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On the Infrared Absorption Intensity of the N—N Stretching Vibration in Some Iridium and Rhenium Dinitrogen Complexes

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The infrared absorption intensity of the N – N stretching vibration has been measured for the complexes

$IrClN_2(PPh_3)_2$, $IrClN_2(C_8H_{12}O_4)(PPh_3)_2$,
$ReClN_2(Ph_2PCH_2PPh_2)_2$, $ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$,
$ReClN_2(Ph_2PCH=CHPPh_2)_2$, $ReClN_2(PMe_2Ph)_4$ and
$ReClN_2(PPh_2Me)_4$

in the solid state and in solution. It has been found that the intensity (A_{NN}) increases with decreasing frequency (ν_{NN}), which is in agreement with a model of $d\pi - p\pi^*$ back donation. The generalization given before [1] has now been extended to cover a greater frequency range. It is concluded that as A_{NN} is greater for Re than for Ir complexes, the degree of backbonding increases from Ir to Re. From the obtained intensities (A_{NN}) in chloroform solution for some of the complexes, the dipole moment derivative $d\mu/dr$, has been calculated. From this quantity and the effective charges on the nitrogen atoms, it was possible to get an approximate value of the variation of charge with interatomic distance dq/dr. An estimation of dq/dr has also been performed from experimentally determined charges on the nitrogen atoms and N – N distances calculated from Badger's rule. By comparison between the dq/dr values obtained in different ways, it has been possible to find out which nitrogen atom that carries which charge. Thus, it has been concluded that the terminal nitrogen atom in the complexes carries the smallest negative charge and that the inner nitrogen atom is the most negative one.

The results of this and the earlier [1] investigation are compared with the result of an infrared study of chemisorbed dinitrogen on nickel by Eischens and Jacknow. The similarities between metal dinitrogen complexes and the adsorbed dinitrogen nickel complex are discussed.

In a previous paper,[1] infrared absorption intensities of the N – N stretching vibration in dinitrogen complexes of ruthenium and osmium have been reported. It was found [1] that the intensity of the N – N stretching vibration (A_{NN}) increases with decreasing frequency (ν_{NN}), which is in agreement with a model of $d\pi - p\pi^*$ back donation. It was concluded that the lower the ν_{NN}

and the higher the A_{NN}, the greater was the disturbance of the dinitrogen molecule. It would therefore be of interest to investigate other dinitrogen complexes both with lower and higher frequencies ν_{NN} in order to cover a great frequency range. Therefore, this infrared study will deal with iridium and rhenium dinitrogen complexes. Collman *et al.*[2-4] have reported the preparation and properties of two iridium dinitrogen complexes, *viz.* $IrClN_2(PPh_3)_2$ and $IrClN_2(C_8H_{12}O_4)(PPh_3)_2$, which show quite different frequencies (ν_{NN}). The infrared absorption intensity of the N-N stretching vibration in these two iridium dinitrogen complexes has been measured in the present investigation. Of special interest are rhenium dinitrogen complexes, which recently have been prepared by Chatt *et al.*[5] These authors find that in some of these complexes, the frequency ν_{NN} is as low as 1922 cm^{-1}. This fact indicates a strong perturbation of the dinitrogen molecule and consequently the metal-dinitrogen bond must be stronger in these complexes than in the previously investigated ruthenium and osmium dinitrogen complexes. Intensity measurements on some rhenium dinitrogen complexes are presented here.

Triphenylphosphine and the other phosphines used show strong absorption in the frequency range 600-400 cm^{-1}. This fact makes it impossible to observe the weak band corresponding to the $M-N_2$ stretching vibration in the complexes. This investigation is therefore limited to intensity measurements on the N-N stretching vibration in the complexes.

