Infrared Absorption Intensities of the N—N and M—N₂ Stretching Vibrations in Ruthenium and Osmium Dinitrogen Complexes

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The infrared absorption intensities of the N—N and M—N₂ stretching vibrations have been measured for the complexes Ru(NH₃)₅N₂X₂ and Os(NH₃)₅N₂X₂, where X = Cl⁻, Br⁻, I⁻, both in the solid state and in solution. It has been found that the intensity of the N—N stretching vibration (Iₐₕₙ) increases with decreasing frequency (vₐₕₙ), which is in agreement with a model of dπ—pπ* back donation. It is concluded that as Aₐₕₙ is greater for Os than for Ru, the degree of such backbonding increases from Ru to Os. A calculation by the fixed charge model of the charge separation between the fragments M(NH₃)₅ and N₂, based on M—N₂ intensities in aqueous solution, has been performed. The calculated values are for Ru 0.72 a.u. and for Os 1.1 a.u. The relation of these to a theoretically calculated value for Fe—N₂ (0.43 a.u.) is discussed.

Since the discovery of the first transition-metal dinitrogen compound,¹ interest in metal complexes containing dinitrogen as a ligand has increased during the last years. These new complexes have opened the possibility of fixation of dinitrogen under mild conditions. Fixation of dinitrogen by mixed systems composed of transition-metal compounds and organometallic compounds has been reported by Vol'pin and Shur,² but so far no complex containing dinitrogen has been isolated from the mixed systems. Soon after these discoveries, complexes of osmium,³ cobalt,⁴ and iridium ⁶ with dinitrogen were also prepared. These complexes show an absorption band in the infrared spectrum in the region 2000—2140 cm⁻¹, the exact position being dependent on the metal to which N₂ is bonded. This band has been assigned to the N—N stretching frequency (vₐₕₙ) of coordinated N₂. The marked shift in vₐₕₙ from the free N₂ (2331 cm⁻¹)⁷ indicates a decrease in the N—N bond order. This is caused by a σ-bond to the metal and by π-back donation from metal d-orbitals into antibonding π-orbitals of N₂. The intensity of the N—N stretching vibration absorption implies that the N₂ is in an unsymmetrical environment.

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coordinated at one end rather than in a symmetrical π-bond configuration. This conclusion is also confirmed by X-ray crystallographic studies on a ruthenium \(^8\) and a cobalt \(^10,11\) dinitrogen complex, which show the M–N–N entity to be linear. A recent report on a rhenium \(^12\) dinitrogen complex also shows that the Re–N–N group is linear.

The dinitrogen complexes of transition metals have generally been hailed as possible models for nitrogenase with dinitrogen on the active site. For a complete analogy one must be able to show the possibility of reduction of the dinitrogen to ammonia. Several attempts to reduce coordinated dinitrogen in some of the complexes have also been performed\(^13\)–\(^15\) These investigations show that the dinitrogen ligand is neither reduced to ammonia by common reducing agents nor affected by protonation of strong acids. The dinitrogen ligand is thus very inert and much more about the chemistry of the dinitrogen ligand must be known before the dinitrogen complexes can be used as initial products in ammonia production.

This infrared spectroscopic investigation was started to increase the knowledge about the bonding and also the polarity of the N–N bond in the dinitrogen complexes. Infrared absorption intensities are known\(^16\) to be related to the charge distribution and its change with interatomic distance in a molecule. Therefore, valuable information of this kind is to be expected from intensity measurements on the dinitrogen complexes.

**EXPERIMENTAL**

**Preparation of Ru(NH\(_3\))\(_2\)X\(_2\)X\(_4\), X = Cl, Br, I.** Commercial ruthenium trichloride (Koch-Light Laboratories) was checked for the absence of ruthenium nitrosyl complexes by its infrared spectrum and then it was used without any purification. Hydrazine hydrate was of *purum* quality.

