static distortions. In the present case an X-ray analysis has shown that a static distortion from C_{3v} symmetry is operative and this alone may account for the observed spectral properties.

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The Infrared Spectra of Ruthenium Derivatives of Nitrogen, Nitric Oxide, and Carbon Monoxide. Experimental Evidence Regarding dπ–pπ Bonding

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The infrared spectra of the compounds *trans*-$[RuClNO(das)_2]Z_2$ (Z^- is Cl^-, Br^-, I^-, PF_6^-, $^1/_2[PtCl_6]^{2-}$, and das is *o*-phenylenebis(dimethylarsine)), *trans*-$[RuINO(das)_2]Z_2$, *trans*-$[RuClN_2(das)_2]Z$, and *trans*-$[RuClCO(das)_2]Z$ have been investigated in the spectral region between 250 and 4000 cm^{-1}. The infrared spectra of the nitrosyl and dinitrogen complexes isotopically substituted with ^{15}N were prepared, and their spectra were utilized for identifying the fundamental vibrational modes of the RuXY moieties. Force constants for the RuXY groups were calculated using a three-body model and a valence force field. On the basis of these results, the band of medium intensity near 490 cm^{-1} in the dinitrogen complex, assigned by other workers to the Ru–N stretching vibration, has been reassigned to the RuNN bending vibration. This three-body model was also successfully applied to the analysis of the infrared spectrum of $[Ru(NH_3)_5N_2]Br_2$. The changes observed in the X–Y force constants upon coordination to ruthenium (Δk_{XY}) have a direct relationship to the ruthenium–ligand force constant, k_{RuX}. These observations are consistent with dπ–pπ bonding between ruthenium and the diatomic ligand.

Introduction

The infrared spectra of coordinated diatomic molecules are important both for elucidating the structures of these complexes and for obtaining information about the bonding between the metal and the ligand.[1–5] The numerous studies of carbon monoxide complexes are well known, and several careful investigations of the infrared spectra of transition metal nitrosyls have been carried out, including normal-coordinate analyses of these data.[6–10] However, only two papers have thus far appeared in which the infrared spectra of the coordinated dinitrogen ligand have been investigated in any detail.[11,12] Many of these earlier studies have been complicated by the presence of other similar ligands and ligand vibrations which may be strongly coupled to the motions of the diatomic molecule under consideration. In addition, there appear to be no comparative infrared studies of isostructural and isoelectronic complexes of the type L_5M–XY (where XY is CO, N_2, and NO and L is not).

In our previous work, the isostructural series of complexes *trans*-$[RuClN_2(das)_2]^+$, *trans*-$[RuClNO(das)_2]^{2+}$, *trans*-$[RuClCO(das)_2]^+$, and some of their ^{15}N-substitution products was prepared.[13] The infrared spectra of these compounds have now been obtained and are discussed below.

Experimental Section

Materials and Analyses.—Ruthenium and trichloronitrosylruthenium were obtained from Englehard Industries, Inc. The isotopically substituted compounds were prepared from ^{15}NO (95%) which was purchased from Bio-Rad Laboratories. Solvents and other common chemicals were obtained from Baker Chemical Co. and Mallinckrodt Chemical Works. The chemicals were of reagent grade and were not further purified unless noted. The elemental analyses were obtained from Huffman Laboratories, Wheatridge, Colo.; Chemalytics, Tempe, Ariz.; and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and are summarized in Table I. In the presence of ruthenium, the carbon analyses have been observed to be as much as 1% high.

Physical Measurements.—The nmr spectra were obtained using a Varian Model HA-100 or T-60 spectrometer and $CDCl_3$ or D_2O as solvent. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer which had been calibrated using polystyrene for the 350–3000-cm^{-1} region and the water band at 202.8 cm^{-1} for the 200–350-cm^{-1} region. A Du Pont curve resolver, Model 310, was used to separate overlapping peaks. The isotopic content of the nitrogen-containing complexes was established by mass spectrometry using a Perkin-Elmer Hitachi Model RMU-6e double-focusing mass spectrometer.

Preparation of the Complexes.—The unsubstituted complexes were prepared as described previously.[13] The ^{15}NO complexes were prepared from $Ru(^{15}NO)Cl_3$. Ruthenium trichloride as obtained from the manufacturers was found to be unreactive with NO. Consequently, $RuCl_3$ was prepared *in situ* and allowed to react with ^{15}NO to form $Ru(^{15}NO)Cl_3$. Ruthenium powder (1.00 g) was stirred for 12 hr together with 250 ml of 5% aqueous NaOCl. The solution was evaporated to 100 ml and cooled in an ice bath and 50 ml of concentrated hydrochloric acid was added followed by 50 ml of methanol. The volume of the solution was reduced by boiling, and after filtering, the filtrate was reduced to dryness in a 500-ml round-bottom flask. The solid material was dissolved in 100 ml of distilled water and 5 ml of concentrated hydrochloric acid. A total of 10.5 mmol

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TABLE I

ELEMENTAL ANALYSIS (%)[a]

	C		H		N		O		X		
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		Calcd	Found
$[RuCl(NO)(das)_2]Cl_2$(anhyd)	29.7	30.1	4.3	4.4	1.7	1.7			(Cl)	13.1	12.2
$[RuCl(NO)(das)_2]Cl_2 \cdot H_2O$[d]	29.0	29.4	4.1	4.0			3.9	3.5	(Cl)	12.8	12.7
		23.35[b]		4.05[b]				4.1[b]			12.75[b]
$[RuCl(NO)(das)_2]Cl_2 \cdot {}^3/_2H_2O$	28.7	29.6	4.2	4.1	1.67	1.63	4.8	4.9	(Cl)	12.7	12.9
$[RuCl(^{15}NO)(das)_2]Cl_2 \cdot {}^3/_2H_2O$					1.79	1.74	4.8	5.0			
$[RuCl(NO)(das)_2]Br_2$									(Cl)	4.1	4.1
									(Br)	18.5	18.4
$[RuCl(NO)(das)_2]I_2 \cdot {}^1/_2H_2O$									(Cl)	3.5	3.2
									(I)	25.0	25.3
$[RuCl(NO)(das)_2](PF_6)_2$	23.4	23.6	3.2	3.4	1.35	1.45			(Cl)	3.4	3.7
									(F)	22.2	21.3
$[RuCl(NO)(das)_2]PtCl_6 \cdot 2H_2O$	20.4	20.3	3.1	3.4	1.2	1.0	4.0	4.5	(Cl)	20.0	19.8
$[RuI(NO)(das)_2]Br_2$[d]									(I)	13.2	13.7
									(Br)	16.7	16.5
$[RuI(NO)(das)_2]I_2$	22.1	22.6	3.0	3.1	1.3	1.1	1.5	1.9	(I)	35.1	35.4
$[RuCl(N_2)(das)_2]Cl$					3.6	3.2			(Cl)	9.2	11.9
$[RuCl(N_2)(das)_2]PF_6$[c]	27.0	27.3	3.7	3.8	3.2	3.3	3.5	4.0	(Cl)	4.0	3.8
									(F)	12.9	13.3
$[RuCl(N_2)(das)_2]SbF_6$	24.7	25.5	3.4	3.4	2.9	2.6			(Cl)	3.6	3.8

[a] All analysis by Huffman Laboratories except where noted. [b] Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] Analysis in ref 13. [d] Because more sample was needed for two analyses, two samples were prepared whose infrared and nmr spectra were identical.

of ^{15}NO was added from a vacuum line, and the mixture was magnetically stirred for 11 days. After removal of the remaining ^{15}NO, the solution was purified using either of the methods described below.