EXPERIMENTAL

Preparation of iridium dinitrogen complexes. *$IrClN_2(PPh_3)_2$* was commercially obtained from Strem Chemicals Inc. as a pure crystalline compound. Its purity was confirmed by elemental analysis of carbon, hydrogen and nitrogen. (Found: C 53.4; H 4.23; N 3.20. Calc.: C 55.4; H 3.88; N 3.58.) The obtained analysis value of nitrogen is about 10 % lower than the calculated one, which may be because the compound is not quite pure or due to difficulties of obtaining a correct analysis value when such an instable compound is analysed. It is thus quite reasonable that the measured intensity value (A_{NN}) is somewhat too low. As this complex has been prepared according to Collman *et al.*[4] from Vaska's [6] iridium complex and α-furoyl azide, the absence of carbonyl absorption in the infrared spectrum has been checked. *$IrClN_2(C_8H_{12}O_4)(PPh_3)_2$* was prepared from the dinitrogen complex above and diethyl maleate according to Collman *et al.*[4] Its purity was checked by the infrared spectrum and by elemental analysis. (Found: C 55.9; H 5.34; N 2.37. Calc.: C 55.5; H 4.41; N 2.94.) For this iridium complex also the analysis value of nitrogen is lower than the calculated one. For the same reasons as above for $IrClN_2(PPh_3)_2$, it is reasonable that the obtained intensity value (A_{NN}) for the diethyl maleate dinitrogen complex can be about 10 % too low.

The two iridium dinitrogen complexes above are not stable in air, but must be kept in a nitrogen atmosphere.

Preparation of rhenium dinitrogen complexes. The starting chemicals, rhenium metal and triphenylphosphine, were of *purissimum* quality. From these chemicals, $ReOCl_3(PPh_3)_2$ was prepared by a minor modification of the method given by Chatt and Rowe.[7] Monobenzoyl hydrazine was prepared from ethyl benzoate and hydrazine hydrate according to a method given by Dilworth.[8] Ethyl benzoate and hydrazine hydrate were of *purum* quality. Then the intermediate chelated benzoylazo complex of rhenium(III) was prepared.[8] Rhenium dinitrogen complexes with various phosphines could then be prepared according to Chatt *et al.*[5,8] The phosphines used, bis(1,2-diphenylphosphino)methane, bis(1,2-diphenylphosphino)ethane, *cis*-bis(1,2-diphenylphosphino)ethylene and methyldiphenylphosphine, were obtained from Strem Chemicals Inc. Dimethylphenylphosphine was obtained from K & K Laboratories Inc. The phosphines were used without further treatment. The following rhenium dinitrogen complexes have been prepared: $ReClN_2(Ph_2PCH_2PPh_2)_2$ (I), $ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$ (II), $ReClN_2(Ph_2PCH=CHPPh_2)_2$ (III), $ReClN_2(PMe_2Ph)_4$ (IV) and $ReClN_2(PPh_2Me)_4$ (V). In the formulas above, Me and Ph stand for methyl and phenyl. The purity of the prepared complexes has been checked only by infrared spectra, *viz.* if the complexes give strong $N-N$ absorption and if the intensity (A_{NN}) of the $N-N$ bands is of about the same order of magnitude as the intensity (A_{NN}) measured for the ruthenium and osmium dinitrogen complexes,[1] then the complexes are assumed to be pure. Only compound V was found to be impure and intensity values for this complex could therefore not be used. The rhenium dinitrogen complexes are generally very stable. They are much more stable than the above mentioned iridium dinitrogen complexes, and can therefore be kept in air for a long time without decomposition.