The first method of Allen and Senoff\(^1\) (reduction of RuCl\(_3\) with hydrazine hydrate) has been found to give impure compounds. The compounds are contaminated with a hydrazine\(^13\) complex and sometimes also with a binuclear ruthenium complex, which is identified by its absorption maximum\(^17\) at 262 nm in the UV-spectrum. For these reasons, it was found impossible to obtain a pure compound and therefore another method was used. First [Ru(NH\(_3\))\(_2\)]Cl\(_4\) was prepared according to Ref. 18. The purity of this compound was checked by elemental analysis of hydrogen and nitrogen and the found values agreed well with the calculated ones. (Found: H 5.22; N 23.6. Calc.: H 5.17; N 23.9.) The UV-spectrum of the Ru(NH\(_3\))\(_2\)Cl\(_4\) ion shows a maximum at 330 nm with a molar absorption coefficient \(\varepsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}\) in agreement with the reported value.\(^13\) To get the Ru(NH\(_3\))\(_2\)N\(_2\)\(^{2+}\) ion, the [Ru(NH\(_3\))\(_2\)]Cl\(_4\) was treated with sodium azide in aqueous solution at a temperature below 40°C and during 25 min. At higher temperatures a considerable amount of the binuclear complex \([\text{Ru(NH}_3)\text{)_2N}_2]^{1+}\) is formed. The solution was filtered, cooled, and solid sodium chloride was added. The precipitate was filtered off, washed and air-dried. The product was rose-coloured and its infrared spectrum showed, besides the peak corresponding to the N–N stretching vibration, a small peak at lower frequency, which is probably the N–N stretching vibration in Ru(NH\(_3\))\(_2\)N\(_2\)Cl\(_4\) which has not reacted completely to the Ru(NH\(_3\))\(_2\)N\(_2\)\(^{2+}\) ion. The product was kept in nitrogen atmosphere overnight and then dissolved in water and precipitated again with solid sodium chloride. Now a yellow precipitate was formed which was treated as before. In this compound only one peak corresponding to the N–N stretching vibration was found, and the purity of the compound was checked by elemental analysis of hydrogen and nitrogen. Ammonia was determined by a colorimetric method,\(^20\) after removing the ammonia of the compound by distillation from strong alkali. (Found: H 5.35; N 34.0; NH\(_3\) 28.5. Calc.: H 5.30; N 34.4; NH\(_3\) 29.9.) The UV-spectrum shows a band with maximum at 221 nm with \(\varepsilon = 1.7 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}\), which is in agreement with the literature.\(^13\)

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The bromide and iodide salts were prepared as above, but the precipitation was done with saturated solutions of the respective anions. The salts were recrystallized from water and analyzed as described above.

\[ \text{Ru(NH}_3\text{)}_3\text{N}_2\text{Br}_3 \text{; Calc.: H 4.04; N 26.2; NH}_3\text{; 21.3.} \]

Preparation of Os(\text{NH}_3\text{)}_3\text{N}_2\text{X}_3, X = \text{Cl, Br, I.} \text{OsO}_4, \text{which was of purum quality, was reduced with ethanol in hydrochloric acid and K}_2\text{OsCl}_4 \text{was precipitated with diluted potassium chloride solution. The red precipitate of K}_2\text{OsCl}_4 \text{was then treated with hydrazine hydrate according to Borod'ko et al.} \]

It was, however, found impossible to get a pure compound. The infrared spectrum of the compound shows, besides a strong band at 2020 cm\(^{-1}\), also two smaller bands at 2100 cm\(^{-1}\) and 2166 cm\(^{-1}\). Three bands in the infrared spectrum of this compound have also been reported by Borod'ko et al. \(\text{N}_2\text{ stretching vibrations in a complex containing two nitrogen molecules, viz. Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_2\text{Cl}_4. Elemental analysis of the compound gave a higher value of nitrogen than the calculated one. Thus, from elemental analysis values of nitrogen, the relative proportions of the two complexes could be determined. This method gives about 65% of the monodinitrogen complex and 35% of the bisdinitrogen complex. At least ten different preparations have been made to get Os(\text{NH}_3\text{)}_2\text{N}_2\text{Cl}_4 \text{and all show a mixture of the above-mentioned two complexes. The amount of the monodinitrogen complex varies from 65 to 75% throughout the preparations. As an example one set of analysis values is given.} \]

Os(\text{NH}_3\text{)}_2\text{N}_2\text{Cl}_4; \text{Calc.: H 4.04; N 26.2; NH}_3\text{; 22.8.} \text{Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_1\text{Cl}_4; Calc.: H 3.14; N 29.1; NH}_3\text{; 17.7. Found: H 4.14; N 37.3; NH}_3\text{; 20.5.} \]

The UV-spectrum of the compound shows a band with maximum at 208 nm corresponding to Os(\text{NH}_3\text{)}_2\text{N}_2 \text{?}^+, but the band is broad and also shows absorption of Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_2^+, which has a maximum at 221 nm.

