

Nitrogen Fixation. II.* On the Charge Distribution in Dinitrogen Complexes of Rhenium, Molybdenum and Tungsten

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ESCA spectra have been recorded for $\text{ReClN}_2(\text{L})_4$, *trans*- $\text{Mo}(\text{N}_2)_2(\text{L})_4$, *trans*- $\text{W}(\text{N}_2)_2(\text{L})_4$, *cis*- $\text{Mo}(\text{N}_2)_2(\text{L})_4$ and *cis*- $\text{W}(\text{N}_2)_2(\text{L})_4$, where $\text{L} = 1/2$ dppe, PMePh_2 or PMe_2Ph . For the *trans* complexes only dppe and PMePh_2 were used, for the *cis* complexes only PMe_2Ph . dppe = $(\text{Ph})_2\text{P}-\text{CH}_2-\text{CH}_2-\text{P}(\text{Ph})_2$.

The binding energies were calibrated against the C_{1s} binding energy measured for the carbon of the phenyl groups. This latter value was obtained from a relation between IR intensity of the CH absorption of the phenyl group and the binding energy. From these data and available correlations between binding energy and effective charge, the charges have been estimated for P, N, Cl and the phenyl group. Typical examples $q_p = -0.22$, $q_{\text{C}_6\text{H}_5} = +0.21$, $q_{\text{N}} = -0.19$ and $q_{\text{N}} = -0.40$. There is no possibility from the ESCA data to decide whether the inner (*endo*) or the terminal (*exo*) nitrogen atom is the most negatively charged one.

From an analysis of the IR intensities of the $\nu_{\text{N}=\text{N}}$ absorption, an estimate can be made of the angle between the N_2 groups in the *cis* complexes ($\theta \approx 98^\circ$). This deviation from 90° is probably caused by electrostatic repulsion between the negatively charged ligands.

Dinitrogen complexes of transition metals have been known for some time. Since their discovery¹ much effort has been made to determine the factors that may make possible a reduction of the N_2 group to ammonia, hydrazine or carbon containing products. These problems have been carefully reviewed recently.²

* Part I in this series: Folkesson, B and Larsson R. *Acta Chem. Scand. A* 33 (1979) 347.

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One of the factors that must favour the reduction is the degree of negative charge donated to the two nitrogen atoms from the central metal atom. It is probable that a further reaction is caused by attack of an electrophilic agent (*e.g.* H^+). Therefore the distribution of charge between the *exo* and the *endo* nitrogen atoms determines the progress of the reaction process.

Several attempts have been made to determine this charge distribution.^{3–7} Work based on ESCA and IR intensity measurements from this laboratory suggested³ that the *endo* atom was the most negative one for the complexes. This view was supported by a qualitative reasoning by Nefedov and Dyatkina.⁴ On the other hand Leigh and coworkers⁵ supported the reverse polarity for a series of rhenium complexes. In a later work Nefedov gave similar evidence.⁶ In a recent paper

Table 1. Collection of data from theoretical calculations on $\text{M}-\text{N}_1-\text{N}_2$.

Ref.	M	q_{N_1}	q_{N_2}
Ref. 8	Cr	-0.672	-0.018
(Extended Hückel)	Fe	-0.944	+0.296
	Ni	-0.192	+0.174
Ref. 9	$\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$	-0.1	+0.2
(CNDO/2)			
Ref. 10	$\text{Ni}(\text{N}_2)_4$	+0.216	-0.092
<i>ab initio</i>			
STO-GTO			
Ref. 11	W_1^a	-0.67	-1.47
(Extended Hückel)	W_9^a	-0.78	-1.47
	W_{13}^a	-1.27	-1.83

^a The examples given correspond to linear $\text{M}-\text{N}-\text{N}$ attachment, many other structures are discussed.

Feltham⁷ discusses the problem and shows that the reactivity pattern for Mo complexes strongly indicates that the *exo* atom is really the most negative one.

Several population analyses from quantum chemical calculations have also been reported⁸⁻¹¹ for the M-N≡N unit (Table 1). As most dinitrogen complexes found in reality contain a set of ligands with a considerable number of atoms – some of these in the lower part of the periodic table – the calculations are sometimes restricted to an idealized compound, *e.g.* M-N₂. In many cases these calculations result in a charge distribution where the *exo* N-atom is negatively charged. The *endo* atom is usually positively charged which is in contradiction to experimental evidence.^{3,7}

As most investigations seem to point to results that are contradictory to the conclusion reached before³ we have set out to search for possible systematic errors in the early work.