Method 1.—A column containing Dowex 50W-X8 cation-exchange resin was prepared. The solution from the reaction described above was passed down the column to remove the large amounts of NaCl present in this solution. The colored fraction was collected and evaporated to dryness. The infrared spectrum of this material had a strong band at 1860 cm^{-1} ($\nu_{^{15}NO}$) and a very weak band at 1895 cm^{-1} ($\nu_{^{14}NO}$). This same procedure was also used to prepare $Ru(^{14}NO)Cl_3$ ($\nu_{^{14}NO} \simeq 1900$ cm^{-1}).

Method 2.—The solution containing NaCl and $Ru(^{15}NO)Cl_3$ was evaporated to dryness and extracted with 200 ml of ethyl acetate. After filtration and removal of the ethyl acetate by evaporation, the residue was redissolved in 50 ml of water, passed through a column packed with Dowex 50, and evaporated to dryness. The red solid thus obtained had an infrared spectrum which was identical with that obtained using method 1, except for bands due to traces of acetic acid. The yields from either method were quantitative (based on ^{15}NO).

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dichloride.—This compound was found to exist in three forms. The material identified as form I was prepared as described previously.[13] Form II was prepared from form I by dissolving 0.037 g of form I in 5 ml of distilled water (or from the reaction of *trans*-$[RuNO_2Cl(das)_2]$ with 5 ml of water and 5 ml of concentrated hydrochloric acid) followed by 12 hr of stirring and final evaporation to dryness. The elemental analysis (Table I) and infrared spectrum allowed identification of this compound as *trans*-$[RuClNO(das)_2]Cl_2 \cdot H_2O$.

A third form, form III, was also obtained by dissolving 0.02 g of form I in 5 ml of concentrated hydrochloric acid and 5 ml of methanol. After stirring for 12 hr, the solution was evaporated to dryness and finally dried for 12 hr at 100° over P_4O_{10}. The elemental analysis of this material allowed its identification as *trans*-$[RuClNO(das)_2]Cl_2 \cdot 1.5H_2O$.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dibromide.—A saturated methanolic solution of LiBr (5 ml) was added to a solution of *trans*-$[RuClNO(das)_2]Cl_2$ (0.05 g) in methanol (5 ml). The dark yellow crystals which formed were collected, washed with methanol, 1:1 methanol–ether (10 ml), and finally diethyl ether. The compound was dried for 12 hr over P_4O_{10}.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Diiodide.—A total of 0.05 g of *trans*-$[RuClNO(das)_2]Cl_2$ was dissolved in methanol (5 ml), and a solution of NaI (0.014 g) in 5 ml of methanol was added. The orange precipitate which formed immediately was removed by filtration, washed with cold methanol, and dried for 12 hr over P_4O_{10}.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dihexafluoroantimonate.—The compound, prepared using the method described above, was dried over P_4O_{10} for 12 hr.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Hexachloroplatinate.—A solution containing 0.02 g of *trans*-$[RuClNO(das)_2]Cl_2$ in distilled water (5 ml) was added to a saturated aqueous solution of K_2PtCl_6 (6 ml). The yellow precipitate which formed was removed by filtration, washed with distilled water (50 ml), and dried at 100° for 12 hr over P_4O_{10}.

Iodonitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Diiodide.—A total of 0.041 g of *trans*-$[RuClNO(das)_2]Cl_2$ and 0.5 g of NaI in 5 ml of methanol was heated at reflux for 3 days. After cooling, the solution was filtered, and the solid product was washed with ice-cold water and dried overnight at 110° over P_4O_{10}. During the drying process, the color of this solid changed from dark orange to dark brown.

Iodonitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dibromide.—Solid LiBr was added to a solution of *trans*-$[RuINO(das)_2]I_2$ (0.06 g) in 50 ml of methanol until an orange precipitate began to form. The solid was collected, washed with methanol, and dried at 100° for 3 hr.

Chlorodinitrogenbis[*o*-phenylenebis(dimethylarsine)]ruthenium Chloride.—A solution (5 ml) containing 0.085 g of *trans*-$[RuClN_2(das)_2][BPh_4]$ and 1:3 hydrochloric acid–acetone was stirred for 12 hr. The solution was evaporated to dryness and washed with benzene until the washings were colorless. The white solid which remained was recrystallized from CH_2Cl_2. After drying over P_4O_{10} at 100°, the elemental analyses and the nmr spectrum allowed identification of the compound as *trans*-$[RuClN_2(das)_2]Cl$.

Chlorocarbonylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Chloride.—This compound was prepared from *trans*-$[RuClCO(das)_2][BPh_4]$ by a procedure analogous to that used for preparation of the dinitrogen complex. An analytical sample was obtained by recrystallization from water.

Calculations.—Force constants for RuNO, RuCO, and RuNN in *trans*-$[RuZ(XY)(das)_2]^{n+}$ were calculated using the three-body model and a valence force field as described by Herzberg.[14] Isotopic shifts of the fundamental frequencies for Ru–NO (^{14}NO and ^{15}NO) and Ru–N_2 ($-^{14}N-^{14}N$, $-^{15}N-^{14}N$, and $-^{14}N-^{15}N$) were calculated and compared with the experimental results. Although treatment of the Ru–X–Y moiety separately from the rest of the molecule is not theoretically justified, it has been shown by Miki[6] that this approximation is valid for the six-coordinate ruthenium complexes $[L_5RuNO]^{2-}$ when L^- is Cl^-, Br^-, or I^-. In addition, the agreement obtained between experimental and calculated results using this model shows that Miki's approximation is also justified for the present cases.

The RuNO, RuCO, and RuNN groups have been assumed to

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be linear by analogy with known compounds of this type. The bond distances were taken from the neutron diffraction studies of $Na_2[Ru(NO_2)_4(OH)(NO)] \cdot 2H_2O$ of Simonsen and Mueller,[15] while the RuNN bond distances were obtained from the X-ray studies of $[Ru(N_3)(N_2)(en)_2]PF_6$ by Davis and Ibers.[16] The RuCO bond distances were obtained from $Ru(CO)_4I_2$.[17] These data are summarized in Table II. Errors of as much as 10° in the bond angle and 0.1 Å in the bond lengths have effects on the calculated force constants and frequencies which are less than or equal to the estimated uncertainties in the experimental data (±1 cm^{-1}).

TABLE II

RUTHENIUM NITROSYL, DINITROGEN, AND CARBONYL BOND DISTANCES AND ANGLES

Compd	—Distance, Å— Ru–X	X–Y	RuXY angle, deg	Ref
$Na_2[Ru(NO_2)_4(OH)NO)] \cdot 2H_2O$	1.748	1.127	179.98	15
$[Ru(N_3)(N_2)(en)_2]^+$	1.894	1.106	179.3	16
$[Ru(CO)_4I_2]$ for CO trans to I	2.02	1.06	171	17

The calculated force constants k_1 (primarily the Ru–X vibration), k_2 (primarily the X–Y vibration), and k_δ (the Ru–X–Y bending vibrations) are listed in Table III. The frequencies calculated from these force constants and the values of the calculated isotopic shifts are compared with the experimentally observed frequencies in Table IV. The agreement between the experimental and calculated results is within experimental error.