The bromide and iodide salts have been prepared through addition of saturated solutions of the respective sodium salts to aqueous solutions of the chloride complex. Elemental analysis values of nitrogen were higher than the calculated ones also for these compounds, and the relative proportions of the two complexes have been determined as described above. UV-spectra of the bromide and iodide salts agreed well with the spectrum of the chloride salt, and also the calculated values of \(\varepsilon\) at 208 and 221 nm, respectively.

Os(\text{NH}_3\text{)}_2\text{N}_2\text{Br}_4; \text{Calc.: H 3.26; N 21.2; NH}_3\text{; 18.4.} \text{Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_1\text{Br}_4; Calc.: H 2.55; N 23.6; NH}_3\text{; 14.4. Found: H 3.25; N 22.0.} \text{Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_1\text{I}_4; Calc.: H 2.71; N 17.6; NH}_3\text{; 15.3. Os(\text{NH}_3\text{)}_2(\text{N}_2\text{)}_1\text{I}_4; Calc.: H 2.13; N 19.7; NH}_3\text{; 12.0. Found: H 2.79; N 18.3; NH}_3\text{; 13.5.} \]

Like the chloride preparations, many different preparations of the bromide and iodide salts have been made and all give about 65 to 75% of the monodinitrogen complex.

Spectral measurements. Ultraviolet spectra were recorded on a Hitachi Recording Spectrophotometer Model EPS-3T. The infrared spectra were recorded with a Perkin Elmer Spectrophotometer Model 531. All spectra on the \(\text{N} \equiv \text{N}\) and \(\text{M} \equiv \text{N}\) stretching vibrations were recorded with a wavenumber scale expansion, so that 1 cm on the chart corresponded to 25 cm\(^{-1}\). The wavenumber readings of the spectrophotometer were checked by recording spectra of carbon monoxide. Measurements on the dinitrogen complexes have been performed both in the solid state and in solution. The solid samples were examined in KBr disks. The concentration of the solid sample was obtained by determination of the weight ratio between sample and KBr before the disk was pressed and by measurements of the volume of the disk afterwards. Water, dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF) have been used as solvents. Unfortunately, not all the complexes were soluble in these solvents. The chloride and bromide salts were soluble only in water, and the iodide salts were soluble in DMSO and DMF. Fisher Scientific Co. “certified reagent” dimethyl sulfoxide and dimethyl formamide were used without further treatment. Cells with CaF\(_2\)-windows were used. For aqueous solutions, 25 \(\mu\) platinum spacers and for DMSO and DMF solutions 0.2 mm teflon spacers were used. The exact cell-thicknesses were determined interferometrically.

Intensity measurements were performed on at least two preparations of each dinitrogen complex and at a number of concentrations. Linear Beer’s law plots were observed for all the complexes in all solvents. A representative example is given in Fig. 1.
When the dinitrogen complexes were not stable in solution for a long time, spectra were recorded immediately after complete dissolution of the compounds. Two spectra were recorded after each other to investigate if there was any decrease in absorbance with time. The decrease was so small that it did not change the intensity of the band, which generally was calculated from the first recorded spectrum. The absorption intensities of the bands have been obtained through graphical integration of the curves \( \epsilon = \epsilon(\bar{v}) \), which were calculated from the transmission bands recorded by the instrument. The obtained values were multiplied with \( \ln 10 \) to get integrated absorption intensities following from the absorption law. It was, however, impossible to obtain the weak band corresponding to the \( M-N_2 \) stretching vibration in solution, depending on strong absorption of the solvents in the region where this vibration occurs and also on the difficulty of dissolving an amount large enough to get any observable absorption band. The intensity of the \( M-N_2 \) band in solution has for every complex been determined by the rule of three from the intensity of the \( N-N \) stretching vibration band in the solid state and in solution and the intensity of the \( M-N_2 \) band in the solid state.