One possibility is that the role of the central metal is essential. There might, *e.g.*, be a difference between the relatively "hard"¹² Ru(NH₃)₂⁺ group and the "soft" (R₃P)₄W(0) and (R₃P)₄Mo(0) groups that gives rise to a differently directed polarity of M-N≡N. Therefore, in this investigation we have not confined the measurements to Re complexes (easy to prepare) but extended them to include some bis dinitrogen complexes of W and Mo. These substances have a rather high reactivity: They are more air-sensitive than those of Re and some of them give NH₃ and N₂H₄ on protonation.²

A direct source of error in the early work might have been the estimate of charges on the nitrogen atoms from ESCA data. These charges, *q*, were used to determine d|*q*|/*dr* from a series of complexes with slightly different N-N distances, *r*. This quantity could also be determined from IR intensity measurements – from which dμ/*dr* results – and the *q* value obtained by ESCA (*cf.* eqn. (1)). A comparison between the two values of d|*q*|/*dr* thus calculated was thought to give an indication if the choice of a certain charge on the *exo* or the *endo* N-atom was the right one. However, when this comparison is made it must be essential that the charge implicit in the entity dμ/*dr* from IR measurements and the ESCA charges are as close to "real" values as ever possible.

In our previous work³ the relation (1) was applied. Later on¹³ we differentiated between the interatomic distance (*R*) and the charge separation in the dipole (*r*). In order to avoid another source of

$$\frac{d|\mu|}{dr} = |q| + r \frac{d|q|}{dr} \quad (1)$$

error one must closely examine the assumptions made^{3,13} on the relation between *r* and *R*.

PROCEDURE

The charge estimates from ESCA measurements are usually dependent on (a) the values of charges derived from theoretical calculations of the model substances used to construct an *E_b versus q_x* curve, and (b) the calibration to a common standard to get rid of the effects due to charging following the X-ray bombardment.

In order to get reliably calibrated binding energies for solid samples we have suggested¹⁴ the following principle: The calibration must be based on an internal standard. As such we have chosen the phenyl group that can be present in the substance as, *e.g.*, (C₆H₅)₃P, (C₆H₅)₄P⁺ or C₆H₅-M. The mean C_{1s} signal of this group is then used as the common reference. In order to know, however, exactly the value of the C_{1s} binding energy in the compound studied, we measure¹⁴ the infrared intensity of the C-H stretching vibration of the aromatic system (*A_{CH}*). As this quantity has been shown¹⁵ to be dependent on the chemical environment of the phenyl group, a relation between C_{1s} binding energy and *A_{CH}* is expected. This was also confirmed¹⁴ and this principle has thereafter been used to establish correlation diagrams between *E_b* and the effective charge (*q*) for chlorine,¹⁶ nitrogen,¹⁷ carbon,¹⁷ sulfur¹⁸ and phosphorus.¹⁹

In all cases (with some exceptions for phosphorus) theoretically calculated *q_x* values were used (*ab initio* or CNDO) for simple compounds, not necessarily of the same structure or total charge. In all cases a linear relation was found over the entire range of charges that was investigated.

In analytical form these relations are

$$\begin{aligned} E_b(\text{Cl}) &= 4.25 q_{\text{Cl}} + 201.2 \text{ eV} \\ E_b(\text{N}) &= 7.00 q_{\text{N}} + 401.4 \text{ eV} \\ E_b(\text{C}) &= 11.5 q_{\text{C}} + 284.8 \text{ eV} \\ E_b(\text{S}) &= 3.38 q_{\text{S}} + 163.8 \text{ eV} \\ E_b(\text{P}) &= 1.67 q_{\text{P}} + 131.6 \text{ eV} \end{aligned}$$

These relations have been tested to a certain extent by measuring¹⁸ complexes of rather com-

plicated structure, containing C, S and N. From the direct determination of the charges by the method sketched above, it was possible to determine — by difference — the charge on a series of metal ions in these complexes. From the very reasonable values of q_M in these examples we have concluded that the method is, pragmatically, a good tool.

In order to join our ESCA data of N_{1s} binding energies of the dinitrogen complexes to the phenyl-internal-standard-scheme we have measured the CH stretching IR intensity for the series of rhenium complexes investigated before.³ These substances are not very unstable and can be easily treated in air. (Actually the preparations of the early investigation³ kept in glass bottles with ordinary screw caps for six years showed excellent N_{1s} signals when remeasured.)

The IR intensity — measured on freshly prepared samples — thus gives us a value for the mean C_{1s} binding energy of the phenyl group in the phosphines of the complexes. As the phenyl carbons outnumber the alkyl ones also present in the phosphines we regard the C_{1s} signal as representative of the phenyl carbons.

The phosphino bis(dinitrogen) complexes of W and Mo, on the other hand, are unstable and tend to decompose in air or in solution. Therefore we have to apply a somewhat more intricate procedure: When presenting the measured binding energies we relate these to the same $E_b(C_{1s})$ as found for the analogous rhenium complex. This does not mean that these binding energy values correspond to the values that a direct determination of A_{CH} for the W or Mo complex would have indicated. Because of this we will present the effective charges derived from the binding energies as a function of A_{CH} . In this way it will be possible to decide how critical the choice of A_{CH} is in determining the charge distribution in the complexes. In order to stress the similarity between the systems, the same treatment is performed also for the Re complexes.

