

## The Influence of Anions on the Infrared Absorption Intensity of the N—N Stretching Vibration in Some Ruthenium and Osmium Dinitrogen Complexes

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The infrared absorption intensity of the N—N stretching vibration of the  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{3+}$  and  $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$  complexes, extracted into butanol and pentanol with suitable reagents, has been measured. As extraction reagents the following anions have been used: Diethyldithiocarbamate, dtc, ethylxanthogenate, exan, diphenylthiocarbazone, dit, and diphenyldithiocarbamate, dpdte. It has been found that the intensities  $A_{\text{NN}}$  are lower in these complexes than in the corresponding halide complexes (*cf.* Table 1, Ref. 1). The frequencies  $\nu_{\text{NN}}$ , on the other hand, have changed very little compared with those in the halide complexes. It is concluded that the decrease in intensity depends on the polarizability of the anion, *viz.* so that it is the change in the dipole moment of the whole extracted unit, *e.g.*  $\text{M}(\text{NH}_3)_5\text{N}_2(\text{dtc})_2$ , during the normal vibration which determines the intensity of the N—N band.

As has been pointed out in an earlier paper,<sup>1</sup> both the frequency and the intensity of the N—N stretching vibration in the ruthenium and osmium dinitrogen complexes were strongly dependent on the counter-ions present in the solid salts. Also in solution an outer-sphere effect on the intensity of the N—N stretching vibration has been found.<sup>1</sup> To get further information about the influence of counter-ions on frequency and intensity of the N—N stretching vibration, some sulphur containing anions have been complexed with the dinitrogen complexes. Since these kinds of ions are strongly polarizable, it could perhaps be expected that they could have an effect on the intensity of the N—N stretching vibration. Attempts have been made to prepare salts of the ruthenium and osmium complexes with these bulky anions, but it was difficult to get a crystalline product. It was, however, possible to extract the complexes into organic solvents and therefore this investigation of the dinitrogen complexes could be performed.

*Determination of intensity from measurements in organic solvents.* As a conventional determination of the metal concentration in the organic phase is

difficult to carry out, the molar absorption coefficient ( $\epsilon_{\text{org}}$ ) has been determined by measuring the absorbance at the maximum of the N—N stretching vibration band after extraction for a series of mixtures with different ratios between the volume of the organic and the aqueous phase,  $v_{\text{org}}$  and  $v_{\text{aq}}$ , respectively.

Then, if  $C_{\text{M}'}$  is the concentration of  $\text{M}(\text{NH}_3)_5\text{N}_2^{2+}$  (M is Ru or Os) in the "original" aqueous solution, which also contains  $\text{C}_\text{L}\text{M}$  anions, the following relation is valid

$$C_{\text{M}'}v_{\text{aq}} = C_{\text{M aq}}v_{\text{aq}} + C_{\text{M org}}v_{\text{org}} \quad (1)$$

If now  $v_{\text{org}}/v_{\text{aq}} = q$  and  $C_{\text{M org}}/C_{\text{M aq}} = \phi$

$$\text{then} \quad C_{\text{M}'} = C_{\text{M org}}(\phi^{-1} + q) \quad (2)$$

This relation presupposes that  $v_{\text{org}}$  and  $v_{\text{aq}}$  do not change on equilibration.

Now Beer's law is introduced

$$(\log T_0/T)_{\text{org}} = \epsilon_{\text{org}} d C_{\text{M org}} \quad (3)$$

and hence

$$\frac{d C_{\text{M}'}}{(\log T_0/T)_{\text{org}}} = \frac{1}{\epsilon_{\text{org}}}(\phi^{-1} + q) \quad (4)$$

Consequently, a plot of  $d C_{\text{M}'}/(\log T_0/T)_{\text{org}}$  against  $q$  will yield the value of  $\epsilon_{\text{org}}$  at the frequency of measurement and thus from eqn. (3) the concentration  $C_{\text{M org}}$ . Then  $\epsilon_{\text{org}}$  can be calculated at any frequency from a spectrum of the organic phase. The intensity of the absorption band could then be calculated through graphical integration as described before.<sup>1</sup> The method given above has been applied by Larsson and Norman<sup>2</sup> and has been used in circular dichroism measurements on the (+)-Coen<sub>3</sub> ion with various ligands in organic solvents.