**RESULTS**

The results of the infrared absorption intensity measurements are given in Table 1. Some observations can immediately be made from the results. The osmium dinitrogen complexes have a higher intensity of the \( N-N \) stretching vibration (\( A_{NN} \)) than the ruthenium dinitrogen complexes. The intensity values measured in the solid state are always lower than the values determined in solution. The frequency of the \( N-N \) stretching vibration (\( v_{NN} \)) is also changed in different solvents. For aqueous solutions, \( v_{NN} \) is larger than for the solid state, whereas \( v_{NN} \) in DMSO and DMF has a lower value than in the solid state. A rough generalization can be made concerning the results, viz. the higher the frequency (\( v_{NN} \)), the lower is the absorption intensity (\( A_{NN} \)). This correlation is shown in Fig. 2. The fact that the \( A_{NN} \ versus \ v_{NN} \) plot shows

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**Fig. 1.** The Beer law plot of the absorption of the \( N-N \) stretching vibration at 2122 cm\(^{-1} \) in Ru(NH\(_3\))\(_4\)N\(_2\)I\(_4\) in the solid state. 

**Fig. 2.** The correlation between intensity \( A_{NN} \) and frequency \( v_{NN} \) for the ruthenium and osmium dinitrogen complexes. Ru(NH\(_3\))\(_4\)N\(_2\)X\(_2\) in KBr (○), H\(_2\)O (○), DMF (●) and DMSO (●). Os(NH\(_3\))\(_2\)N\(_2\)X\(_2\) in KBr (▲), H\(_2\)O (△), DMF (▽) and DMSO (▽).
Table 1. The results of the absorption intensity measurements on the $M(\text{NH}_3)_2\text{N}_4^{2+}$ complexes; $M = \text{Ru}$ and $\text{Os}$.

<table>
<thead>
<tr>
<th>Metal complex</th>
<th>Dispersion medium</th>
<th>$\nu_{\text{NN}}$ cm$^{-1}$</th>
<th>$\nu_{\text{M-N}}$ cm$^{-1}$</th>
<th>$\varepsilon_{\text{NN}}$ M$^{-1}$ cm$^{-1}$</th>
<th>$\varepsilon_{\text{M-N}}$ M$^{-1}$ cm$^{-1}$</th>
<th>$A_{\text{NN}} \times 10^{-4}$ M$^{-1}$</th>
<th>$A_{\text{M-N}} \times 10^{-3}$ M$^{-2}$ cm$^{-1}$</th>
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<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{Cl}_2</td>
<td>KBr</td>
<td>2008</td>
<td>512</td>
<td>390 ± 40</td>
<td>43 ± 3</td>
<td>4.6 ± 0.4</td>
<td>1.75 ± 0.1</td>
</tr>
<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{Cl}_2</td>
<td>H$_2$O</td>
<td>2120</td>
<td>760 ± 70</td>
<td>5.4 ± 0.4</td>
<td>2.1 ± 0.2</td>
<td>5.8 ± 0.5</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{Br}_2</td>
<td>KBr</td>
<td>2108</td>
<td>504</td>
<td>420 ± 40</td>
<td>44 ± 3</td>
<td>4.0 ± 0.4</td>
<td>1.45 ± 0.1</td>
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<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{Br}_2</td>
<td>H$_2$O</td>
<td>2117</td>
<td>640 ± 60</td>
<td>5.8 ± 0.5</td>
<td>2.0 ± 0.2</td>
<td>5.8 ± 0.5</td>
<td>2.0 ± 0.2</td>
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<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>KBr</td>
<td>2122</td>
<td>495</td>
<td>390 ± 40</td>
<td>40 ± 3</td>
<td>4.2 ± 0.4</td>
<td>1.45 ± 0.1</td>
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<td>Ru(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>DMF</td>
<td>2100</td>
<td>930 ± 50</td>
<td>5.8 ± 0.5</td>
<td>2.0 ± 0.2</td>
<td>5.8 ± 0.5</td>
<td>2.0 ± 0.2</td>
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<tr>
<td>Ru(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>DMSO</td>
<td>2085</td>
<td>625 ± 50</td>
<td>5.0 ± 0.5</td>
<td>1.7 ± 0.2</td>
<td>5.0 ± 0.5</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>Os(\text{NH}_3)_2\text{N}_4\text{Cl}_2</td>
<td>KBr</td>
<td>2020</td>
<td>518</td>
<td>550 ± 50</td>
<td>60 ± 5</td>
<td>6.5 ± 0.5</td>
<td>3.3 ± 0.3</td>
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<tr>
<td>Os(\text{NH}_3)_2\text{N}_4\text{Cl}_2</td>
<td>H$_2$O</td>
<td>2035</td>
<td>1350 ± 100</td>
<td>8.8 ± 1.0</td>
<td>4.5 ± 0.5</td>
<td>8.8 ± 1.0</td>
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<td>Os(\text{NH}_3)_2\text{N}_4\text{Br}_2</td>
<td>KBr</td>
<td>2032</td>
<td>510</td>
<td>1000 ± 100</td>
<td>64 ± 5</td>
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<td>Os(\text{NH}_3)_2\text{N}_4\text{Br}_2</td>
<td>H$_2$O</td>
<td>2035</td>
<td>1200 ± 100</td>
<td>8.5 ± 1.0</td>
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<td>Os(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>KBr</td>
<td>2037</td>
<td>498</td>
<td>1100 ± 100</td>
<td>60 ± 5</td>
<td>8.5 ± 0.5</td>
<td>3.0 ± 0.3</td>
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<tr>
<td>Os(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>DMF</td>
<td>2020</td>
<td>2150 ± 100</td>
<td>11.8 ± 0.7</td>
<td>4.3 ± 0.5</td>
<td>11.8 ± 0.7</td>
<td>4.3 ± 0.5</td>
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<tr>
<td>Os(\text{NH}_3)_2\text{N}_4\text{I}_2</td>
<td>DMSO</td>
<td>2007</td>
<td>1600 ± 100</td>
<td>13.5 ± 1.0</td>
<td>4.9 ± 0.5</td>
<td>13.5 ± 1.0</td>
<td>4.9 ± 0.5</td>
</tr>
</tbody>
</table>

