepared. The infrared spectrum of the chloride salt is shown in Figure 1. It should be noted that the relative intensities of the peaks at 2120 and 2175 cm^{-1} are the same within experimental error for the three preparations, and are, moreover, constant for successive croppings of crystals from a single solution. *Anal.* Calcd for $(NH_3)_4Os(N_2)_2Cl_2$: H, 3.14; N, 29.09; Cl, 18.40. Found: H, 3.22; N, 28.98 Cl, 18.38. Calcd for $(NH_3)_4Os(N_2)_2Br_2$: H, 2.55; N, 23.63; Br, 33.70. Found: H, 2.53; N, 23.43; Br, 33.95. More convincing support of our formulation than the elementary composition, which does not discriminate between ammonia and $N\equiv N$, is the gas chro-

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[10] The preparation of a nitrogen-containing complex of osmium by heating osmium compound with hydrazine has also been reported by Yu. G. Borod'ko, V. S. Burkeev, G. I. Kozub, M. L. Khidekel, and A. E. Shilov, *Zh. Strukt. Khim.*, **8**, 542 (1967).

matographic analysis performed after addition of Ce(IV), which in duplicates showed 1.82 ± 0.11 and 1.77 ± 0.07 moles of N_2 for each osmium. In blank experiments using $(NH_3)_5OsN_2^{2+}$, it was shown that 95% of the theoretical yield of N_2 is obtained and that excess Ce(IV) does not produce N_2 from coordinated NH_3.

The analytical results constitute a strong case for the formulation of the cation as $(NH_3)_4Os(N_2)_2^{2+}$. Splitting of the carbon monoxide stretching mode is observed when these are located in the *cis* position.[11-13] By analogy we are inclined to ascribe the splitting observed in the N≡N stretch to the same kind of effect, and on this basis suggest that the N_2 molecules in the new complex $Os(NH_3)_4(N_2)_2^{2+}$ are located *cis* to each other.

The ion $Os(NH_3)_4(N_2)_2^{2+}$ which we have prepared is probably the trace component reported by Borod'ko, *et al.*,[10] as present in the preparation[9] of $Os(NH_3)_5N_2^{2+}$ by the hydrazine method. In one preparation of $Os(NH_3)_5N_2I_2$ we also observed two weak lines at somewhat higher frequency than 2035 cm^{-1}, which is characteristic of the mononitrogen complex. Borod'ko, *et al.*, suggest three states of combination on the basis of the infrared spectra of the unpurified material; in view of our work, two suffice since the *cis*-dinitrogen complex shows two lines in the infrared spectra.[14]

The thermal stability of the dinitrogen complex is much less than that of $Os(NH_3)_5N_2^{2+}$. On heating a solution of the former complex over *ca.* 50°, the solution turns dark.

It is interesting that when $Ru(NH_3)_5N_2^{2+}$ is treated with nitrous acid under conditions similar to those described, the reaction does not follow the course as outlined for $Os(NH_3)_5N_2^{2+}$. Nitrogen is released essentially quantitatively, and a nitrosyl complex is the major ruthenium-containing product. This kind of reaction may explain why Jordan, *et al.*,[15] failed in their attempt to prepare a nitrogen-containing complex by the reaction of a Ru(II) azide complex with nitrous acid.

The rapid diazotization of NH_3 in $Os(NH_3)_5N_2^{2+}$ is remarkable in itself. From the observation that the pentaammine is consumed completely within 1 min, we calculate a lower limit for the specific rate of reaction of HONO with H_3NOs^{II} to be 1 M^{-1} sec^{-1}, a value which can be compared with 2.8×10^{-4} M^{-1} sec^{-1} as reported[16] for HONO reacting with NH_4^+. The rapid diazotization of coordinated NH_3 is by no means a general phenomenon. Thus, when an excess of nitrous acid is added to $Ru(NH_3)_5N_2^{2+}$ and the mixture is left for an extended period of time, the amount of N_2 formed is not materially greater than that observed with an equivalent amount of nitrous acid. On this basis we estimate the specific rate for the reaction of HONO with NH_3 in $Ru(NH_3)_5NO^{3+}$ (this is, the major product of the N_2 elimination reaction) to be less than 2×10^{-3} M^{-1} sec^{-1}.

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On the Mechanism of Energy Transfer from n,π* Triplet State of Carbonyl Compounds to Simple Olefins

Sir:

Electronic energy transfer is a rapidly expanding subject of current interest.[1] The process involves the transfer of electronic excitation energy from a donor to an acceptor which leads to the electronic excitation of the acceptor. Energy transfer from a triplet donor to an acceptor occurs readily when the triplet energy level of the donor is higher than that of the acceptor.[2] The accepted mechanism for such transfer is that of a collisional interaction between the donor and the acceptor with a rate approaching that of the diffusion-controlled process.[3] Although energy transfer from the triplet states of carbonyl compounds to simple olefins has been noted in several isolated instances, the detailed mechanism of such processes has not been investigated.[4] *One specific interesting aspect of these transfers is that there may be insufficient energy in the triplet state of carbonyl compounds to be transferred into the planar triplet state of simple olefins.*

The lowest planar triplet energy level of ethylene was measured by Evans to be 82 kcal/mol (28,700 cm^{-1}), and he reported that alkyl substituents had little effect on the triplet energy levels of conjugated unsaturated compounds.[5] Substitutions of hydrogens by alkyl groups on ethylene may lower the triplet energy level, but the exact magnitude of this decrease is not known. The n,π* triplet energy levels of phenyl carbonyl compounds have been well characterized and range from 66 to 73 kcal/mol (24,000–25,800 cm^{-1}),[6] values substantially below that of ethylene. The triplet energy level of an olefin depends on the angle of twist around the axis connecting the two carbon atoms, and the minimum energy level is reached when the angle of twist is 90° from the planar configuration.[7] A distinct possibility exists that, after the energy transfer, the olefinic acceptor has a geometry different from its ground state, an apparent deviation from the Franck–Condon princi-

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