Infrared spectral measurements. The infrared spectra were recorded with a Perkin Elmer Spectrophotometer Model 521 equipped with a linear absorbance potentiometer. All spectra on the $N-N$ stretching vibration 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. Chloroform, benzene, and tetrahydrofuran (THF) were used as solvents. Chloroform and benzene were of spectroscopic grade and tetrahydrofuran of analytical grade. The solvents were dried by shaking with molecular sieves 5 Å for a few minutes before use. Cells with CaF_2-windows and 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. The measurements on iridium and rhenium dinitrogen complexes in solution were performed rapidly, since it was found that the complexes were not stable in solution. Spectra were recorded immediately after complete dissolution of the compounds. Two or three spectra were recorded after each other, and a small decrease in absorbance for each spectrum was found. The decrease in intensity was, however, very small for spectra recorded in this way after each other. Reported intensity values are generally those calculated from the first recorded spectrum. Only $IrClN_2(C_8H_{12}O_4)(PPh_3)_2$ was found to decompose more rapidly than the other complexes investigated. This complex shows an $N-N$ band at 2105 cm^{-1} in the infrared spectrum of the chloroform solution besides the $N-N$ band at 2200 cm^{-1}. This fact indicates that the complex decomposes and also gives the complex from which it has been prepared. As $IrClN_2(PPh_3)_2$ has been measured before, it was possible to determine its concentration and thereby also the concentration of the iridium diethylmaleate dinitrogen complex, which gives the band at 2200 cm^{-1}. The intensity of the band at 2200 cm^{-1} was found to decrease with time. The reported intensity value on this iridium complex has been obtained through extrapolation to zero time. It was also found that the decrease in absorbance of the $N-N$ band at 2105 cm^{-1} was greater than when $IrClN_2(PPh_3)_2$ alone was measured. When the two $N-N$ bands at 2105 cm^{-1} and 2200 cm^{-1} decrease in absorbance and intensity with time a new band at 2250 cm^{-1} appears. This band increases in intensity with time, and can probably be assigned to a common decomposition product of the two iridium dinitrogen complexes.

The areas under the bands were determined with a planimeter. The values obtained were then multiplied with ln 10 to get integrated absorption intensities relating to Beer's law. The reported intensity values are the mean values of the intensities determined at different concentrations. The error limits give the maximum deviation from the mean value.

RESULTS

The results of the intensity measurements on the iridium dinitrogen complexes are given in Table 1. The good agreement of the intensity values (A_{NN}) determined in various dispersion media for the complex $IrClN_2(PPh_3)_2$ shows that the intensity is not dependent on the medium. The agreement of the intensity values for $IrClN_2(C_8H_{12}O_4)(PPh_3)_2$ is not so good, probably depending

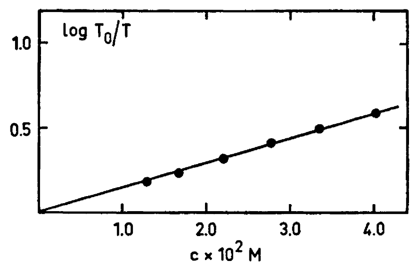

Fig. 1. The Beer's law plot of the absorption of the N–N stretching vibration at 2105 cm^{-1} in $IrClN_2(PPh_3)_2$ in chloroform solution.

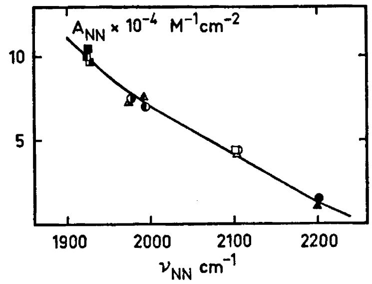

Fig. 2. The correlation between intensity A_{NN} and frequency ν_{NN} for the iridium and rhenium dinitrogen complexes. $IrClN_2(PPh_3)_2$ in KBr (○), $CHCl_3$ (△) and C_6H_6 (□). $IrClN_2(C_8H_{12}O_4)(PPh_3)_2$ in KBr (●) and $CHCl_3$ (▲). $ReClN_2(Ph_2PCH_2PPh_2)_2$ in KBr (◐) and $CHCl_3$ (◭). $ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$ in KBr (◑) and $CHCl_3$ (◮). $ReClN_2(PMe_2Ph)_4$ in KBr (■), $CHCl_3$ (◧) and C_6H_6 (◨).

on the instability of this complex in solution and thereby the difficulty of obtaining a correct intensity value. The frequencies (ν_{NN}) in the two iridium dinitrogen complexes are quite different. In the diethylmaleate complex, the frequency (ν_{NN}) is about 100 cm^{-1} higher than in $IrClN_2(PPh_3)_2$. This fact indicates a reduction of the $d\pi - p\pi^*$ back donation, which is as expected since the olefin competes with dinitrogen for the available *d*-electrons. A corresponding decrease in the absorption intensity is to be expected and is also found.