A rather large scattering indicates that more than one factor influences this relation. The fact that the chloride and the bromide salts of osmium have equal values of both intensity ($A_{\text{NN}}$) and frequency ($\nu_{\text{NN}}$) in aqueous solution indicates that these salts are completely dissociated in water. Especially the equal values of the frequency is an indication of no influence of the counterions. The same is also valid for the corresponding ruthenium salts.

The near contact with halide ions in the solid salts can cause several effects. To understand these, another striking effect must be regarded. This is the large increase in intensity $A_{\text{NN}}$ for Os(\text{NH}_3)_2\text{N}_4\text{I}_2 dissolved in DMSO and DMF. This increase in intensity is followed by a decrease in $\nu_{\text{NN}}$ and therefore a change in electronic structure of the $M$–N–N entity must be suggested. This trend is not so noticeable for the corresponding ruthenium compound. It is plausible that the $\sigma$-S–O and $\sigma$-C–O groups in the respective solvents solvate the osmium complex ions so that the antibonding $\varepsilon^*$-$d$-orbitals are engaged in an electron-donation process. Thereby, there will be a higher electron density in these orbitals which causes a higher degree of $\pi$-back donation within the $M$–N–N entity, viz. $M$–N–N. This weakens the N–N bond and the change in polarity on an N–N stretching vibration will increase and thereby also the intensity, $A_{\text{NN}}$. Such charge-transfer association of outer-sphere ligands has been found and discussed earlier for complexes like Co(\text{NH}_3)$_2^{5+}$ and Coen$_2^{3+}$ (cf., e.g., Refs. 23 and 24). As osmium has a somewhat greater ion-radius than ruthenium, the possibility of near contact between the solvating molecules and the mentioned $d$-orbitals must be greater for osmium than for ruthenium.

In Fig. 3, intensity values for the osmium and ruthenium complexes in the solid state are plotted against the frequency. It is evident that the intensities for the chloride and the bromide of each complex within the error limits.
are practically equal, whereas the intensity value for the ruthenium iodide is smaller than the chloride and bromide values. For osmium iodide, the value is greater than the corresponding chloride and bromide values. It is then plausible that an outer-sphere effect is responsible for the high value of the osmium iodide. The result will be that the iodide ion, with the greatest tendency for electron donation, causes a change of the trend, viz. gives a higher intensity than the chloride and the bromide. It is, however, disturbing that the frequency increases with increasing intensity, a circumstance which is contradictory to the generalization made earlier.