Another consequence of the low stability of the tungsten and molybdenum complexes is a certain difficulty to measure the infrared spectra in solution. Therefore A_{NN} as well as ν_{NN} have been measured in the solid state with KBr as the dispersion medium. This is probably allowed as the previous measurements on Re and Ir complexes³ showed that both A_{NN} and ν_{NN} were seemingly independent of the dispersion medium.

The A_{CH} values of the rhenium complexes were

measured in solution ($CDCl_3$). In this way the data are directly compatible with those that were used to derive the $q_{C_6H_5} - A_{CH}$ relation^{14,17} and the $E_b(C_{1s}) - A_{CH}$ relation.¹⁴

From these preliminaries, we now have — in principle — the necessary data for a detailed discussion of the charge distribution in the complexes and, *e.g.*, to use the formalism developed earlier.^{3,14}

EXPERIMENTAL

The complexes $ReClN_2(dppe)_2$,²⁰ $ReClN_2(PMePh_2)_4$,²⁰ $ReClN_2(PMe_2Ph)_4$,²⁰ and $Mo(N_2)_2(dppe)_2$,²¹ $W(N_2)_2(dppe)_2$,²² $Mo(N_2)_2(PMePh_2)_4$,²¹ $W(N_2)_2(PMePh_2)_4$,²³ $W(N_2)_2(PMe_2Ph)_4$,²² were prepared following established methods. XPS data were obtained with an AEI ES200 electron spectrometer using Mg $K\alpha$ radiation (1253.6 eV) and following the procedure described previously.²⁴ It was necessary to cool the samples as dinitrogen was lost during irradiation by X-rays. Satisfactory spectra were obtained at 173 K. Several runs were performed for the $N(1s)$ signal for each sampling and at least two different samplings were done on each of the complexes. The binding energy values tabulated are generally the average of at least two measurements and are accurate to ± 0.2 eV.

The IR spectra were run on a Perkin Elmer 580 B. The solutions (for recording ν_{CH}) were made under nitrogen atmosphere. All weighing procedures for the preparation of the KBr pellets (for recording ν_{NN}) were also made in a nitrogen flashed dry box. The areas of the absorption curves were measured with a planimeter.

RESULTS

The frequencies and integrated absorption values of the N—N vibration are collected in Table 2. In Table 3 we present the results of the A_{CH} measurements of the rhenium complexes. From these and the correlation line between $E_b(C_{1s})$ and A_{CH} (Ref. 14) we have found the C_{1s} binding energies in the dppe and the $PMePh_2$ complexes to be equal to 285.1 eV. For the PMe_2Ph complex the corresponding value is 284.9 eV. If these values are also used for the analogous Mo and W complexes we get calibrated binding energies as reported in Table 4.

Some typical spectra of the N_{1s} signal are recorded in Figs. 1–2. As the splitting of the N_{1s}

Table 2. Infrared data of the ν_{N-N} vibration in the complexes investigated.

Compound	Dispersion medium	ν_{NN} cm^{-1}	$A_{NN} \times 10^{-4}$ $\text{M}^{-1}\text{cm}^{-2}$	$A_{NN}(\text{MEAN}) \times 10^{-4}$ $\text{M}^{-1}\text{cm}^{-2}$
$\text{ReClN}_2(\text{dppe})_2^a$	CHCl_3	1975	7.3	
$\text{ReClN}_2(\text{PMePh}_2)_4^a$	CHCl_3	1922	—	
$\text{ReClN}_2(\text{PMe}_2\text{Ph})_4^a$	CHCl_3	1924	10.0	
<i>trans</i> - $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$	Nujol	1985	—	
<i>trans</i> - $\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4$	KBr	1923	8.5	
<i>cis</i> - $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$	KBr	1935	3.5	3.05
		2015	2.6	
<i>trans</i> - $\text{W}(\text{N}_2)_2(\text{dppe})_2$	KBr	1947	11.1	
<i>trans</i> - $\text{W}(\text{N}_2)_2(\text{PMePh}_2)_4$	KBr	1898	10.3	
<i>cis</i> - $\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$	KBr	1912	4.0	
		1989	3.2	3.6

^a From Ref. 3.

band was not very pronounced for the Mo and W complexes the spectra were analyzed with the help of a Tektronix 4051 minicomputer. In this way it was possible to estimate the band separation and the absolute values of the binding energies to an accuracy of about 0.05 eV (Table 4). As the peak separation in the rhenium complexes was definitely larger than the halfwidth of each of the peaks these spectra were easily analyzed.

It was found that the type of resolution that gave the best fit to the original curve usually gave a narrow peak of high binding energy and a peak of low binding energy that was somewhat broader. The areas of the peaks were found, with one exception, to be of equal size. Examples of this analysis are also given in Figs. 1–2.