The results of the infrared absorption intensity measurements on the rhenium dinitrogen complexes are collected in Table 2. It can immediately be seen that there is a good agreement in the measured intensity values (A_{NN}) for different dispersion media. The intensity is thus apparently not dependent on the medium. The complexes I and II show in the infrared spectrum in the solid state (KBr) two bands assigned to the N–N stretching vibration. This fact indicates a crystal effect, since in solution only one N–N band is found.

Table 1. The results of the absorption intensity measurements on the iridium dinitrogen complexes.

Metal complex	Dispersion medium	ν_{NN} cm^{-1}	ε_{NN} M^{-1} cm^{-1}	$A_{NN} \times 10^{-4}$ M^{-1} cm^{-2}
$IrClN_2(PPh_3)_2$	KBr	2103	690 ± 25	4.2 ± 0.3
	$CHCl_3$	2105	725 ± 25	4.2 ± 0.3
	C_6H_6	2103	925 ± 25	4.4 ± 0.3
	THF	2103	900 ± 25	4.2 ± 0.3
$IrClN_2(C_8H_{12}O_4)(PPh_3)_2$	KBr	2202	340 ± 40	1.5 ± 0.2
	$CHCl_3$	2200	200 ± 20	1.1 ± 0.1

Table 2. The results of the absorption intensity measurements on the rhenium dinitrogen complexes.

Metal complex	Dispersion medium	ν_{NN} cm^{-1}	ε_{NN} $M^{-1}\ cm^{-1}$	$A_{NN} \times 10^{-4}$ $M^{-1}\ cm^{-2}$
I. $ReClN_2(Ph_2PCH_2PPh_2)_2$	KBr	1973	870 ± 50	7.0 ± 0.7
		1995	800 ± 50	
	$CHCl_3$	1993	1350 ± 50	7.6 ± 0.4
II. $ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$	KBr	1978	1350 ± 100	7.5 ± 0.4
		1930	500 ± 50	
	$CHCl_3$	1975	1000 ± 50	7.3 ± 0.3
III. $ReClN_2(Ph_2PCH=CHPPh_2)_2$	KBr	1965	700 ± 50	6.0 ± 0.4
	$CHCl_3$	1970	850 ± 50	5.7 ± 0.3
IV. $ReClN_2(PMe_2Ph)_4$	KBr	1925	1600 ± 150	10.5 ± 0.5
	$CHCl_3$	1924	1600 ± 50	10.0 ± 0.3
	C_6H_6	1928	2600 ± 100	9.7 ± 0.3
V. $ReClN_2(PPh_2Me)_4$	KBr	1928		
	$CHCl_3$	1922		
	C_6H_6	1925		

The complex III gives a somewhat lower intensity value than the complexes I and II, even though the frequency ν_{NN} is lower in complex III than in the complexes I and II. This is probably because the complex III is not quite pure. The frequencies ν_{NN} in the rhenium dinitrogen complexes are generally lower than in the iridium dinitrogen complexes investigated above. Consequently, the intensities (A_{NN}) are found to be higher in the rhenium complexes than in the iridium complexes. The highest intensity is found for complex IV, which also shows the lowest N – N stretching frequency. In accordance with the results given before,[1] the degree of $d\pi - p\pi^*$ back donation must be greater in the rhenium than in the iridium dinitrogen complexes. It will also mean that the disturbance of the dinitrogen molecule and the decrease in the N – N bond order must be greater in the rhenium than in the iridium dinitrogen complexes. A high intensity value of the N – N stretching vibration also gives indication of a strong metal – dinitrogen bond. In agreement with this, it may be noted that the rhenium dinitrogen complexes are more stable to chemical attack than the corresponding iridium complexes both in the solid state and in solution. In Fig. 2, the intensities A_{NN} are plotted against the frequency ν_{NN} for the rhenium and the iridium dinitrogen complexes. The generalization found before,[1] *viz.* the lower the frequency the higher the intensity, is found also for the rhenium and the iridium complexes. This correlation now covers a larger frequency range than before when only osmium and ruthenium dinitrogen complexes were available. It is evident from Fig. 2 that the intensity (A_{NN}) approaches zero, when the frequency (ν_{NN}) approaches the limiting value for the free dinitrogen molecule, *i.e.* 2331 cm^{-1} (*cf.* Ref. 9, p. 72). The previously [1] determined intensities (A_{NN}) for the ruthenium and osmium dinitrogen complexes are not given in Fig. 2, but on comparison with Figs. 2 and 4 in Ref.