A similar effect is found if one regards the intensities of the M–N₂ stretching vibration in the solid state. How correct intensity values of the M–N₂ band for the osmium dinitrogen complexes have been obtained is described later, when the results of the osmium bisdinitrogen complexes are discussed. From Table I it can be seen that the frequency of the M–N₂ stretching vibration decreases in the order Cl⁻ > Br⁻ > I⁻. The intensity of the M–N₂ band also decreases in this order. On comparison of the frequencies νₚₚ and νₚₚ', it is found that while νₚₚ decreases in the order Cl⁻ > Br⁻ > I⁻, νₚₚ increases. It is thus reasonable that an effect which causes a weakening of the M–N₂ bond strengthens the N–N bond to a corresponding extent and vice versa.

It is of interest to observe the X-ray crystal structure analysis results of Ru(NH₃)₅N₂X₂.²⁵ The authors find that the cell dimensions in the series X = Cl⁻, Br⁻, I⁻ do not increase as much as is expected from the ion-radius. This suggests a contact between the central group and the outer-sphere ligands. This is also in accordance with the frequency changes with the nature of the anion, which have been obtained.

Fig. 3. Intensity values Aₚₚ in the solid state plotted against the frequency νₚₚ for Ru(NH₃)₅N₂X₂ and Os(NH₃)₅N₂X₂. Ru(NH₃)₅N₂X₂: X = Cl⁻ (o), Br⁻ (●), I⁻ (□). Os(NH₃)₅N₂X₂: X = Cl⁻ (△), Br⁻ (▲), I⁻ (▽).

Fig. 4. Intensity values Aₚₚ for Os(NH₃)₄(N₂)₂X₄ as a function of the frequency νₚₚ. X = Cl⁻, Br⁻, I⁻; Cl⁻ in KBr (o), Br⁻ in KBr (●), I⁻ in KBr (□), and I⁻ in DMSO (■).

Another interesting fact from the literature, that supports the suggestion that the effects discussed depend on outer-sphere association, is the observation of Chatt et al.²⁶ that the N–N stretching frequency in salts of [ReClN₄]-
[Ph₂P(CH₂)₂PPh₂]⁺ is independent of the nature of the anion. This would suggest that the observed effects for Ru(NH₃)₆N₂²⁺ and Os(NH₃)₆N₂²⁺ are specific for these complexes. All in all, the investigations on counter-ion influences on νₙₙ and Aₙₙ show that to get the best information about the charge distribution within the complexes, intensity values measured in aqueous solution must be used, since the concentration of counter-ions is small in these solutions and the outer-sphere association can be neglected.

As mentioned in the description of the preparation of Os(NH₃)₆N₂X₂, a bisdinitrogen complex, viz. Os(NH₃)₄(N₂)₂X₂, which could not be separated from the monodinitrogen complex, is also obtained. The bisdinitrogen complex gives two absorption bands corresponding to N–N stretching vibrations. It is a cis-complex as has been pointed out by Taube et al.[22] The results of the

<table>
<thead>
<tr>
<th>X</th>
<th>Dispersion medium</th>
<th>νₙₙ cm⁻¹</th>
<th>εₙₙ M⁻¹ cm⁻¹</th>
<th>Aₙₙ × 10⁻⁴ M⁻¹ cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>KBr</td>
<td>2166</td>
<td>450 ± 50</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>Br</td>
<td>KBr</td>
<td>2105</td>
<td>670 ± 70</td>
<td>4.7 ± 0.2</td>
</tr>
<tr>
<td>I</td>
<td>KBr</td>
<td>2110</td>
<td>900 ± 50</td>
<td>4.8 ± 0.3</td>
</tr>
<tr>
<td>I</td>
<td>DMSO</td>
<td>2170</td>
<td>350 ± 50</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>I</td>
<td>DMSO</td>
<td>2115</td>
<td>650 ± 75</td>
<td>3.2 ± 0.3</td>
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</tbody>
</table>

intensity measurements on these complexes are given in Table 2. The chloride and bromide salts have been investigated only in the solid state, since the complexes were not soluble enough in any solvent to permit measurements to be made. The iodide complex, on the other hand, could be investigated also in DMSO.