As said above, it was difficult to measure A_{CH} for the Mo and W complexes with the necessary accuracy. To describe the dependence of the charges on the value of A_{CH} a graphical presentation can be made.

In Fig. 3 we present the results for $\text{ReClN}_2(\text{dppe})_2$ of an estimation of the charges q_{N_1} , q_{N_2} , q_{P}

and q_{Cl} from the ESCA binding energy data reported in Table 4 and the charge on the phenyl group, $q_{\text{C}_6\text{H}_5}$, derived from the $A_{\text{CH}} - q_{\text{C}_6\text{H}_5}$ relation (Ref. 19). As mentioned above, these data are presented as a function of A_{CH} . One immediately observes that, as far as the q_{N} values are concerned, the variation with A_{CH} is not very pronounced. For the other complexes similar relations can be constructed in the form $q_{\text{X}} = a_{\text{X}} A_{\text{CH}} + b_{\text{X}}$ (Table 5).

In Fig. 3 and Table 5 we have included the function $q_{\text{M}} + nq_{\text{CH}_3}$ or $q_{\text{M}} + nq_{\text{CH}_2}$ where n is the number of CH_3 or CH_2 groups present in the complex under discussion. One also immediately observes that this function is characterized by a very strong dependence on A_{CH} . It is not possible with the available data, however, to split up this sum into the component terms. To proceed further in this analysis some extra assumptions have to be introduced. As we are interested mainly in the nitrogen charges and not the metal ones the following procedure has been adopted: Two values of q_{M} are chosen, $q_{\text{M}} = 0$ and $q_{\text{M}} = +0.3$ (Table 6). For the methyl and methylene groups we adopt $q_{\text{Me}} = +0.1$. More positive values than +0.1 on the Me groups in the present complexes would give extremely negative charges on the metal atoms. Such negative charges are not compatible with chemical intuition. When good correlations between E_{b} (M) and q_{M} are established for the metals in question and within the scheme of internal calibration one will, however, get the possibility to check the choice in a better way.

The value $q_{\text{Me}} = +0.1$ may seem a little surprising as we have estimated the charge on the phenyl

Table 3. IR absorption data for the rhenium complexes. A_{CH} is given per phenyl group.

Substance	$A_{\text{CH}} \times 10^{-2}$ $\text{M}^{-1}\text{cm}^{-2}$	C_{1s} (eV) From Ref. 14
$\text{ReClN}_2(\text{PMe}_2\text{Ph})_4$	15.3	284.9
$\text{ReClN}_2(\text{PMePh}_2)_4$	12.3	285.1
$\text{ReClN}_2(\text{dppe})_2$	12.0	285.1

Table 4. ESCA data for the complexes investigated.

Compound	E_b NIs eV	NIs binding energy separation eV	Half width of NIs peaks eV	Ratio between the areas of the NIs peaks	E_b P2p eV	E_b Cl2p _{3/2} eV	E_b M3d _{5/2} or M4f _{7/2}	Ref. E_b Cls eV
ReCl(N ₂ (dppe) ₂)	400.6;398.7	1.9			131.6	198.3	41.1	285.1
ReCl(N ₂ (PMePh ₂) ₄)	400.4;398.5	1.9			131.7	198.3	41.0	285.1
ReCl(N ₂ (PMe ₂ Ph) ₄)	400.3;398.4	1.9			131.4	197.9	41.0	284.9
<i>trans</i> -Mo(N ₂) ₂ (dppe) ₂	400.0;398.55	1.45	1.45;1.45	1.38:1	131.2		227.4	285.1 ^a
<i>trans</i> -Mo(N ₂) ₂ (PMePh ₂) ₄	400.25;398.75	1.50	1.45;1.55	1.08:1	131.2		227.4	285.1 ^a
<i>cis</i> -Mo(N ₂) ₂ (PMe ₂ Ph) ₄	399.9;398.45;397.15	1.45;1.30	1.50;1.40;1.35	0.99:1:0.50	131.2		227.1	284.9 ^a
<i>trans</i> -W(N ₂) ₂ (dppe) ₂	400.35;398.75	1.60	1.50;1.65	1.15:1	131.2		30.6	285.1 ^a
<i>trans</i> -W(N ₂) ₂ (PMePh ₂) ₄	400.35;398.75	1.60	1.45;1.70	0.98:1	131.3		31.0	285.1 ^a
<i>cis</i> -W(N ₂) ₂ (PMe ₂ Ph) ₄	399.9;398.25	1.65	1.40;1.50	0.96:1	131.1		30.6	284.9 ^a

^a In analogy to the Re complexes, cf. the text.Table 5. Coefficients of the formula $q_x = a_x A_{CH} + b_x$ derived for relations like that in Fig. 3.