1, it is obvious that these intensity values (A_{NN}) fall on this curve. The only exceptions are the intensity values for $Os(NH_3)_5N_2I_2$ dissolved in DMSO and DMF, which are higher than the highest intensity value for the rhenium dinitrogen complexes. The present results thus give further support for the theory that some special effect, *e.g.* a charge-transfer association of outer-sphere ligands, causes the high intensity of the N−N stretching vibration in $Os(NH_3)_5N_2I_2$ dissolved in DMSO and DMF.

To get approximate information about the polarity of the N−N bond, the fixed charge model has been applied. The complexes are considered as two-atomic molecules, *viz.* consisting of, *e.g.*, $(PhMe_2P)_4ClReN$ and N. For a two-atomic molecule, the absorption intensity is related to the dipole moment of the molecule by the formula (*cf.* Refs. 1 and 10)

$$A = \frac{\pi \cdot N}{3c^2 \times 10^3 \times \mu_{\text{red}}} \left(\frac{\mathrm{d}\mu}{\mathrm{d}r}\right)^2 \tag{1}$$

Here N and c stand for the Avogadro number and the velocity of light. μ_{red} is the reduced mass and has thus in the present case been calculated from the above mentioned molecular fragments. μ is the dipole moment and r the interatomic distance. In the calculation of $\mathrm{d}\mu/\mathrm{d}r$, intensities of the N−N stretching vibration measured in chloroform solution were used. Calculations have been performed on $IrClN_2(PPh_3)_2$ and on three of the rhenium dinitrogen complexes, *viz.* complex I, II, and IV (those which were obtained in pure form). If it is assumed that the charges on the molecular fragments are $+q$ and $-q$ (atomic units), the dipole moment is

$$\mu = rq \tag{2}$$

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

$$\mathrm{d}\mu/\mathrm{d}r = q \tag{3}$$

If, on the other hand, there is a variation of charge with interatomic distance, a term relating to this, *viz.* $\mathrm{d}q/\mathrm{d}r$, is easily derived from eqn. (2), *i.e.*

$$\mathrm{d}\mu/\mathrm{d}r = q + r\mathrm{d}q/\mathrm{d}r \tag{4}$$

Table 3. Calculated values of $\mathrm{d}\mu/\mathrm{d}r$ and the experimentally obtained charges on the nitrogen atoms ($M-N_1-N_2$) in the dinitrogen complexes of iridium and rhenium.

Metal complex	$\lvert\mathrm{d}\mu/\mathrm{d}r\rvert$ a.u.	Extended Hückel		CNDO		*Ab initio* SCF MO	
		$-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.	$-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.	$-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.
$IrClN_2(PPh_3)_2$	2.43	0.90	0.20	0.40	0.23	0.47	0.27
$ReClN_2(Ph_2PCH_2PPh_2)_2$	3.30	1.20	0.25	0.47	0.24	0.56	0.28
$ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$	3.24	1.20	0.25	0.47	0.24	0.56	0.28
$ReClN_2(PMe_2Ph)_4$	3.78	1.30	0.30	0.50	0.25	0.60	0.30