It may be mentioned here that in a later investigation of the decomposition of the Os(NH₃)₆N₂²⁺ ion in acid solution, it was found that the bisdinitrogen complex was quite stable and could be isolated from the monodinitrogen complex. This investigation will be presented in a later paper.[27] When the bisdinitrogen complex could be isolated in this way, more accurate values of the intensity Aₙₙ could be obtained, and it was found that the values agreed well with those determined from the mixture of the two complexes. This also indicates that the intensities determined for the monodinitrogen complex must be correct. The intensity of the M–N₂ stretching vibration in the bisdinitrogen complexes has not been determined because of the uncertainty in assigning the band that corresponds to this vibration. In the case of the monodinitrogen complexes, the assignments of the M–N₂ stretching vibrations given by Borod'ko et al.[21] are followed. It was sometimes found that the M–N₂ band was broad, when the compound contained a considerable amount of the bisdinitrogen complex. This is due to overlapping of the M–N₂ band in the monodinitrogen complex of a band from the bis-

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dinitrogen complex. This fact could be concluded after the infrared spectrum of the pure bisdinitrogen complex was obtained. The intensities of the $M-N_2$ bands in the monodinitrogen complexes could then be corrected for this effect and it is the corrected values that are reported in Table 1. The correction amounts to about 10%.

The results of Table 2 show that the frequencies $v_{NN}$ are higher than corresponding $v_{NN}$ in the monodinitrogen complexes. This is also reasonable if it is the $d\pi - p\pi^*$-interaction which to the greatest extent determines the change in $v_{NN}$ (and $A_{NN}$), since the available $d$-electrons now have to go to two nitrogen molecules. A corresponding decrease in the absorption intensity is to be expected and is also found. These values are also found to follow the generalization given before in Fig. 2. This is demonstrated in Fig. 4. It can be seen from Fig. 4 that there is no large increase in intensity $A_{NN}$ for Os(NH$_3$)$_4$(N$_2$)$_2$I$_2$ dissolved in DMSO, which was found for the corresponding monodinitrogen complex. This large increase in intensity for the monodinitrogen complex has been suggested above to depend on solvation of the osmium complex ions by the $\geq S=O$ groups in the solvent. The association of the $\geq S=O$ groups to the metal ion must be strongest if the metal ion carries a high positive charge. As we observe a greater influence from the solvent for the monodinitrogen complex, it is reasonable that there is a smaller charge on the metal ion in the bisdinitrogen complex.

DISCUSSION

Qualitatively, the observed intensities of the $N-N$ stretching vibration can be discussed in terms of the degree of $d\pi - p\pi^*$ back donation from the metal ion to the dinitrogen ligand and the degree of $\sigma$-bonding from the lone-pair of the dinitrogen ligand to the metal ion. The situation is thus analogous to that for, e.g., cyanide complexes (cf. Ref. 28).

A high electron density in the antibonding $\pi$-orbitals of the dinitrogen group corresponds to an increase in the $N-N$ distance. Conversely, when the $N-N$ distance increases during the vibration there will be a flow of electrons into these antibonding $\pi$-orbitals. The $N-N$ stretching vibration is thus followed by a change of the electron density over the $M-N-N$ entity. This corresponds to a large variation of the dipole moment during the vibration which means a high infrared absorption intensity. As the osmium complexes have higher intensities of the $N-N$ stretching vibration than the ruthenium complexes, it is quite reasonable that the degree of $d\pi - p\pi^*$ back donation is greater for osmium than for ruthenium. As has been pointed out above, an effect that causes a weakening of the $N-N$ bond strengthens the $M-N_2$ bond to a corresponding extent. Thus, when the degree of $d\pi - p\pi^*$ back donation is high, the disturbance of the dinitrogen molecule must be considerable and there will be a decrease in the $N-N$ bond order. A high intensity value of the $N-N$ stretching vibration thus gives an indication of a strong metal-dinitrogen bond. It has been reported that the osmium dinitrogen complexes are more stable than the ruthenium dinitrogen complexes both in the solid state and in solution.

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To get approximate information about the polarity of the $M-N_2$ bond, the fixed charge model has been applied. The complex is considered as a two-atomic molecule consisting of $(\text{NH}_3)_5M$ and $N_2$. For a two-atomic molecule, the absorption intensity is related to the dipole moment of the molecule by the formula (cf., e.g., Ref. 29):

$$A = \frac{\pi N}{3c^2 \times 10^8 \mu_{\text{red}}} \left( \frac{d\mu}{dr} \right)^2$$

