using a Portland Electronics conductivity bridge and an evacuable conductance cell which could be attached to the vacuum line for introduction of solvent by distillation. Esca measurements were made on an AEI E.S.-100 instrument modified so that air-sensitive samples could be introduced.

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Registry No. [$ReCl_2(N_2COPh)(PPh_3)_2$], 34347-22-3; [ReCO], 25259-88-5; [$(ReN_2)_2TiCl_4(CH_2Cl_2)_2$], 42934-19-0; [$ReN_2$], 25263-89-2; [$TiCl_3(thf)_3$], 18039-90-2; [$(ReN_2)_2TiCl_4(C_6H_6)_{1.5}$], 42934-20-3; [$(ReN_2)TiCl_4(thf)$], 42934-21-4; [$(ReN_2)(Ti_2Cl_6O)(Et_2O)$], 39455-32-8; [$(ReCO)_2TiCl_4$], 43070-52-6.

Notes

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Nitrogen-15-Labeled Complexes of [$Ru(NH_3)_5N_2$]Br_2

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Although the positions of the bands in the infrared spectrum of [$Ru(NH_3)_5N_2$]Br_2 have been reported in detail,[1] only brief references[2,3] have been made to the exact positions of some of the dinitrogen-labeled complexes. Several years ago,[4] we began to compile data on the dinitrogen-28 and -29 complexes. Only recently, we have developed an efficient method for preparing pure samples of the dinitrogen-29 complex.[5] In the course of our work, we also prepared the dinitrogen-30 sample for another investigator. Quinby and Feltham[6] recently published estimates for the dinitrogen bands in Ru-^{14}N-^{15}N and Ru-^{15}N-^{14}N based upon curve resolution of our earlier data. We now have a complete set of more accurate results. While their conclusions do not need to be altered, the actual positions of the bands are sufficiently shifted to warrant a further report. In addition, a complete description of the dinitrogen bands in the infrared spectrum of [$Ru(NH_3)_5N_2$]Br_2 (when N_2 is 28, 29, or 30) will be presented. We believe that such a compilation will prove useful for future investigators seeking to assess the exact origin of the transitions and pursuing the mechanistic details of other dinitrogen formation reactions

Experimental Section

[$Ru(NH_3)_5{}^{28}N_2$]Br_2 was prepared by any one of several synthetic procedures.[1,5,7,8] [$Ru(NH_3)_5{}^{29}N_2$]Br_2 was prepared by reaction of Cr^{2+} with $Ru(NH_3)_5N_2O^{2+}$ [4] with the N_2O labeled in either the endo or exo positions (^{15}N-N-O or N-^{15}N-O). Alternatively, the treatment of alkaline solutions of $Ru(NH_3)_6{}^{3+}$ with ^{15}NO also results in the formation of the $^{29}N_2$ complex.[5] [$Ru(NH_3)_5{}^{30}N_2$]Br_2 was prepared by Cr^{2+} reduction of [$Ru(NH_3)_5{}^{15}$N-^{15}N-O]$^{2+}$. The latter was formed in solution upon the treatment of $Ru(NH_3)_5OH_2{}^{2+}$ with ^{15}N-^{15}N-O.[8] All compounds were checked for their purity using the λ_m at 221 nm, ϵ 1.8 × 10^4 M^{-1} cm^{-1}. Of the compounds described above, only the [$Ru(NH_3)_5{}^{30}N_2$]Br_2 displayed a significant impurity (and it was the [$Ru(NH_3)_5Br$]Br_2 complex (~17%)).

Ir spectra in the range 4000-250 cm^{-1} were recorded as Nujol mulls on KBr plates using a Perkin-Elmer 180 ir spectrometer. A few room-temperature spectra were recorded using KBr disks. The 2180-cm^{-1} region was calibrated using atmospheric CO_2 (2350 cm^{-1}). The 500-cm^{-1} region was calibrated using atmospheric water vapor.[9] Low-temperature spectra were obtained by mounting the KBr plates (~30 mg of Ru complex, 2 drops Nujol) against a copper cold finger filled with liquid nitrogen. This unit was placed inside a glass sleeve through which cold, dry nitrogen was purged. The flow of cold nitrogen over the faces of the KBr disks prevented the formation of significant amounts of ice on the faces of the disk. The glass sleeve was clamped into position in the sample beam and encased within a large plastic sheet taped to the instrument. Reproducible low-temperature spectra were obtained within 3 min after pouring liquid nitrogen into the copper cold finger.

Results and Discussion

The data in Table I summarize the dinitrogen frequencies for the four possible isomers obtained using ^{14}N and ^{15}N sources of nitrogen. The values for ^{14}N-^{15}N and ^{15}N-^{14}N frequencies are based upon equilibrated samples of ^{14}N-^{15}N *or* ^{15}N-^{14}N (prepared *via* the appropriately labeled samples of the nitrous oxide complexes). In addition, the value for the ^{14}N-^{15}N frequency has been confirmed by the direct reaction of ^{15}NO with the coordinated ammine.[5] While the definition of the bands varied as a function of the preparation, the apparent increase in intensity and sharpening of the bands at low temperature did provide an opportunity to assign the bands in Table I. On lowering the temperature, all the bands for δ_{Ru-N_2} were shifted ~4 cm^{-1} toward higher energy.