Calculated values of $\mathrm{d}\mu/\mathrm{d}r$ from eqn. (1) are given in Table 3. The values are relatively high, so it is reasonable to suppose that the charge varies with the interatomic distance. To determine $\mathrm{d}q/\mathrm{d}r$, the charges on the nitrogen atoms and the interatomic distance r must be known. The charges on the nitrogen atoms have been determined from ESCA measurements.[11] Nitrogen 1*s* electron spectra of the above mentioned dinitrogen complexes show two peaks indicating [12] different effective charges on the nitrogen atoms. ESCA measurements have also been performed on a number of nitrogen compounds and the obtained nitrogen 1*s* binding energies plotted against calculated charge on nitrogen atoms to get a correlation diagram. As different methods of charge calculation give different results, *viz.*, *e.g.*, extended Hückel, CNDO, and *ab initio* SCF MO calculations, three different correlation diagrams have been made. The charges on the nitrogen atoms in the dinitrogen complexes can thus be obtained if the measured nitrogen 1*s* binding energies are compared with the correlation diagrams. This will be presented in more detail in a subsequent paper.[11] The charges obtained on the nitrogen atoms in the various dinitrogen complexes are given in Table 3. The error in the determined charges is of course dependent on the error in the measured binding energies, which amounts to ± 0.1 eV. The error in the charges from extended Hückel calculations amounts then to about ± 0.05 a.u. In the other two methods of charge calculation, the error in the obtained charges is about ± 0.01 a.u.

When $\mathrm{d}\mu/\mathrm{d}r$ is calculated from eqn. (1), the absolute value of this quantity is obtained. Since the negative charge on the terminal nitrogen atom (q) increases from the iridium dinitrogen complex to the rhenium dinitrogen complexes (*cf.* Table 3), as does the $N-N$ distance calculated from Badger's rule [13] (see below), it follows that $\mathrm{d}q/\mathrm{d}r < 0$. Further, as also $q < 0$, both the terms on the right side of eqn. (4) get a negative sign and thus the negative sign on $\mathrm{d}\mu/\mathrm{d}r$ must be used in the calculations from eqn. (4).

The value of the distance r is more difficult to obtain, as it is the distance between two charge centers and it is difficult to know where the charge center on the big molecular fragment of the complex (*cf.* p.281) should be placed. To use the $N-N$ distance in eqn. (4) to obtain a value of $\mathrm{d}q/\mathrm{d}r$ is thus not correct. If one uses the $N-N$ distance in eqn. (4), a limit for the highest possible value of $-\mathrm{d}q/\mathrm{d}r$ is obtained. Similarly, a limit for the least possible value of $-\mathrm{d}q/\mathrm{d}r$ is obtained if the M-terminal N distance is used in the calculation. As an example, the complex $\mathrm{ReClN_2(PMe_2Ph)_4}$ is considered. A calculation of $-\mathrm{d}q/\mathrm{d}r$ on this complex $(M-N_1-N_2)$ from eqn. (4), using the distances [14] $r_{N_1-N_2}$ and r_{M-N_2} and under the assumption that the terminal nitrogen atom carries the greatest negative charge (CNDO calculated charges are used), yields the values 1.55 a.u. and 0.54 a.u., respectively. If the terminal nitrogen atom carries the smallest negative charge, the $-\mathrm{d}q/\mathrm{d}r$ values become 1.67 a.u. and 0.58 a.u., respectively. A corresponding calculation of $-\mathrm{d}q/\mathrm{d}r$ from *ab initio* SCF MO calculated charges gives the same values as those above. A true value of $-\mathrm{d}q/\mathrm{d}r$ is thus difficult to obtain, but probably this lies closer to the smallest than the highest of the two calculated values above. Calculations on the other dinitrogen complexes are more difficult to perform, since interatomic distances are not known. On the other hand, it is expected that the values of $-\mathrm{d}q/\mathrm{d}r$ do not deviate much from those obtained above for $\mathrm{ReClN_2(PMe_2Ph)_4}$.

From the example above it can also be seen that there is only a small difference in $-\mathrm{d}q/\mathrm{d}r$, when the terminal nitrogen atom carries the greatest or the smallest negative charge.