	$a_x \times 10^5$ (charge unit M cm ²)		P	C ₆ H ₅	Cl	b_x (charge unit)		N ₁	P	C ₆ H ₅	Cl
	M+CH ₂	N ₁				M+CH ₂	N ₁				
ReCl(N ₂) (dppe) ₂ (Fig 3)	408	-10.1	-10.1	-41.7	-24.0	-16.4	+0.01	+0.50	+0.50	+0.49	-0.49
ReCl(N ₂) (PMePh ₂) ₄	406	-8.8	-10.1	-41.7	-22.7	-17.7	-0.04	+0.55	+0.55	+0.46	-0.48
ReCl(N ₂) (PMe ₂ Ph) ₄	308	-10.1	-8.8	-42.9	-24.0	-17.7	-0.01	+0.52	+0.52	+0.49	-0.53
<i>trans</i> -Mo(N ₂) (dppe) ₂	410	-10.1	-10.1	-45.5	-25.2	-4.5	-0.08	+0.31	+0.31	+0.50	
<i>trans</i> -Mo(N ₂) (PMePh ₂) ₄	409	-8.4	-10.0	-42.1	-25.3	-4.6	-0.06	+0.26	+0.26	+0.50	
<i>cis</i> -Mo(N ₂) (PMe ₂ Ph) ₄	314	-8.8	-10.1	-41.7	-22.7	-3.0	-0.07	+0.38	+0.38	+0.47	
<i>trans</i> -W(N ₂) (dppe) ₂	413	-11.8	-13.5	-43.8	-25.3	-4.6	-0.07	+0.29	+0.29	+0.51	
<i>trans</i> -W(N ₂) (PMePh ₂) ₄	415	-11.4	-10.1	-44.2	-26.5	-4.9	-0.01	+0.35	+0.35	+0.52	
<i>cis</i> -W(N ₂) (PMe ₂ Ph) ₄	311	-11.8	-10.1	-42.1	-21.9	-2.7	-0.04	+0.33	+0.33	+0.46	

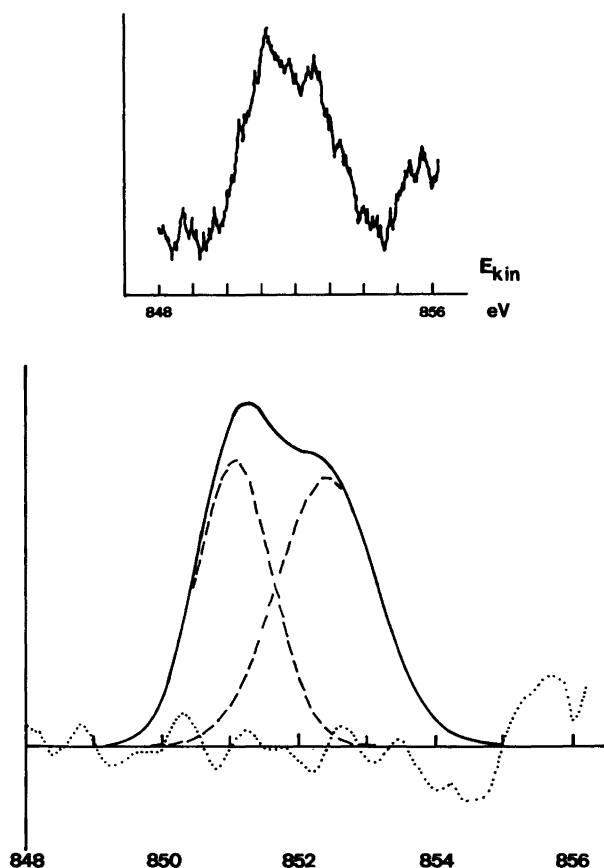


Fig. 1. Representative example of ESCA spectrum of the N_{1s} signal for $cis\text{-W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$. The computer-analyzed spectrum is depicted below.

group to be about +0.2 from the A_{CH} values of the complexes (Fig. 3) and +0.14 for Ph_3P (Ref. 19).

The inductive coefficients given by Kabachnik²⁵ would tend to put a more positive charge on methyl groups than on phenyl groups in R_3P molecules. Furthermore, calculations by Raevskii *et al.*^{26,27} on R_3PO confirm this trend. We have chosen, however, to use the rough estimate of $q_{\text{Me}} \approx +0.1$ when presenting some examples of the charge distribution (Table 6). One observes that there is really a very small variation of q_{N_1} and q_{N_2} for the two choices, $q_{\text{M}} = 0$ or $q_{\text{M}} = +0.3$.

The difficulty in determining a correct A_{CH} is clearly seen from Table 6. The low values (around $12 \times 10^2 \text{ M}^{-1} \text{ cm}^{-2}$) given for $\text{ReClN}_2(\text{PMePh}_2)_4$ and $\text{ReClN}_2(\text{dppe})_2$ in Table 2 would give rise to very negative values of q_{Re} and most probably are

in error. On the other hand, they fit very well to the values found appropriate for the Mo and W complexes. One must remember that the determination of infrared intensities is usually done with an error of about $\pm 5\%$. To this are added the possible effects of decomposition and/or impurities in the preparations.