When one allows for the affect of counterion[10] on the exact positions of dinitrogen frequencies in the ir spectrum, our values are found to be internally consistent with previously published values in the 2100-cm^{-1} region.[2,3] Shifts on the order of $\Delta\nu$ ~70 cm^{-1} for $Ru^{28}N_2$ *vs.* Ru-$^{30}N_2$ have been reported in the past.[11-13] However, one report[2] claims that Ru-^{14}N-^{15}N absorbs at 2098 cm^{-1} (as the I^- salt), while Ru-^{15}N-^{14}N absorbs at 2094 cm^{-1}. Within the resolution afforded by our instruments in this spectral region, we did not observe any splitting of equilibrated mixtures of the Br^- salts for Ru-^{14}N-^{15}N or Ru-^{15}N-^{14}N in Nujol mulls. In addition, KBr disks of our Ru-$^{29}N_2$ samples demonstrated no discernible

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[1] A. D. Allen, F. Bottomley, R. D. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 89, 5595 (1967).

[2] Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Russ. J. Phys. Chem.*, 44, 349 (1970).

[3] J. Chatt, A. B. Nikolsky, R. L. Richards, J. R. Sanders, J. E. Fergusson, and J. L. Love, *J. Chem. Soc. A*, 1479 (1970).

[4] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 92, 2560 (1970).

[5] S. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 94, 686 (1972).

[6] M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, 11, 2468 (1972).

[7] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *Inorg. Syn.*, 12, 5 (1970).

[8] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 93, 6476 (1971).

[9] L. R. Blaine, E. Plyler, and W. Benedict, *J. Res. Nat. Bur. Stand., Sect A*, 66, 223 (1962).

[10] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Chem. Soc. A*, 3168 (1971).

[11] A. K. Shilova, A. E. Shilov, and Z. N. Vastroknutova, *Kinet. Katal.*, 9, 924 (1968).

[12] Yu. G. Borod'ko and V. S. Lyutov, *Kinet. Katal.*, 12, 1 (1971).

[13] J. Chatt, E. Fergusson, R. Richards, and J. L. Love, *Chem. Commun.*, 1522 (1968).

Table I. Positions of the Dinitrogen Infrared Bands in $[Ru(NH_3)_5N_2]Br_2$[a]

	δ_{Ru-N_2} (±1 cm^{-1})			ν_{N_2} (±5 cm^{-1})	
Ru-N-N	Obsd (low temp)	Obsd (room temp)	Calcd[b] (room temp)	Obsd (room temp)	Calcd[b] (room temp)
$Ru-^{14}N-^{14}N$	511	508	507.7	2105	2106.7
$Ru-^{14}N-^{15}N$	505	501	502.7	2070	2071.4
$Ru-^{15}N-^{14}N$	499	496	495.9	2070	2071.4
$Ru-^{15}N-^{15}N$	495	492	490.7	2040	2035.5

[a] Nujol mulls. [b] The force constants obtained from the calculation are $k_{NN} = 18.298 \pm 0.061$ mdyn/A and $H_\delta = 0.788 \pm 0.008$ mdyn/A.

splitting of the band at 2075 ± 0.5 cm^{-1}. The maximum separation of possible, unresolved bands under this envelope at 2075 cm^{-1} is ±3 cm^{-1}.

Our observations have recently been confirmed by Quinby and Feltham.[6] In addition, they reported only a small splitting of ν_{N_2} in only one salt (SbF_6^-) of *trans*-$[RuCl(^{15}N-^{14}N)(das)_2]^+$ (2094 and 2089 cm^{-1}). In all other salts only a single ν_{N_2} frequency was observed, and in no case was a splitting in ν_{RuN_2} at 446.5 cm^{-1} observed. However there was a splitting of the degenerate bending frequency δ_{RuN_2} near 490 cm^{-1} for almost every salt. They concluded that shifts for $\nu_{Ru^{14}N^{15}N}$ and $\nu_{Ru^{15}N^{14}N}$ could only be ~1 cm^{-1}; however, in order to explain the shifts of ~9 cm^{-1} which we observed for the band at 508 cm^{-1} in $[Ru(NH_3)_5N_2]Br_2$, they suggested that the band at 508 cm^{-1}, previously assigned[1,2] as ν_{RuN_2}, be reassigned as δ_{RuN_2}. More importantly, they concluded that the assignment of the 508-cm^{-1} band to ν_{RuN_2} would require an observed shift of ~9 cm^{-1} for this band and should demand a corresponding shift of ~35 cm^{-1} for ν_{N_2}. No bands of significant intensity were observed for $[Ru(NH_3)_5N_2]Br_2$ which could be assigned to ν_{RuN_2}. In addition, they reported that they were unable to see any splitting of the 2070-cm^{-1} $[Ru(NH_3)_5N_2]Br_2$ bands (to better than 5 cm^{-1}).