Results and Discussion

A. Ruthenium Nitrosyl Complexes.—The compound $Ru(^{15}NO)Cl_3$ served as the starting material for all of the ^{15}N-substituted compounds reported in this paper. The isotopic purity of this compound was determined by curve resolution and integration of the ^{14}NO and ^{15}NO bands present in the infrared spectrum of this material. Using this method of analysis, the ^{14}N content of $RuNOCl_3$ was found to be 7%. The ^{15}NO supplied by Bio-Rad contained 5% ^{14}NO, and the discrepancy between these two figures (5 *vs.* 7%) can be taken as the error inherent in this type of analysis.

To ensure that any differences observed between the infrared spectra of the ^{14}N and ^{15}N complexes are due to isotopic effects, $Ru(^{14}NO)Cl_3$ was prepared using procedures identical with those used for the preparation of $Ru(^{15}NO)Cl_3$. The complexes of *o*-phenylenebis(dimethylarsine) were prepared using these samples of $Ru(^{15}NO)Cl_3$, $Ru(^{14}NO)Cl_3$, and commercial $RuNOCl_3$. No differences were noted between the complexes prepared from $Ru(^{14}NO)Cl_3$ and commercial $RuNOCl_3$. Consequently, all spectral differences between $Ru(^{15}NO)Cl_3$ and $Ru(^{14}NO)Cl_3$ complexes are attributed to the effects of isotopic substitution.

Three different forms of *trans*-$[RuClNO(das)_2]Cl_2$ were initially identified by small but easily observable differences in the 1900- and 600-cm^{-1} regions of the infrared spectrum. An examination of the nmr spectra of these different forms dissolved in $CDCl_3$ and D_2O proved that the trans geometry was maintained for all three forms, while the presence of ν_{Ru-Cl} near 330 cm^{-1} in all three forms showed that no substitution in the coordination sphere had occurred. Elemental analyses of all three forms showed that they differ only by the amount of water present in the samples.

4000–650-cm^{-1} Region.—To facilitate the identification of all the ruthenium–nitrosyl frequencies, a variety of salts were prepared in which both the coordinated chloride and the uncoordinated chloride were substituted by other anions. The complete infrared spectra of these compounds including *trans*-$[RuClNO(das)_2]Cl_2$ (forms I–III) and *trans*-$[RuINO(das)_2]I_2$ as well as *trans*-$[RuCl_2(das)_2]$ are summarized in Table V. The infrared absorption bands of the ligand *o*-phenylenebis(dimethylarsine) have been assigned by Green, *et al.*, and Deacon and Green.[18]

The bands near 3000 cm^{-1} correspond to C–H vibrational frequencies of the *o*-phenylenebis(dimethylarsine), ligand, while O–H stretching vibrations were observed between 3200 and 3500 cm^{-1} for forms II and III of *trans*-$[RuClNO(das)_2]Cl_2$, *trans*-$[RuClNO(das)_2]I_2$, and *trans*-$[RuClNO(das)_2][PtCl_6]$. The number, position, and relative intensity of all of the bands between 650 and 1600 cm^{-1} were essentially identical for all of the compounds listed in Table V.

650–250-cm^{-1} Region.—There are six bands due to *o*-phenylenebis(dimethylarsine) found in this region of the infrared spectrum (Table VI and ref 18). The four bands of *o*-phenylenebis(dimethylarsine) between 500 and 250 cm^{-1} are well separated and were identified following Green's assignments.[18] The Ru–Cl vibration is also found in this region. A band of medium intensity at 330 cm^{-1} in *trans*-$[RuClNO(das)_2]Cl_2$ was identified as ν_{RuCl} by its failure to shift upon ^{15}N substitution and its disappearance upon substitution of chloride by iodide in the coordination sphere. Lewis[19] has identified Ru–Cl vibrations in other complexes between 310 and 340 cm^{-1}.

The infrared spectra of these compounds between 500 and 600 cm^{-1} are more complicated. Comparison with other *o*-phenylenebis(dimethylarsine) complexes requires the presence of two bands near 600 cm^{-1}. The work of Green[18] indicated that, unlike the other *o*-phenylenebis(dimethylarsine) bands, the positions of the two bands near 600 cm^{-1} are sensitive to changes in the coordination sphere of the metal and to changes in lattice structure. Consequently, the identification of the Ru–NO frequencies required isotopic substitution with ^{15}N. A maximum of three bands and a minimum of two bands in the 500–600-cm^{-1} region undergo shifts with ^{15}N substitution. In those cases wherein three bands shift with ^{15}N substitution, two of these frequency shifts are identical within experimental error (Table IV) and are greater than the other observed frequency shift.

In *trans*-$[RuINO(das)_2]I_2$, all five bands (two from *o*-phenylenebis(dimethylarsine) and three from Ru–N–O) are observed between 550 and 650 cm^{-1} (Figure 1). The positions of these bands were established by curve fitting. Four of these bands (621.5, 597, 588.5, and 565.5 cm^{-1}) are of medium intensity, while the shoulder at 570.0 cm^{-1} is considerably weaker than the other four bands. Substitution of ^{15}N in this complex results in the spectrum shown in Figure 2. There are still four bands of medium intensity, two of which are unshifted from the ^{14}N derivative (622.0 and 597

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TABLE III

FORCE CONSTANTS CALCULATED FOR THE RuNO, RuN_2, AND RuCO COMPLEXES[a]

Compd	k_1	$k(^{14}N)$ $k(^{15}N)$	k_2	$k(^{14}N)$ $k(^{15}N)$	$k_{\delta 1}$	$k(^{14}N)$ $k(^{15}N)$	$k_{\delta 2}$	$k(^{14}N)$ $k(^{15}N)$
$[RuCl(NO)(das)_2]Cl_2$ (I)	5.45	5.44 5.46	13.84	13.84 13.85	0.991	0.992 0.990		
$[RuCl(NO)(das)_2]Cl_2 \cdot H_2O$ (II)					1.002	1.002 1.001	0.974	0.973 0.975
$[RuCl(NO)(das)_2]^3/_2H_2O$ (III)	5.83	5.82 5.84	13.80	13.82 13.78	1.002	1.000 1.003	0.972	0.972 0.973
$[RuCl(NO)(das)_2]Br_2$					0.994	0.995 0.994		
$[RuCl(NO)(das)_2]I_2$					0.996	0.995 0.996	0.983	0.983 0.983
$[RuCl(NO)(das)_2](PF_6)_2$	5.68	5.65 5.70	13.78	13.85 13.71	0.992	0.992 0.992		
$[RuCl(NO)(das)_2]PtCl_6$	5.72	5.73 5.72	13.44	13.43 13.46	1.024	1.024 1.025	0.985	0.985 0.985
$[RuCl_3(NO)das]$	5.90	5.94 5.87	13.30	13.25 13.35	0.998	0.998 0.998	0.956	0.953 0.958
$[RuI(NO)(das)_2]Br_2$					0.986	0.986 0.987	0.916	0.918 0.915
$[RuI(NO)(das)_2]I_2$	4.92	4.91 4.93	13.85	13.84 13.86	0.982	0.982 0.983	0.906	0.906 0.906
$[RuCl(N_2)(das)_2]Cl$					0.693	0.693 0.693		
$[RuCl(N_2)(das)_2]PF_6$	2.78	2.79 2.78	17.98	17.98 17.97	0.694	0.693 0.694		
$[RuCl(N_2)(das)_2]SbF_6$	2.75	2.76 2.74	17.98	17.98 17.97	0.694	0.693 0.694		

[a] $k(^{14}N)$ and $k(^{15}N)$ refer to the value of each respective force constant calculated from the ^{14}N or ^{15}N data only; force constants are in mdyn/Å.