## EXPERIMENTAL

**Chemicals.**  $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$  and  $\text{Os}(\text{NH}_3)_5\text{N}_2\text{Cl}_2$ , prepared and analyzed as described before,<sup>1</sup> have been used. As extraction reagents the following anions have been used: Diethyldithiocarbamate, dtc, ethylxanthogenate, exan, diphenylthiocarbazone, dit, and diphenyldithiocarbamate, dpdte. All these chemicals were of *purissimum* quality or better. Concentrated aqueous solutions of the anions were prepared and the solutions were filtered before use. Diphenylthiocarbazone could not be dissolved in water but was dissolved in diluted ammonia to get the enol form of this reagent. Water-saturated butanol and pentanol were used as organic solvents. To avoid changes of  $v_{\text{org}}$  and  $v_{\text{aq}}$  on equilibration, the butanol and the pentanol were water-saturated before use. The solutions were equilibrated by shaking by hand for a few minutes and then the solutions were centrifuged and infrared spectra were recorded on the organic phase.

**Measurements.** The infrared spectra were recorded on the same instrument as mentioned before.<sup>1</sup> As the absorption bands were of low intensity, all spectra were recorded with  $5 \times$  ordinate expansion. Cells with  $\text{CaF}_2$ -windows and 0.2 mm teflon spacers were used. At least two series of measurement on each complex with different  $C_{\text{M}'}$  in the two organic solvents have been performed. To check if the above-mentioned extraction reagents have any absorption band in the region  $2200-2000 \text{ cm}^{-1}$ , where the N—N stretching vibration band appears, infrared spectra have been recorded on the reagents

in the solid state. Ethylxanthogenate and diphenylthiocarbazono show no absorption in this spectral region but for the diethyldithiocarbamate a small absorption band appears. Depending on the low concentration of anion in the organic phase, no influence on the N-N absorption band has been found. This has also been checked by extraction of  $\text{Zn}(\text{dte})_2$  of about the same concentration as the extracted Ru and Os complexes into butanol. The butanol shows no absorption within  $2200-2000\text{ cm}^{-1}$ . Diphenyldithiocarbamate, on the other hand, appears to have a strong absorption band between  $2100\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$  and it was also found that the sodium diphenyldithiocarbamate itself was extracted into the organic solvent. For these reasons it was impossible to distinguish the N-N band of the extracted osmium complex. The N-N stretching vibration band in  $\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dpdte})_2$  could, however, be detected if the reference cell contained organic solvent shaken with the dpdte solution. As the N-N absorption bands had a very low intensity and it thus was difficult to determine  $\epsilon_{\text{org}}$  with any accuracy, only one series of measurement of surveying character in butanol has been performed.

The measurements on the complexes  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  and  $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$  with the anions dte and exan could be performed in both butanol and pentanol without any complications.

When the dit solution was added to the aqueous solution of  $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$  to get the "original" aqueous solution, a precipitate was formed. The precipitate was, however, soluble in the organic solvents used. The mixing procedure was changed so that at first the  $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$  solution was poured into tubes and then the same volume of the dit solution was added to each tube. Each tube contained then the complex  $\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$  in the same amount. Then various volumes of the organic solvent were added to the tubes and  $\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$  could be extracted into the organic phase and the measurements could be performed. This complication was not met with  $\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$ .

Attempts to extract the above-mentioned complexes into other organic solvents like 1-octanol, methyl isobutyl ketone and chloroform have also been made, but it was found that the complexes were extracted very poorly into these solvents and therefore only butanol and pentanol have been used.