A way to obtain a more accurate value of the charge parameter $\mathrm{d}q/\mathrm{d}r$ is from experimentally determined charges on the nitrogen atoms and interatomic distances calculated from Badger's rule.[13] This rule is used in the following form:

$$r_e = \left(\frac{c_{ij}}{k_e}\right)^{1/3} + d_{ij} \tag{5}$$

Here r_e is the equilibrium interatomic distance in Ångström units and k_e is the force constant in megadynes per centimeter. c_{ij} and d_{ij} are constants characteristic of all diatomic molecules made up of one element in the ith row and one in the jth row of the periodic system. The force constants of the N–N bond in the dinitrogen complexes have been determined from the formula (*cf.*, *e.g.*, Ref. 9, p. 8)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu_{red}}} \tag{6}$$

μ_{red} is the reduced mass and has been calculated from the above mentioned molecular fragments (*cf.* p. 281) of the dinitrogen complexes. Then the interatomic distances could be determined from eqn. (5). The result is presented in Table 4. The charge on the nitrogen atoms in the various complexes is then

Table 4. The N–N distances in the dinitrogen complexes of iridium and rhenium calculated from Badger's rule.

Metal complex	ν_{NN} cm^{-1} in chloroform	k_{N-N} megadyn/cm	r_{N-N} Å
$IrClN_2(PPh_3)_2$	2105	3.61	1.052
$ReClN_2(Ph_2PCH_2PPh_2)_2$	1993	3.25	1.065
$ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$	1975	3.19	1.068
$ReClN_2(PMe_2Ph)_4$	1924	3.01	1.075

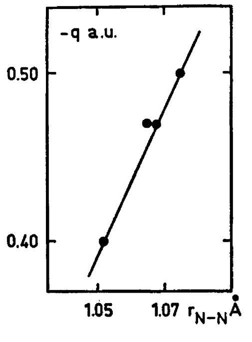

Fig. 3. A plot of CNDO calculated charges on the nitrogen atoms against N–N distances from Badger's rule.

plotted against the N – N distance determined from eqn. (5) and dq/dr is obtained from the slope of the straight line. A typical plot is given in Fig. 3. dq/dr has been determined both when the terminal nitrogen atom has the largest and the smallest negative charge. The result is presented in Table 5.

Table 5. The variation of charge with interatomic distance (dq/dr) determined from the obtained charges on the nitrogen atoms and the interatomic distances from Badger's rule.

Method of charge calculation	– dq/dr a.u. Terminal nitrogen atom carrying the largest negative charge	Terminal nitrogen atom carrying the smallest negative charge
Extended Hückel	8.5 ± 2.0	2.0 ± 1.0
CNDO	2.2 ± 0.4	0.5 ± 0.3
Ab initio SCF MO	2.8 ± 0.4	0.7 ± 0.3

It can be seen that the – dq/dr values vary with the method of charge calculation. On the other hand, the largest values of – dq/dr are obtained if the terminal nitrogen atom carries the largest negative charge. The error in the – dq/dr values is about 25 %. Considerably smaller values of – dq/dr are obtained if it is assumed that the terminal nitrogen atom carries the smallest negative charge. As the charge on the nitrogen atom in this case does not vary very much from one complex to another (*cf.* Table 3), the error in the – dq/dr values is about 50 %. Nevertheless, as these last values of – dq/dr are more in agreement with those obtained from infrared intensity data (*cf.* the example given above), it is concluded that the terminal nitrogen atom carries the smallest negative charge.

DISCUSSION

Recently, infrared intensity measurements of the N – N and C – O stretching vibrations in iridium(I) complexes have been reported by Darensbourg and Hyde.[15] These authors find that more meaningful conclusions about the π^*-acceptor ability of the dinitrogen and carbonyl ligands can be obtained from intensity measurements than in any other of the earlier investigations [4,16,17] based only on frequency data. It has been found [15] that the intensity of the N – N stretching vibration in $IrClN_2(PPh_3)_2$ is much smaller than the intensity of the C – O stretching vibration in $IrCl(CO)(PPh_3)_2$. From this fact it was concluded that the acceptor ability of the dinitrogen π^*-orbital is much smaller than that of carbonyl. This interpretation is in accordance with the result of the present investigation, *viz.* the higher the intensity of the N – N stretching vibration the greater the degree of $d\pi - p\pi^*$ back donation (measured by the effective charges on the nitrogen atoms determined with ESCA [11]). The intensity value (A_{NN}) obtained by Darensbourg and Hyde [15] is about 25 % lower than that obtained in the present investigation. Probably their compound $IrClN_2(PPh_3)_2$ was not pure. One preparation of $IrClN_2(PPh_3)_2$