TABLE IV

OBSERVED AND CALCULATED ISOTOPIC SHIFTS (CM^{-1}) FOR Ru–N–O[a]

	ν_{NO} str			ν_{RuN} str			δ_{RuNO}					
							No. 1			No. 2		
Compd	^{14}N	^{15}N	$\Delta\nu_2$	^{14}N	^{15}N	$\Delta\nu_2$	^{14}N	^{15}N	$\Delta\nu_2$	^{14}N	^{15}N	$\Delta\nu_2$
$[RuCl(NO)(das)_2]Cl_2$ (I)	1881.5 (1883.0)	1843.0 (1842.0)	38.5 (41.0)	595.5[b] (595.4)	592.0[b] (590.7)	3.5 (4.7)	591.0 (591.3)	576.5 (576.5)	14.5 (14.7)	c		
$[RuCl(NO)(das)_2]Cl_2$ (II)	1899.0	1860.5	38.5	c	c	c	594.5 (594.6)	579.5 (579.7)	15.0 (14.9)	586.0 (586.2)	572.0 (571.6)	14.9 (14.6)
$[RuCl(NO)(das)_2]Cl_2$ (III)	1890.0 (1889.0)	1846.5 (1847.5)	43.5 (41.5)	613.0 (613.0)	609.0 (608.0)	4.0 (5.0)	594.0 (594.6)	580.0 (579.7)	14.0 (14.9)	585.5 (585.9)	571.5 (571.3)	14.0 (14.6)
$[RuCl(NO)(das)_2]Br_2$	1882.0	1842.5	39.5	c	c	c	592.5 (592.2)	577.0 (577.4)	15.5 (14.8)	c		
$[RuCl(NO)(das)_2]I_2$	1875.0	1837.0	38.0	c	c	c	592.5 (592.8)	578.0 (578.0)	14.5 (14.8)	589.0 (588.9)	574.5 (574.2)	14.5 (14.7)
$[RuCl(NO)(das)_2](PF_6)_2$	1877.0 d	1839.0	38.0	605.0[b] d	603.0[b]	2.0	591.5 (591.6)	577.0 (576.9)	14.5 (14.7)	c		
$[RuCl(NO)(das)_2]PtCl_6$	1865.0 (1864.0)	1826.0 (1824.0)	39.0 (40.0)	607.5 (607.0)	602.5 (602.0)	5.0 (5.0)	601.5 (601.1)	586.5 (586.1)	15.0 (15.0)	589.5 (589.5)	575.5 (574.8)	14.0 (14.7)
$[RuCl_3(NO)das]$	1858.0 (1860.0)	1821.5 (1820.0)	36.5 (40.0)	616.0 (616.0)	609.5 (612.0)	6.5 (4.0)	593.5 (593.4)	578.5 (578.6)	15.0 (14.8)	580.0 (580.8)	567.0 (566.3)	13.0 (14.5)
$[RuI(NO)(das)_2]Br_2$	1873.0	1832.0	41.0	c	c	c	590.0 (589.8)	575.5 (575.1)	14.5 (14.7)	569.0 (568.5)	554.5 (554.3)	14.5 (14.2)
$[RuI(NO)(das)_2]I_2$	1872.0 (1872.0)	1833.5 (1832.0)	38.5 (40.0)	570.0 (570.0)	565.0 (565.0)	5.0 (5.0)	588.5 (588.6)	574.5 (574.0)	14.0 (14.7)	565.5 (565.4)	551.5 (551.3)	14.0 (14.1)

[a] Calculated values in parentheses. [b] Very doubtful assignment. [c] Not observed. [d] Not calculated.

cm^{-1}), while the other two bands have shifted by 14.0 cm^{-1} each to 574.5 and 551.5 cm^{-1}. In addition, the weak shoulder at 570.0 cm^{-1} is now well resolved at 565.0 cm^{-1}. This weak band at 565.0 cm^{-1} in the ^{15}N complex is not due to residual ^{14}N since its relative intensity is too large compared with the ^{15}N band at 551.5 cm^{-1}. It should also be noted that there are no observable residual peaks due to the ^{14}N species at 588.5 and 570 cm^{-1}. The results for the other ruthenium nitrosyl complexes are similar to those obtained for the iodide salt.

Assignment of the Ru–NO Frequencies.—There have been several other vibrational analyses of the infrared spectra of transition metal nitrosyl complexes.[6–10] Khanna, Brown, and Jones found that the bending motions of Fe–NO occur at frequencies higher than the stretching frequency and assigned a band at 666 cm^{-1} in $Na_2Fe(CN)_5NO \cdot 2H_2O$ to δ_{FeNO} and the band at 656.8 cm^{-1} to the Fe–N stretch (ν_{FeN}).[10] The bending frequency was also observed to be considerably more intense than the stretching frequency in this iron complex.

Conflicting assignments have been made for ruthenium nitrosyl complexes.[9] Miki,[6] Gans,[7] and Sinitsyn[8] have previously studied ruthenium nitrosyl complexes including $[RuCl_5NO]^{2-}$, $[RuBr_5NO]^{2-}$, $[RuI_5NO]^{2-}$, and $[Ru(OH)(NO)(NH_3)_4]^{2+}$. Using ^{15}N substitution, Miki assigned the Ru–NO stretching vibrations to weak bands occurring at frequencies higher than the more intense bending vibrations in the series of compounds $[RuX_5NO]^{2-}$. Miki also investigated the normal-coordinate analysis of these compounds and

Table V

Observed Infrared Frequencies (cm^{-1}) for Ruthenium Nitrosyl Complexes[a]