DISCUSSION

Treatment of the IR data of the cis - complexes. (1) The IR frequency values of the ν_{NN} stretching for the *cis* complexes allow a determination of the interaction force constant in a similar way as that used by Cotton and coworkers,^{28,29} a procedure followed by many others, among those, *e.g.*

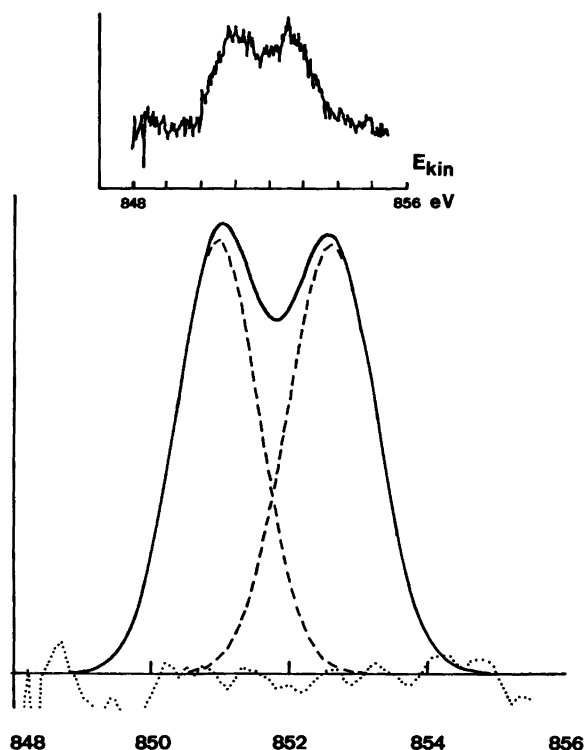


Fig. 2. ESCA spectrum of $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ analogously presented as in Fig. 1.

Rebenstorf and Larsson.³⁰ In that approach one considers the CO — or in this case N_2 — ligands as nonmechanically coupled, *i.e.* the force constants refer to the XY molecule, the vibration conditions of which are altered by electronic influence from the metal and the other ligands.

From the reasoning of Cotton and Kraihanzel²⁸ it follows that for a *cis* complex the A_1 vibration (symmetric stretch) is represented by eqn. (2) and the B_1 vibration (asymmetric stretch by eqn. (3), where $\lambda = 5.889 \times 10^{-7} \bar{\nu}^2$, μ = the reduced mass of the XY molecule expressed in atomic weight units, k = the X—Y stretch force constant, and k_c = the X—Y, X—Y interaction constant. Implicit in this approach²⁸ is that k_c is a positive quantity.

$$\lambda = \mu^{-1}(k + k_c) \quad (2)$$

$$\lambda = \mu^{-1}(k - k_c) \quad (3)$$

In Table 7 we present the results from such a calculation on the Mo and W *cis* complexes

investigated in this work. One can observe that the stretching force constant k is somewhat smaller for the W complex than for the Mo one. This can be interpreted as a larger electron occupancy of the antibonding N—N-orbitals in the former complex than in the latter. This finding is in agreement with the somewhat larger polarity found for the W—N—N unit than for the Mo—N—N one (*cf.* Table 6).

(2) Now, when the two ν_{NN} bands in the spectrum of the *cis* complexes have been identified from the condition that k_c in the above analysis should be positive, one can try to use the intensity ratio of the bands to get some indication on the angle between the two N_2 units.

Following Steele³¹ and Beck, Melnikoff and Stahl³² we apply the formula

$$A_{\text{asym}}/A_{\text{sym}} = \text{tg}^2 \theta/2$$

where θ is the above-mentioned angle.

In Table 7 we report the results of such a calculation. Although the precision in the measure-