Here $N$ and $c$ stand for the Avogadro number and the velocity of light. $\mu_{\text{red}}$ is the reduced mass and has, in the present case, been calculated from the above-mentioned molecular fragments. $\mu$ is the dipole moment and $r$ the interatomic distance. In the calculation of $d\mu/dr$, the mean values of the intensities of the $M-N_2$ stretching vibration for the chloride and bromide complexes in aqueous solution were used; for the Ru complexes $A = 2.05 \times 10^3 \text{ M}^{-1} \text{ cm}^{-2}$ and for the Os complexes $A = 4.20 \times 10^3 \text{ M}^{-1} \text{ cm}^{-2}$. If it is assumed that the charges on the molecular fragments are $+q$ and $-q$ (atomic units), the dipole moment is

$$\mu = rq$$

(1)

If, as stated in the fixed charge model, it is assumed that $q$ does not change with $r$, it follows that

$$d\mu/dr = q$$

(2)

For the Ru complexes one obtains

$$d\mu/dr = \pm 3.45 \times 10^{-10} \text{ e.s.u.}$$

If the value of $d\mu/dr$ is expressed by using the electronic charge, $4.8 \times 10^{-10}$ e.s.u., as the unit one obtains

$$d\mu/dr = q = 0.72 \text{ a.u.}$$

Correspondingly, for the Os complexes one obtains

$$d\mu/dr = \pm 5.1 \times 10^{-10} \text{ e.s.u.}$$

and

$$d\mu/dr = q = 1.1 \text{ a.u.}$$

It is of interest to compare these values with a theoretical calculation for a hypothetical $\text{Fe(O)}-N_2$ complex, made by Kruglyak and Yatsimirskii. These authors found the following charge distribution within the complex

$$\text{Fe} \quad -0.432 \quad +1.01 \quad -0.576$$

In this calculation, both the $\sigma$-bond and the $\pi$-bond are taken into consideration. In Fig. 5, the $q$-values have been plotted against the atomic number of the metal together with the theoretical value of the $\text{Fe}-N_2$ complex (0.43). The atomic number of the metal ($Z_M$) is an arbitrary choice. A monotonous

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Fig. 5. The charge separation $q$ as a function of the atomic number of the metal ($Z_M$), Fe (○), Ru (△), and Os (□).

The function is obtained and the value of the Fe–N₂ complex falls on the curve. Now it must be pointed out that the fixed charge model is an oversimplification. It is quite reasonable that there is a variation of charge with the interatomic distance. A better approach is then to include in eqn. (2) a term relating to this, viz. $\frac{dq}{dr}$ which can be derived from eqn. (1), i.e.

$$\frac{d\mu}{dr} = q + r \frac{dq}{dr}$$

(3)

$q$ in eqn. (3) is, however, not known and therefore it is difficult to determine $\frac{dq}{dr}$. None the less, the trend in the calculated values of charge separations is of importance, viz. that the charge separation increases when the diminishing of the N–N bond order becomes greater. It is also of interest to observe that as the charge calculated on the Fe atom is negative, it must be the $\sigma$-bond from the dinitrogen group to the metal atom that to the greatest extent determines the equilibrium charge distribution within the complex. The $\sigma$-bond thus increases in the order Fe < Ru < Os. This is to be compared with the earlier suggestion that it is the $d\pi - p\pi^*$ back donation that to the greatest extent determines the change in frequency and intensity. Consequently, it is a co-operation of the two types of bonding that is responsible for the charge distribution within the complexes.

The results of the investigation of the osmium and ruthenium dinitrogen complexes show that the lower $\nu_{NN}$ is and the higher $\Delta_{NN}$ is, the greater is the disturbance of the dinitrogen molecule. It would therefore be of interest to investigate other dinitrogen complexes both with lower and higher frequencies $\nu_{NN}$, in order to cover a large frequency range and to see if the connection between $\nu_{NN}$ and $\Delta_{NN}$ also holds for other dinitrogen complexes. Of special interest are rhenium dinitrogen complexes, which have recently been prepared by Chatt et al. The authors find that in some of the complexes, $\nu_{NN}$ is as low as 1922 cm⁻¹. This indicates a strong perturbation of the dinitrogen molecule and consequently the metal-dinitrogen bond must be stronger in these complexes than in the ruthenium and osmium dinitrogen complexes investigated here. It could perhaps be expected that, depending on the strong bond between metal and nitrogen, it would be possible to find in

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these systems a reduction-oxidation cycle which could result in nitrogen fixation. It could therefore be of importance to investigate such complexes as well. Measurements on rhenium dinitrogen complexes together with two iridium dinitrogen complexes have also been performed and will be described later.32

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