Cl, Cl_2, (I)	Cl, Cl_2 (II)	Cl, Cl_2 (III)	Cl, Br_2	Cl, I_2	Cl, $(PF_6)_2$	Cl, $PtCl_6$	das, Cl_3	I, Br_2	I, I_2
b	3400 br	3400 br	*b*	3400 br	3020 vbr	3200–3600 br		3400 w, br	
	3040 m		3040 w	3030 w				3290 m	
b	2978 s	2970 s	2976 w	2978 mw	2940	2800–3000 br	2995	2980 m	2980 m
				2910 w					
	2900 m	2900 br	2920 w	2880 w				2900 w	2900 br
1881.5 vs	1899 s	1890 vs	1882 s	1875 vs	1873 br, s	1865 vs	1858 vs	1873 s	1872 vs
	1865 br, sh			1830 vw		1620 s		1620 w	
b	1640 m	1620 m	1630 m	1615 w	1563 m	1560 m		1560 w	1563 w
	1563 m	1565							
1453 m	1450 m	1450 m	1450 ms	1450 m	1455 s	1455 br, s	1450 w	1455 m	1453 m
1421 m	1420 br	1424 ms	1420 ms	1419 br, s	1421 s	1418 ms	1420 s, br	1420 s	1419 br, s
					1290 m	1370 ms			
	1275 mw		1285 w	1280 w, sh	1275 s	1280 w	1280 w		1268 s
1271 s	1261 m	1260 s	1270 ms	1265 ms	1260 sh, s	1261 s	1260 m	1270 ms	
1260 sh, s	1239 mw	1245 sh, s	1260 sh	1253 m		1245 sh			
1253		1230 w	1248			1163 w		1130 br	
1109 m	1102 ms	1108 m	1108 ms	1108 ms	1108 s	1107 s	1109 m	1109 m	1108 m
1096 mw		1090 sh	1034 w				1090 sh		
		1060 sh							
1035 m	1031 m	1035 m	1030 w	1034 w	1034 m	1030 m	1030 ms	1029 m	1030 w
935 s	939 s	933 s	930 s	924 s, sh	920 s	915 s	930 s	930 s	923 s
892 vs	888 vs	886 s	895, 885 s	883 vs	870 s	870 vs	890 vs	890 vs	888 vs
			870 sh	865 sh	830 vs	830 w	840 m, sh	830 w	830 w
840 w	835 w	830 w	830 s	830 w	765 s	760 s	765 s	765 s	758 s
768 m	777 s	769 s	761 s	756 s	705 w	720 w	700 w		
625.5	622	622.5	624.5	621.0	621.5 m	622.5	625 s	623.5	621.5 m
		613		605.0	605 w	607.5	616 w		
604.5 m	600	600	601	600.0	596	601.5	601 s	600.5	597 m
595.5 m	594.5 m	594	592.5	592.5	591.5	598	593.5	590	589 m
591 m	586	585.5		589.0		589.5	580 m	569.5	570 w
					556 vs				565.5 m
435.5 m	439 m	441.5 m	434 m	433 m	441 m	437.5 m	440 ms	433 m	432 m
377 m	375 m	377 m	376 ms	376 ms	378 m	374 s	372 m	375 m	373 s
363 m	363 m	362 m	361 ms	361 ms	363 s	362 s	365 s	363 m	361.5 s
330 mw		330 mw	330 m	332 w	330 w		335 s	*b*	
310 w				310 w	310 w		308 s	*b*	
275 w									276 w

[a] In the compounds $[RuZ(NO)(das)_2]^{2+}Z'_n$, the first anion used as the column heading is Z and the second is Z'_n. Key: strong, s; medium, m; weak, w; shoulder, sh; very, v; broad, br. [b] Not observed.

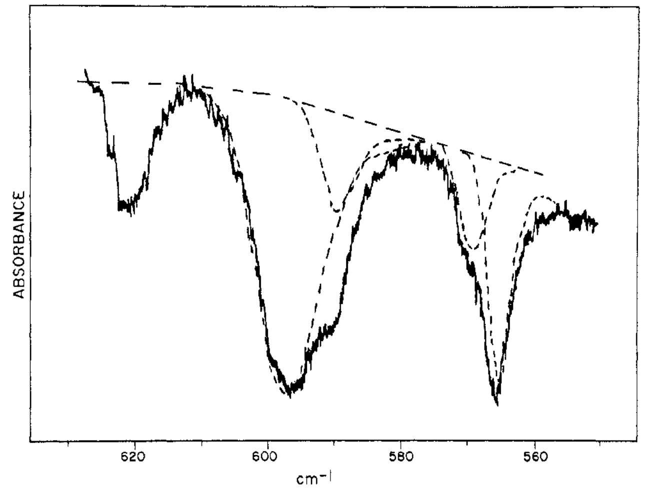

Figure 1.—The infrared spectrum of *trans*-$[RuI(^{14}NO)(das)_2]I_2$ between 540 and 630 cm^{-1}.

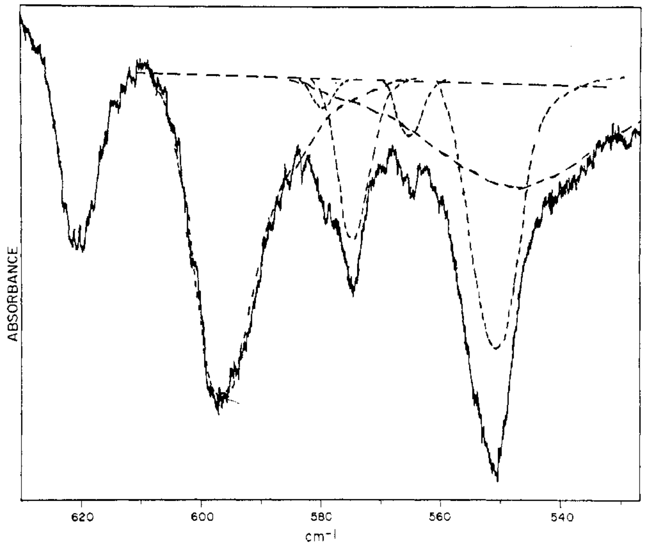

Figure 2.—The infrared spectrum of *trans*-$[RuI(^{15}NO)(das)_2]I_2$ from 540 to 630 cm^{-1}.

found that a three-body model gave agreement between the calculated values and experimental results which were indistinguishable from the values calculated using a more complicated eight-body model.

Substitution of ^{14}N by ^{15}N in *trans*-$[RuXNO(das)_2]^{2+}$ shifts a maximum of four infrared bands. In no case is there an observable shift of any of the absorption bands below 550 cm^{-1}. These observations show conclusively that none of the fundamental vibrational modes of the RuNO moiety occur below 500 cm^{-1}. The band in the 1800-cm^{-1} region shifts by approximately 40 cm^{-1}. From its position, intensity, and frequency shift, it is readily identified as ν_{NO}. For those compounds in which three bands in the 600-cm^{-1} region are affected by ^{15}N substitution, two of these three bands have identical shifts (14 cm^{-1}), are of

TABLE VI

OBSERVED FREQUENCIES OF REFERENCE COMPOUNDS[a]

Diarsine	*trans*-$RuCl_2(das)_2$	*cis*-$RuCl_2(das)_2$	$RuCl_3(NO)$	$KSbF_6$	KPF_6	$NaB(C_6H_5)_4$
3058 sh						3060 s
3040 m	3040 w	3030 w				3017 sh
2980 s	2980 w	2980 w				2990 s
2900 s	2900 w	2905				2970
						2900 w
1610 w			1895 s			1960 m
1587 vw						1900 m
						1840 m
1563 w	1545 w	1555				1785 w
1560 w						1578 s
1441 m	1439 m	1440				1480 s
						1450 sh
1421 s	1420 m	1418				1421 s
1412 sh	1405 sh					1395 w
1383 sh						1310 w
1261 m	1266 s	1268 s				1265 sh
1250 ms	1250 m	1245 m				1253 ms
1235 sh	1238 w					1185 m
1160 w						1150 s, br
1119 w				1100 br		1128 sh
1090 m	1094 s	1100 s				1110–1090 s, sh
1033 w						1070 m
1024 m						1031 ms
980 vw						990 w
941 w						929 vw
885 s	903 s	905 s				870 s
865 sh						853 s
846 s	856 vs	860 vs				
826 sh					823 s	
785 w						
744 s	768 s	762 s				750 vs
719 w						718 vs
692 w						
645 w						626 m
576 s	607 s	606 s		620 m		609 vs
				610 m	561 vs	
568 s	590 s	592 s		530, 550 vw		561 vw
495 w				470 w		487 ms
433 s	443 s					468 ms
	377 s	375 s				420 vvw
344 s	350 vs	357 vs	345 s			
	319 w					
	280 w					
278 s	271 m	270–280 br, m	298 w			
231 m	256		223 w			