No bands of significant intensity were observed for the Br^- salt that could be attributed to ν_{RuN_2}. (The I^- salt has been reported[2] to display a band at 516 cm^{-1}.) Examination of the infrared (at a readout of 1 cm^{-1}/division) spectrum to 400 cm^{-1} indicated no change in any of the other band positions (at 466, 448, 440, and 430 cm^{-1}) upon ^{15}N substitution. To confirm the assignments of the δ_{RuN_2} bands near 500 cm^{-1} and the ν_{N-N} bands in the 2100-cm^{-1} region, a simple normal-coordinate calculation was made (using the programs of Schachtschneider[14] as modified by Mann[15]) involving the linear triatomic system Ru-N-N. The bond distances were obtained from the work of Bottomley and Nyburg.[16] Since no data were available for ν_{Ru-N}, it was impossible to obtain a complete set (k_{N-N}, N-N stretch; k_{Ru-N}, Ru-N stretch; H_δ, Ru-N-N bend; $k_{Ru-N,N-N}$, the stretch-stretch interaction term) of force constants for this model. However, by performing a preliminary calculation, using as starting guesses the force constants obtained in the work of Feltham,[6] the assignment of the bands for the four isomers became readily apparent: three bands were predicted for the ν_{N-N} region, two for the ν_{Ru-N} region, and four for δ_{Ru-N-N}. The force constants k_{N-N} and H_δ were then allowed to refine, and the results obtained are displayed in Table I. It can be seen that regardless of the value of the bending force constant H_δ, the δ_{Ru-N_2} frequencies will always be in the following order: $Ru-^{14}N-^{14}N > Ru-^{14}N-^{15}N > Ru-^{15}N-^{14}N > Ru-^{15}N-^{15}N$. By using the central atom as a point of reference, one might have anticipated the bending mode for $Ru-^{15}N-^{14}N$ to be more like that for $Ru-^{14}N-^{14}N$ than that for $Ru-^{15}N-^{15}N$. Since this would have given rise to a set of frequencies different from those observed, this assumption is not correct. It is further seen that, to the extent to which the triatomic model is valid, only two bands will occur in the ν_{Ru-N} region (one for the two $Ru-^{14}N$ isomers and one for the two $Ru-^{15}N$ molecules) and three in the ν_{N-N} region, with coincident frequencies for the two $Ru-^{29}N_2$ ν_{NN} stretches. In order to validate this assignment, the value of the stretch-stretch interaction term $k_{Ru-N,N-N}$ was arbitrarily assigned inordinately large values. The resulting calculation yielded no further splitting of the bands.

In conclusion we have presented the complete description of the observed bending and stretching modes for the four isomers of $[Ru(NH_3)_5{}^{28,29,30}N_2]Br_2$. No splitting is observed for ν_{N_2} in the $^{29}N_2$ isomer, while a significant splitting is observed for δ_{Ru-N_2} in the same isomer. The latter is very useful in identifying[5,8,17] the products of dinitrogen formation reactions. The relative energies of the observed bands for δ_{Ru-N_2} can be correctly assigned by considering the isotopic shifts expected for a stretching mode of Ru-N. Using the data presented, the conclusions of Feltham regarding the reassignment of ν_{Ru-N_2} and δ_{Ru-N_2} have been confirmed.

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Registry No. $[Ru(NH_3)_5-^{14}N-^{14}N]Br_2$, 15246-25-0; $[Ru(NH_3)_5-^{14}N-^{15}N]Br_2$, 42402-14-2; $[Ru(NH_3)_5-^{15}N-^{14}N]Br_2$, 42402-15-3; $[Ru(NH_3)_5-^{15}N-^{15}N]Br_2$, 42402-16-4.

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(14) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules," Vol. V and VI, Shell Development Co., Emeryville, Calif., 1964.

(15) L. H. Ngai and R. H. Mann, *J. Mol. Spectrosc.*, 38, 322 (1971).

(16) F. Bottomley and S. Nyburg, *Chem. Commun.*, 897 (1966).

(17) S. D. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 95, 7625 (1973).

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Reactions of Some Lithium Alkyltrimethylsilylamides with Dichlorophenylborane and Chlorodimethylaminophenylborane[1]

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Reactions of alkali metal derivatives of bis(trimethylsilyl)-amine with haloboranes (eq 1) have been used for the prepara-

$$(Me_3Si)_2NM + XB< \rightarrow (Me_3Si)_2NB< + MX \qquad (1)$$

$$M = Li, Na; X = F, Cl$$

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(1) Taken from the Ph.D. dissertation of R. H. Neilson, Duke University, Durham, N. C., 1973.