## RESULTS

A typical plot for the determination of  $\epsilon_{\text{org}}$  at the maximum of the N-N absorption band in  $\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$  is shown in Fig. 1 both in butanol and pentanol and at two values of  $C_M'$ . From the parallelism of the lines it follows that  $\epsilon_{\text{org}}$  is not dependent on  $C_M'$ . The different intercepts for  $q = 0$ , indicating

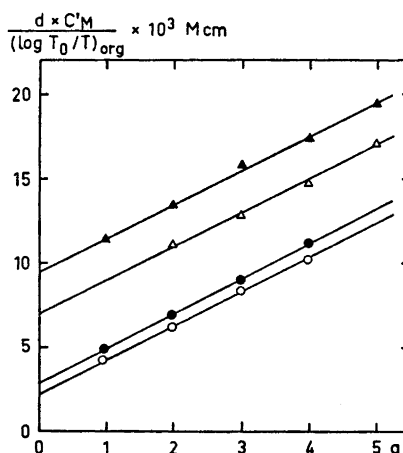


Fig. 1. Determination of  $\epsilon_{\text{org}}$  at the maximum of the N-N absorption band in  $\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$  in butanol ( $C_M' = 10.7\text{ mM}$  (O) and  $C_M' = 13.4\text{ mM}$  (●)) and in pentanol ( $C_M' = 12.4\text{ mM}$  (Δ) and  $C_M' = 16.3\text{ mM}$  (▲)).

different partition quotients  $\phi$ , originate from the fact that the concentration of free anions is smaller with higher  $C_M'$  than with lower  $C_M'$  and that  $\phi$  increases with the concentration of free anions. The measurements in the two solvents give almost parallel lines, so  $\epsilon_{\text{org}}$  must be about the same. On the other hand, the result of the measurements in pentanol shows greater intercepts at  $q=0$ , which indicates that pentanol has a lower extraction ability than butanol.

The results of the measurements on the other complexes give also parallel lines in the determination of  $\epsilon_{\text{org}}$  in analogy with Fig. 1, but the slopes of the lines were different for the investigated complexes.

The absorption intensity  $A_{\text{NN}}$  of the N–N stretching vibration in the various complexes has been calculated as described above and the results are given in Table 1. The intensities  $A_{\text{NN}}$  for the osmium complexes are higher than

Table 1. Intensity measurements on ruthenium and osmium dinitrogen complexes in organic solvents.

Metal complex	Solvent	$\nu_{\text{NN}}$ $\text{cm}^{-1}$	$\epsilon_{\text{NN}}$ $\text{M}^{-1}\text{cm}^{-1}$	$A_{\text{NN}} \times 10^{-4}$ $\text{M}^{-1}\text{cm}^{-2}$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$	Butanol	2105	$250 \pm 25$	$2.8 \pm 0.3$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$	Pentanol	2105	$320 \pm 30$	$2.4 \pm 0.3$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{exan})_2$	Butanol	2110	$425 \pm 50$	$4.2 \pm 0.4$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{exan})_2$	Pentanol	2110	$425 \pm 50$	$3.3 \pm 0.3$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$	Butanol	2110	$260 \pm 25$	$2.1 \pm 0.2$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$	Pentanol	2110	$260 \pm 25$	$1.6 \pm 0.2$
$\text{Ru}(\text{NH}_3)_5\text{N}_2(\text{dpdte})_2$	Butanol	2110	$170 \pm 25$	$1.2 \pm 0.1$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$	Butanol	2027	$480 \pm 50$	$4.5 \pm 0.4$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$	Pentanol	2027	$500 \pm 50$	$3.7 \pm 0.4$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{exan})_2$	Butanol	2033	$900 \pm 100$	$7.8 \pm 0.7$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{exan})_2$	Pentanol	2033	$900 \pm 100$	$6.5 \pm 0.5$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$	Butanol	2033	$400 \pm 40$	$3.2 \pm 0.3$
$\text{Os}(\text{NH}_3)_5\text{N}_2(\text{dit})_2$	Pentanol	2033	$400 \pm 40$	$2.7 \pm 0.3$