[a] Key: strong, s; medium, m; weak, w; shoulder, sh; very, v; broad, br.

equal intensity (medium), and consequently are assigned to the bending vibrations δ_{RuNO}. The identification of ν_{RuN} presents a more complicated problem. The presence of three or four strong bands in the 600-cm^{-1} region often tends to obscure the weak Ru–N stretching band. In addition, the isotopic shift of this band is small (3–5 cm^{-1}). However, ν_{RuN} and its ^{15}N counterpart are observed in a sufficient number of compounds (six) to ensure its proper identification. The three-body model previously used by Miki for $[RuX_5NO]^{2-}$, is also applicable to the RuNO vibrations of *trans*-$[RuXNO(das)_2]^{2+}$. The use of this model is justified because of the agreement obtained between the observed and calculated frequencies (Table IV).

All of the RuNO vibrations of the *trans*-$[RuXNO(das)_2]^{2+}$ are somewhat sensitive to the nature of the counteranion. The maximum frequency differences observed are 34 cm^{-1} for ν_{NO}. These differences are useful in demonstrating that the bands in the 500–600-cm^{-1} region assigned to Ru–^{14}N–O and Ru–^{15}N–O are not due to impurities. However, by far the largest effect on ν_{NO} is caused by water of crystallization. The presence of water in the solid was established by elemental analyses and by the observation of H_2O bands in the ir spectra of these compounds. The three forms of *trans*-$[RuClNO(das)_2]Cl_2$ differ only in the water content of the solid. The water which is present is probably an integral part of the crystal since it is not removed by vacuum drying over P_4O_{10} at 100° for 12 hr. A similar effect of water on ν_{NO} was noted by Sinitsyn[8] in the pentahalonitrosylruthenates. The Russian workers attributed these effects to hydrogen bonding between the water molecule and the NO group. We have also observed a similar shift (30 cm^{-1}) in ν_{NO} between $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and anhydrous $Na_2[Fe(CN)_5NO]$. However, the crystal structure of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ shows that the nitrosyl group is not hydrogen bonded to the water molecules.[20] Consequently, the large effect which water has on ν_{NO} must remain unexplained.

The replacement of chloride by iodide in *trans*-$[RuClNO(das)_2]^{2+}$ leads to a small decrease in all of the Ru–NO frequencies (Table V). Fenske and De-

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(20) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

Kock[21] and Clark and Crosse[3] have shown that substitution of chloride by bromide and iodide in the series $Mn(CO)_5X$ has little effect on the low-frequency vibrations of the trans carbonyl group, in complete agreement with our results for the ruthenium nitrosyl complexes.

B. Ruthenium Dinitrogen Complexes.—The preparations of *trans*-$[RuClN_2(das)_2]^+$ and its $^{15}N^{14}N$ derivative, *trans*-$[RuCl(^{15}N^{14}N)(das)_2]^+$, have been reported by us previously. The trans geometry was established by its nmr spectrum. The isotopic identity of the coordinated dinitrogen ligand containing ^{15}N was established by mass spectrometric examination of the dinitrogen gas evolved from the thermal decomposition of the ^{15}N-substituted complex and by examination of the infrared spectra described below. The mass spectrum of the gas evolved from the complex containing ^{15}N consists exclusively of $^{15}N^{14}N$ and background $^{14}N^{14}N$. No $^{15}N-^{15}N$ peak is present in the mass spectrum.

4000–650-cm^{-1} Region.—As in the case of the nitrosyl derivatives, the absorption bands in the infrared spectrum above 650 cm^{-1} are easily identified. The strong band found between 2125 and 2132 cm^{-1} is in the region usually associated with the linearly coordinated dinitrogen ligand.[22,23] This band shifts to lower frequencies by 36 cm^{-1} upon substitution of a single ^{15}N, thus unequivocally identifying this band as ν_{NN}. The other absorption bands in this region are *o*-phenylenebis(dimethylarsine) or anion frequencies (Table VI).

650–250-cm^{-1} Region.—Although one band of medium intensity has been observed between 400 and 500 cm^{-1} by other workers,[11,22–24] the additional $Ru-N_2$ frequencies expected in this region have not been properly identified. The infrared spectra of several salts of *trans*-$[RuClN_2(das)_2]^+$ obtained from KBr pellets or highly concentrated Nujol mulls are listed in Table VII. A band of medium intensity is found near 490 cm^{-1}. Upon substitution of a single ^{15}N this band shifts by 12 cm^{-1} thus identifying it as a dinitrogen vibration. In addition, a weak band at 453 cm^{-1} in the SbF_6^- salt is also observed to undergo a shift (7.5 cm^{-1}) upon substitution by ^{15}N. Although this weak band is observed only as a shoulder in the ^{14}N complex, it is well resolved in the ^{15}N complex.

The infrared spectra of some samples of *trans*-$[RuCl(^{15}N^{14}N)(das)_2]^+$ are time dependent. It has been shown by Douglas[25] that the ^{15}N in the dinitrogen complex *trans*-$[RuCl(^{15}N^{14}N)(das)_2]^+$ initially occupies the endo position. Consequently, the appearance of the additional bands in the SbF_6^- salt must be due to isomerization of the endo to the exo complex. This type of isomerization of dinitrogen complexes was first observed and explained by Armor and Taube.[24] Examination of the infrared spectrum of this mixture of endo and exo isomers in the 2000-cm^{-1} region shows the presence of a strong doublet at 2094 and 2089 cm^{-1}. No similar splitting is observed in any of the other salts nor in the unsubstituted $^{14}N-SbF_6^-$ salt. In any case, the separation between the ν_{NN} bands of the endo and exo isomers is 5 cm^{-1} or less. After isomerization, two bands of equal intensity are found near 490 cm^{-1}, but only a *single* weak band is observed at 446.5 cm^{-1} in this mixture of endo and exo isomers. These results are in total agreement with those for the endo and exo isomers of $[Ru(NH_3)_5(^{15}N^{14}N)]Br_2$ found by Armor,[26] who observed only a single band at 2070 cm^{-1} but reported two bands of medium intensity[24] at 503 and 494 cm^{-1}.