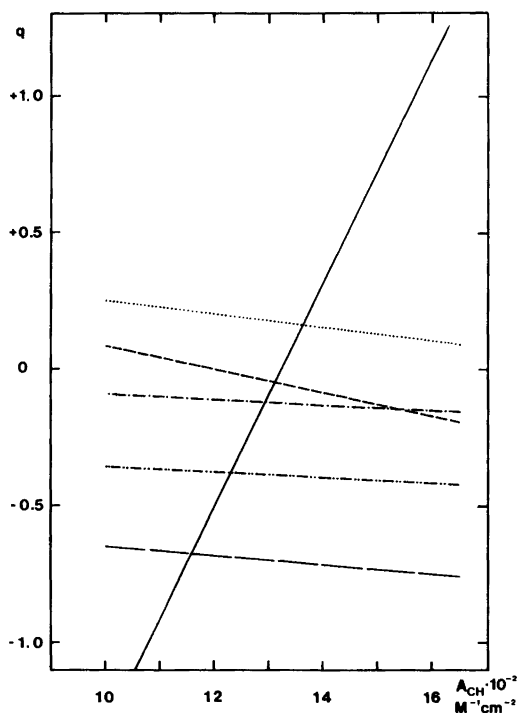


Fig. 3. The effective charges of the components of $\text{ReCl}(\text{N}_2)(\text{dppe})_2$ presented as functions of A_{CH} , the integrated absorption of the C-H stretching vibrations of the phenyl groups. —, $q_{\text{M}} + nq_{\text{Me}}$ (cf. text); \cdots , $q_{\text{C}_6\text{H}_5}$; $---$, q_{P} ; $- \cdot -$, q_{N_1} ; $- \cdot \cdot -$, q_{N_2} ; $---$, q_{Cl} .

ments does not allow us to draw any conclusions about differences between the two complexes, one observes that both angles are larger than 90 degrees. We prefer to interpret this effect as caused by electrostatic repulsion between the two N_2 units which have a rather considerable negative charge (Table 6).

(3) In a previous work³⁰ from this laboratory we tried to extend the correlation for CO complexes between k_c (or k_i in relevant cases and using Cotton's nomenclature) and the stretching force constant k suggested by Cotton.²⁹ If one now applies a scaling on the present N_2 data by multiplying with the ratio between force constants for gaseous CO and N_2 it would be possible to compare them with analogous CO data. Thus multiplication by 18.55/22.40 gives $k_{\text{corr}} = 13.0$ for W and 13.3 for Mo. As indicated in Fig. 4 the N_2 complexes are then placed in parity with such CO

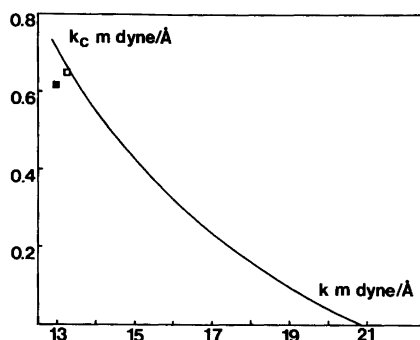


Fig. 4. The relation between k_c and k for carbonyl complexes from Cotton²⁹ and from Rebenstorff and Larsson³⁰ (fulldrawn line) and for the two *cis*-dinitrogen complexes studied in this work. \square , Mo; \blacksquare , W.

complexes where the CO bond is regarded as considerably weakened. Also this finding agrees with the interpretation of rather large negative charges on the dinitrogen units.

On the polarity of the M-N-N group. From the data given in Tables 4 and 6 it follows that the charges estimated for the N_1 and N_2 atoms differ very little from one complex to another. Indeed in most cases $\Delta q_{\text{N}_1} = \Delta q_{\text{N}_2}$. This means that, whatever value one assigns to r_{NN} for the complexes, $\frac{d|q|}{dr}$ will have the same numerical value, whether one considers the N_1 or the N_2 atom. In spite of the possibility of calculating this quantity for *exo*-N atom in the same manner as made by Folkesson³ we have now no possibility of using that quantity to differentiate between the charges on the *exo*- and *endo*-N-atoms.

Obviously a more careful calibration gives better and more accurate values of the binding energies. This, in its turn, means that the charges derived from ESCA are more accurate and are thus comparable in a more correct way with those related to IR intensity measurements. The deductions reported before must be considered as unfounded, in the sense that the charges derived from the ESCA data were not accurate enough. With this statement, one of the objects of this study has been achieved. In order, however, to illuminate in greater detail the problems inherent in such calculations we have applied the ideas of Folkesson³ to the *trans*-systems, the most easily treated ones.

Consider the schematic presentation of the *trans*

Table 6. Estimation of effective charges from Fig. 3 and the relations described in Table 5. The assumption is made that $q_{\text{CH}_2} = q_{\text{CH}_3} = +0.1$. The two parts of the table correspond to two different values of q_{M} .