those for the ruthenium complexes. This is also to be expected since the frequencies  $\nu_{\text{NN}}$  are lower in the osmium complexes than in the ruthenium complexes. On the other hand, the intensities  $A_{\text{NN}}$  are found to be *lower* than those measured on the halide complexes (*cf.* Table 1, Ref. 1). This is found for both the ruthenium and the osmium complexes as can be seen from Table 1. Only the xanthogenate complexes measured in butanol give intensities ( $A_{\text{NN}}$ ), which are about the same as those found for the halide complexes in the solid state. The frequency ( $\nu_{\text{NN}}$ ) in these extracted complexes has only been changed very little compared with the frequency  $\nu_{\text{NN}}$  in the halide complexes. This fact indicates that if intensity is plotted against frequency the values fall outside the rough generalization given in Ref. 1. It can also be seen from Table 1 that the frequencies  $\nu_{\text{NN}}$  are almost the same, independent of the anion within the ruthenium and osmium complexes, despite the variation in intensity. One

also observes that the intensity becomes lower as the size of the anion increases. This fact must denote that the anion influences the intensity of the N-N stretching vibration.

On comparison between the intensities measured in butanol and pentanol, it was always observed that the values in butanol were about 20 % higher than those in pentanol, despite the fact that the  $\epsilon_{\text{NN}}$ -values were about the same. This is a remarkable solvent effect on the intensity and will be discussed below.

### DISCUSSION

The fact that the intensity of a stretching vibration in a metal complex is dependent on the anion has been dealt with earlier.<sup>3,4</sup> Thus it has been found that for, *e.g.*,  $\text{Co}(\text{NH}_3)_6^{3+}$  with iodide as anion the intensity of the Co-N stretching vibration was lower than if the anions were, *e.g.*,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ .<sup>4</sup> It has been suggested<sup>4</sup> that the explanation of these results is the greater polarizability of the iodide ion. As the anions used in this investigation contain sulphur and are therefore strongly polarizable, it is reasonable that they also could effect the intensity of the N-N stretching vibration. Thus, it is quite probable that it is the dipole moment of whole the extracted unit, *e.g.*  $\text{M}(\text{NH}_3)_5\text{N}_2(\text{dte})_2$ , the change of which during the normal vibration determines the intensity for the observed band. As the M-N-N group gives rise to strong infrared absorption, charges will move to and fro over the group during the vibration. This charge change induces a dipole moment in the easy polarizable outer-sphere, which is of opposite direction to that of the M-N-N group. Thus, the total dipole moment will be smaller which causes a lower intensity of the N-N stretching vibration. The fact that the intensity  $A_{\text{NN}}$  decreases with increasing size of the anion supports the view that it is the polarizability of the anion that influences the dipole moment change of the entire extracted unit. It is, however, remarkable that the frequency  $\nu_{\text{NN}}$  does not change when the intensity  $A_{\text{NN}}$  is changed. This probably means that the electronic structure within the M-N-N entity is not changed and that the force constant of the N-N band is practically constant.

The dependence of infrared intensity on solvent parameters, *e.g.* dielectric constant, has been discussed frequently.<sup>5,6</sup> In a recent paper by Tanaka *et al.*<sup>7</sup>, it has been suggested rather that intermolecular forces play a more important role compared to the effect due to the bulk medium. It has also been found by Larsson<sup>8</sup> that the halfwidth and also the intensity of the Hg-Cl asymmetric stretching vibration band were different in various solvents. It has then been suggested<sup>8</sup> that the halfwidth of the absorption band could be used as a measure of the solute-solvent interaction. A broad band would thus indicate low solute-solvent interaction. From the work of Shimozava and Wilson<sup>9</sup> it follows that the broadness of an absorption band of a stretching vibration is a measure of the ease of rotation of the molecule in question. In the present investigation, the absorption bands of the N-N stretching vibration were found to be broader in butanol than in pentanol. Thus, the possibility of easy rotation of the molecules could be greater in butanol than in pentanol. The solute-solvent interaction could be smaller in butanol than in pentanol. These

results are of course remarkable as the solvents butanol and pentanol are very alike. On the other hand, as has been pointed out above, the used solvents were water-saturated. Thus, as butanol contains more water than pentanol, it is quite reasonable that it could be the water content in the alcohols, which causes that the intensity of the N – N stretching vibration band is different in the two solvents.

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