TABLE VII

OBSERVED FREQUENCIES OF RuN_2 AND RuCO COMPLEXES[a]

$[RuCl(N_2)(das)_2]Cl$	$[RuCl(N_2)(das)_2]SbF_6$	$[RuCl(N_2)(das)_2]PF_6$	$[RuCl(CO)(das)_2]Cl$
3020 w	3060 }	Weak peaks	
2970 m	3040 } w	near 3000	
2900 m	2990 }		
	2910 }		
2125 s	2130 s	2130.5 s	1945 s
	2030 w		1930 s
	1700 m		
	1553 w		
	1445 m		
1454 w	1420 br	1445 m	1450 w
	1360 m		
1420 br, ms	1279 }	1420 br, m	1420 m
1275 sh	1261 } m	1279 }	1280
1261 ms	1251 }	1261 } mw	1260 m
	1220 m	1251 }	
1102 m	1102 s	1102 m	1102 mw
1035 w	1030 s	1030 w	1030 m
908 s	905 br, s	918 w	915 m
901 w			
876 s		864	865 br, s
861 s	860 br, s	837 vs	
810 w	815 w		
783 s	755 br, s	758 m	750 s
702 w	700 m		710 br, w
	666 vs	648 w	
616 m	613 m	613 m	615 m
595 m	594.5 m	594 m, 556 vs	598 m
489 m	490	489 s	588 m
	453	455 m	545 m
445 m	441 s	441 s	435 m
373.5 m	376 s	378 m	378 m
358 s	357 s	359 m	360 m
310 w	318 m		

[a] Key: strong, s; medium, m; weak, w; shoulder, sh; very, v; broad, br.

Assignment of the $Ru-N_2$ Frequencies.—The $Ru-N_2$ bands of the pentaammine complexes have been assigned previously.[11,12] The band of medium intensity near 490 cm^{-1}, observed in all of the dinitrogen complexes thus far examined, was assigned by Borod'ko and coworkers[11] to the Ru–N stretching vibration, ν_{RuN}, while a weak band at 516 cm^{-1} was assigned to the bending vibration, δ_{RuNN}. However, these previous assignments are not in accord with the observed isotopic shifts nor with the relative intensities of these two bands (the stretching vibration is expected to be *less* intense than the bending vibration, *vide supra*).

On the basis of the observed isotopic shifts and relative intensities, the fundamental vibrations of the RuNN moiety have been reassigned. The bands of medium intensity near 490 cm^{-1} in *trans*-$[RuClN_2(das)_2]^+$ are now assigned to δ_{RuNN}, while the weak band at 453 cm^{-1} is assigned to the ruthenium–nitrogen

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[21] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

[22] (a) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965); (b) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

[23] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 955 (1970).

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

[25] P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, **94**, 5254 (1972).

[26] J. N. Armor, unpublished results.

TABLE VIII

OBSERVED AND CALCULATED ISOTOPIC SHIFTS (CM^{-1})[a] FOR THE RuN_2 COMPLEXES

		ν_{NN} str			ν_{RuN} str			δ_{RuNN}		
Compd	Ref	^{14}N	^{15}N	Δ_{calcd}	^{14}N	^{15}N	Δ_{calcd}	^{14}N	^{15}N	Δ_{calcd}
$[RuCl(N_2)(das)_2]Cl$		2125.0						489.0		
$[RuCl(N_2)(das)_2]PF_6$		2130.5	2095.5	35.0	455.0	448.5	7.5	489.0	477.8	11.2
	b	(2130.0)	(2092.0)	(38.0)	(455.0)	(448.5)	(7.5)	(489.2)	(477.6)	(11.6)
	c	(2130.0)	(2097.0)	(33.0)	(455.0)	(448.0)	(8.0)	(489.2)	(485.0)	(3.8)
$[RuCl(N_2)(das)_2]SbF_6$		2130.5	2094.0	35.5	453.0	446.5	6.5	490.0	486.0	4.0
			2089.0	41.5					477.8	12.2
	d	(2130.0)	(2091.0)	(39.0)	(452.0)	(446.0)	(6.0)	(489.6)	(477.9)	(11.6)
	e	(2130.0)	(2096.5)	(33.5)	(452.0)	(446.0)	(6.0)	(489.6)	(485.2)	(4.7)

[a] Calculated values in parentheses. [b] Calculated for $Ru^{15}NN$. [c] Calculated for $RuN^{15}N$. [d] Calculated for $Ru^{15}NN$. [e] Calculated for $RuN^{15}N$.

stretching vibration, ν_{RuN}. The strong band near 2130 cm^{-1} is readily identified as ν_{NN} from its intensity, position, and shift upon isotopic substitution. Using the product rule and the observed frequencies of ν_{NN} (all three complexes: $Ru^{14}N^{14}N$, $Ru^{15}N^{14}N$, and $Ru^{14}N^{15}N$) and ν_{RuN} ($Ru^{14}N^{14}N$ only), the frequencies of the stretching vibration ν_{RuN} were calculated for both the endo and exo isomers (Table VIII). These calculations show that ν_{RuN} for the exo and endo isomers differ by only 1 cm^{-1} and consequently would not be resolvable. This prediction is in full accord with the experimental results for the salts of *trans*-$[RuClN_2(das)_2]^+$ in which only a *single weak band* was observed for the mixture of endo and exo isomers. Using the assignments of Borod'ko[11] for ν_{RuN} and the product rule, the *minimum* separation expected for ν_{NN} of the exo and endo isomers is 35 cm^{-1}. A frequency difference of this magnitude would easily be observed and resolved in the 2000-cm^{-1} region, contrary to the experimental results. These calculations confirm the present assignment of the band of medium intensity near 490 cm^{-1} to δ_{RuNN} and the weak band at 453 cm^{-1} to ν_{RuN}. Using these assignments and the three-body model, the frequencies of the endo and exo isomers were calculated and are compared with the observed isotopic shifts (Table VIII). The derived force constants are summarized in Table III.

Since there was disagreement between the assignments of the RuN_2 frequencies made for $[Ru(NH_3)_5N_2]^{2+}$ and for *trans*-$[RuClN_2(das)_2]^+$, the pentaammine complexes were reinvestigated. Armor[26] and Borod'ko[11] have prepared the appropriate ^{15}N derivatives of $[Ru(NH_3)_5N_2]^{2+}$ and Borod'ko made the assignments discussed above on the basis of the isotopic shifts observed for these compounds. Unfortunately, not all of the ir bands for these compounds were reported. The positions of the two bands of medium intensity (503 and 494 cm^{-1}), were obtained by curve resolution of the published spectrum[24] of the mixture of exo and endo complexes $[Ru(NH_3)_5(^{15}N^{14}N)]Br_2$. Armor[26] has kindly supplied us with the other frequencies observed for the endo and exo ^{15}N isomers as well as with the frequencies of unsubstituted $[Ru(NH_3)_5N_2]Br_2$. Armor observed only a single ν_{NN} frequency in the mixture of endo and exo isomers, in agreement with our experience with the *trans*-$[RuCl(^{15}N^{14}N)(das)_2]^+$ complexes. In any case, the separation between ν_{NN} of the exo and endo isomers of $[Ru(NH_3)_5(^{15}N^{14}N)]^{2+}$ must be less than 5 cm^{-1}.