obtained from Strem Chemicals Inc. by the present author gave the same intensity value A_{NN} as that reported in Ref. 15 and this compound was found impure. A further proof that the complex $IrClN_2(PPh_3)_2$, used by Darensbourg and Hyde,[15] probably was impure, is that intensity measurements of the C–O stretching vibration in $IrCl(CO)(PPh_3)_2$ by the present author gave the same intensity value as that reported by Darensbourg and Hyde,[15] *viz.* 8.7×10^4 M^{-1} cm^{-2}.

An essential result of the present investigation is that, through a combination of infrared intensity data with experimentally determined charges on atoms, it was possible to determine the variation of charge with interatomic distance ($\mathrm{d}q/\mathrm{d}r$). This quantity gives increased characterisation of the electronic structure of a molecule by indicating the degree of mobility of charges over the bond in question. In the estimation of $\mathrm{d}q/\mathrm{d}r$ it was also found possible to elucidate which nitrogen atom that carries which charge. In a recent paper by Leigh *et al.*[18] on ESCA measurements of two rhenium dinitrogen complexes, the smallest nitrogen 1*s* binding energy was assigned to the terminal nitrogen atom and consequently this is the most negative one. In the present work it has been shown rather that the terminal nitrogen atom carries the smallest negative charge.

It is also of interest to compare the result of the present investigation and the earlier results [1] of intensity measurements with an investigation of chemisorbed dinitrogen on nickel performed by Eischens and Jacknow.[19] It has been found [19] that dinitrogen chemisorbed on nickel gives rise to strong infrared absorption at 2202 cm^{-1}. This band has been assigned to the N–N stretching vibration in the structure $Ni-N\equiv N^+$. Further evidence for a linear structure is given by Chernikov *et al.*[20] The integrated absorption intensity of this N–N band has been calculated [21] to 3.96×10^4 M^{-1} cm^{-2}. This value is, however, somewhat uncertain, depending on the calculation procedure used. The frequency (ν_{NN}) of chemisorbed dinitrogen is the same as that obtained for the iridium diethylmaleate dinitrogen complex (*cf.* Table 1). The intensity value is somewhat higher, but still of the same order of magnitude (3.96×10^4 compared with 1.5×10^4). An estimation of the charge separation between Ni and N_2 has also been made in the following way. The intensity values of the $M-N_2$ stretching vibration in the ruthenium and osmium dinitrogen complexes (*cf.* Table 1, Ref. 1) are plotted against the N–N stretching frequency. The curve is drawn so that it passes through the point (0,2331), *i.e.* the limiting value for the free dinitrogen molecule (*cf.* Ref. 9, p. 72). This gives a maximum value of A_{M-N_2} at 2202 cm^{-1} of about 0.6×10^3 M^{-1} cm^{-2}, which can be seen in Fig. 4.

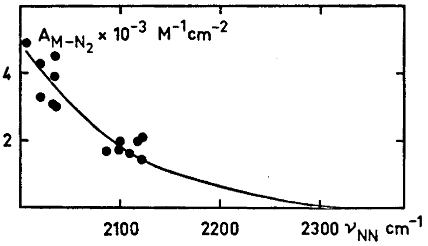

Fig. 4. An estimation of the intensity of the $Ni-N_2$ stretching vibration in the adsorbed dinitrogen complex from intensities (A_{M-N_2}) of ruthenium and osmium dinitrogen complexes (Table 1, Ref. 1) plotted against the N–N stretching frequency.

Then $d\mu/dr$ is calculated from eqn. (1) and the value 0.35 a.u. is obtained. This value can be compared with the corresponding values of charge separation calculated for the ruthenium and osmium dinitrogen complexes in a previous paper.[1] This illustrates the similarities between metal dinitrogen complexes and dinitrogen chemisorbed on a metal surface. It is therefore of great interest to perform ESCA measurements on gases adsorbed on metal surfaces and especially dinitrogen adsorbed on metal surfaces to get more information about the electronic structure of adsorbed species.

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