If the band of medium intensity at 507 cm^{-1} in the unsubstituted compound $[Ru(NH_3)_5N_2]Br_2$ is assigned to the ruthenium–nitrogen stretching vibration ν_{RuN}, then the minimum separation between the ruthenium–nitrogen stretching vibration of the exo and endo isomers is 6 cm^{-1} (from the apparent band maxima) or 9 cm^{-1} (from curve resolution). This separation of 6–9 cm^{-1} between ν_{RuN} of the exo and endo isomers would lead to a frequency separation of between 16 and 38 cm^{-1} for the N–N stretching vibration of the exo and endo isomers which is not in accord with the experimental observations. A frequency difference of this magnitude would certainly have been observed if it were present. However, these apparent discrepancies between the calculated and experimental results can be eliminated by reassigning the band of medium intensity to the bending vibration δ and by assigning the weak band at 516 cm^{-1} in $[Ru(NH_3)_5N_2]I_2$ to the ruthenium–nitrogen stretching vibration ν_{RuN}.

C. Ruthenium Carbonyl Complexes.—The *trans*-$[RuCl(CO)(das)_2]Cl$ complex was prepared by treatment of the tetraphenylborate salt *trans*-$[RuCl(CO)(das)_2][BPh_4]$ with HCl. The stereochemistry of the resultant product was confirmed by nmr spectroscopy. The Ru–CO frequencies were identified by comparison with the infrared spectra of the ruthenium nitrosyl complexes, the ruthenium dinitrogen complexes, and *trans*-$[RuCl_2(das)_2]$ (Table VI). The carbonyl stretching vibration is split with the two bands occurring at 1930 and 1945 (vs) cm^{-1}. Two additional bonds can be identified in the 250–600 cm^{-1} region. These bands were assigned by analogy with the nitrosyl and dinitrogen complexes, since no isotopically substituted compounds were available. In the other complexes of *o*-phenylenebis(dimethylarsine) there are two ligand bands, one near 620 cm^{-1} and one near 600 cm^{-1}. Accordingly, the bands at 615 and 598 cm^{-1} were assigned to the *o*-phenylenebis(dimethylarsine) frequencies, leaving the bands at 588 (m) and 545 (m) cm^{-1} for assignment as Ru–CO frequencies. Other workers have assigned the more intense bands at higher frequencies to δ_{MCO}, while the weaker bands at lower frequencies have been assigned to ν_{MC}.[1-3] These previous assignments of the MCO frequencies are similar to those already made for the nitrosyl and dinitrogen complexes. Accordingly, the weaker band at 545 cm^{-1} has been assigned to the Ru–C stretching motion, and the band at 588 cm^{-1} has been assigned to the Ru–C–O bending motion. Using these assignments, force constants were calculated using the three-body model and are $k_1 = 13.3 \times 10^5$, $k_2 = 4.1 \times 10^5$, $k_\delta = 0.84 \times 10^5$ mdyn/Å.

Conclusions

The vibrational spectra of the diatomic species N_2, NO^+, and CO, when coordinated to ruthenium, can be

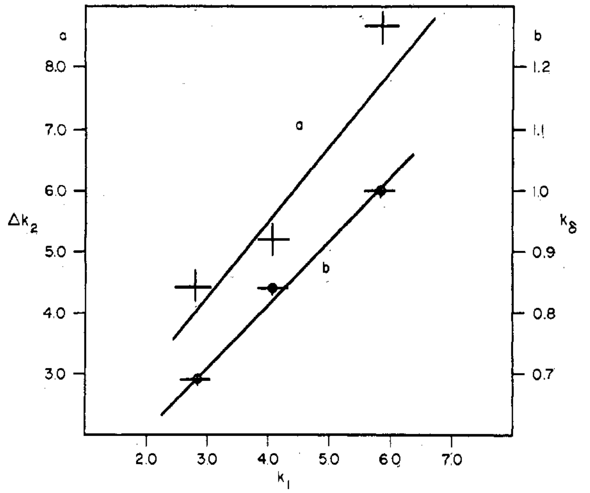

Figure 3.—Plots of (a) Δk_2 and (b) k_δ *vs.* k_1. The lengths of the lines at each data point represent the relative uncertainties of the force constants.

described by use of a valence force field and consideration of only three atoms, RuXY. The observed isotopic shifts are in complete accord with this model for the complexes *trans*-[RuClN$_2$(das)$_2$]$^+$ and *trans*-[RuXNO(das)$_2$]$^{2+}$. The presence of other light atoms in the coordination sphere of ruthenium (*i.e.*, [Ru(NH$_3$)$_5$N$_2$]$^{2+}$) could conceivably lead to a breakdown of this model by introducing vibrations of similar frequency and of the same symmetry as those of the RuXY group. However, it also proved possible to explain the isotopic shifts observed for the ^{15}N-substituted pentaammine complexes [Ru(NH$_3$)$_5$N$_2$]$^{2+}$ using this three-body model.

We have shown that the three complexes *trans*-[RuClNO(das)$_2$]$^{2+}$, *trans*-[RuClN$_2$(das)$_2$]$^+$, and *trans*-[RuClCO(das)$_2$]$^+$ are isostructural. In addition, these complexes are normally considered isoelectronic since they all formally involve Ru(II) coordinated to the isoelectronic ligands (N$\equiv$O)$^+$, (N$\equiv$N), and (C$\equiv$O). The remainder of the coordination sphere is identical. Therefore it is of interest to compare the derived force constants for these three complexes.

The infrared spectra of MCO complexes are often interpreted in terms of the π-bonding model first placed on a firm theoretical basis by Dewar, Chatt, and Craig, *et al.*,[27] and subsequently utilized by authors too numerous to mention. However, in a recent review, Petit[28] has pointed out that definitive experimental evidence for "back-π-bonding" is scarce, and the use of this model is generally contentious. For example, it is nearly always *assumed* that k_{MC} increases linearly with decreasing values of k_{CO}, but such a relationship has seldom been experimentally demonstrated. Fritz and Paulus[29] found that $\nu_{\mathrm{MC}} + \nu_{\mathrm{CO}}$ is approximately constant for a large number of metal carbonyls, but the ν_{MC} frequencies were not properly assigned. Bigorgne and Zelwer[30] have also observed a linear relationship between k_{NiC} and k_{CO} for a series of phosphine-substituted nickel carbonyl complexes, Ni(CO)$_{4-n}$P$_n$.

In Figure 3, the change in the stretching force constant from that of the uncoordinated ligand (Δk_2) is plotted *vs.* the force constant for the metal–ligand stretching vibration and metal–ligand bending vibration. In order to compare the force constants of the complexes of NO$^+$, N$_2$, and CO with those of the free ligand, the force constants of the uncomplexed diatomic species were calculated directly from the observed vibrational frequencies[31] using the harmonic oscillator approximation. The force constants calculated for these diatomic species are $k_{\mathrm{NO^+}} = 22.5$, $k_{\mathrm{CO}} = 19.0$, and $k_{\mathrm{NN}} = 23.0$ mdyn/Å.

There are three features of these data which support the π-bonding model. First, as can be seen from Figure 3 there is a surprisingly good relationship between the strength of the ruthenium–ligand bond and the decrease in the XY force constant upon coordination to the metal. Second, k_1 increases with the increasing stability of the RuXY complexes: N$_2$ < CO < NO$^+$. Third, the bending force constant, k_δ, increases with the increasing strength of the Ru–X bond. Since these complexes possess the same molecular geometry and identical ligands, the increase in the RuXY force constants can be directly attributed to the increasing π bonding between ruthenium and N$_2$, CO, and NO$^+$. Similar conclusions were also reached by Darensbourg from comparative studies of the intensities of ν_{XY} of some osmium complexes of N$_2$ and CO.[32]

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