	$A_{\text{CH}} \times 10^{-2}$ $\text{M}^{-1}\text{cm}^{-2}$	q_{N_1}	q_{N_2}	q_{P}	$q_{\text{C}_6\text{H}_5}$	q_{Cl}
$q_{\text{M}} = 0.0$						
ReClN ₂ (dppe) ₂	14.2	-0.13	-0.40	-0.09	+0.15	-0.72
ReClN ₂ (PMePh ₂) ₄	14.6	-0.16	-0.43	-0.05	+0.14	-0.72
ReClN ₂ (PMe ₂ Ph) ₄	13.3	-0.13	-0.40	-0.05	+0.17	-0.75
<i>trans</i> -Mo(N ₂) ₂ (dppe) ₂						
<i>trans</i> -Mo(N ₂) ₂ (PMePh ₂) ₄	12.1	-0.15	-0.37	-0.24	+0.20	
<i>cis</i> -Mo(N ₂) ₂ (PMe ₂ Ph) ₄	12.1	-0.18	-0.39	-0.12	+0.20	
<i>trans</i> -W(N ₂) ₂ (dppe) ₂						
<i>trans</i> -W(N ₂) ₂ (PMePh ₂) ₄	12.8	-0.15	-0.38	-0.21	+0.19	
<i>cis</i> -W(N ₂) ₂ (PMe ₂ Ph) ₄	11.2	-0.17	-0.40	-0.14	+0.22	
$q_{\text{M}} = +0.3$						
ReClN ₂ (dppe) ₂	14.95	-0.14	-0.41	-0.12	+0.13	-0.73
ReClN ₂ (PMePh ₂) ₄	15.4	-0.17	-0.44	-0.08	+0.12	-0.74
ReClN ₂ (PMe ₂ Ph) ₄	14.25	-0.15	-0.41	-0.10	+0.15	-0.77
<i>trans</i> -Mo(N ₂) ₂ (dppe) ₂						
<i>trans</i> -Mo(N ₂) ₂ (PMePh ₂) ₄	12.85	-0.17	-0.38	-0.27	+0.18	
<i>cis</i> -Mo(N ₂) ₂ (PMe ₂ Ph) ₄	13.1	-0.19	-0.40	-0.16	+0.18	
<i>trans</i> -W(N ₂) ₂ (dppe) ₂						
<i>trans</i> -W(N ₂) ₂ (PMePh ₂) ₄	13.5	-0.16	-0.38	-0.25	+0.17	
<i>cis</i> -W(N ₂) ₂ (PMe ₂ Ph) ₄	12.15	-0.18	-0.41	-0.18	+0.20	

bis N₂ complex in Fig. 5. In this model we idealize the M–N≡N vibration as one of a variation of the distance of the *exo* N atom from the center of the molecule. In this way we can treat the vibration as one of a linear XY₂ molecule. The mass of the central atom X is taken as the entire rest of the complex, *i.e.* (M(PR₃)₄N₂). The mass of Y = the mass of N. Thus we can apply the treatment of XY₂ intensities used, *e.g.*, by Robinson,³³ and arrive at a $\frac{\partial \mu}{\partial R}$ value, reported here in Table 8. In interpreting this value in terms of charges we once more must consider the model depicted in Fig. 5. The bond

dipole moment is as eqn. (4), where r is the distance between the centers of charge.

$$|\mu| = |q||r| \quad (4)$$

When the molecule is vibrating this distance no longer coincides with the geometrical M–N₂ distance (R) [eqns. (5) and (6)]. Now differentiating eqn. (4) gives eqn.(7).

$$r = R + a \quad (5)$$

$$\frac{dr}{dR} = 1 + \frac{da}{dR} \quad (6)$$

Table 7. Assignment of the infrared bands of the ν_{NN} vibration for *cis*-M(N₂)₂(PMe₂Ph)₄. $A_{\text{asym}}/A_{\text{sym}} = \text{tg}^2\theta/2$.

M	ν_{asym} (B ₁) cm ⁻¹	ν_{sym} (A ₁) cm ⁻¹	$A_{\text{asym}} \times 10^{-4}$ M ⁻¹ cm ⁻²	$A_{\text{sym}} \times 10^{-4}$ M ⁻¹ cm ⁻²	$A_{\text{asym}}/A_{\text{sym}}$	θ degrees	k mdyn/Å	k_{c} mdyn/Å
Mo	1935	2015	3.5 ± 0.1	2.6 ± 0.1	1.35	99 ± 2	16.09	+0.65
W	1912	1989	4.0 ± 0.1	3.2 ± 0.1	1.25	97 ± 2	15.69	+0.62

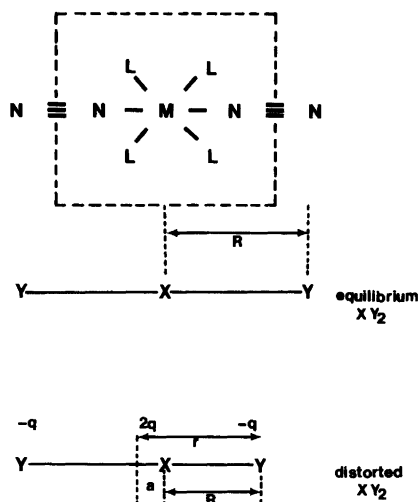


Fig. 5 Model of the $\text{N}\equiv\text{N}$ vibration of the *trans*-dinitrogen complexes as the ν_3 vibration of an XY_2 molecule.

$$\frac{d|\mu|}{dR} = |q| \frac{dr}{dR} + |r| \frac{d|q|}{dR} \quad (7)$$

As the center has a mass that is considerably greater than that of the *exo* N atom, the change of R that is caused by a displacement of the center is probably rather small. Even so, it is difficult to assess the displacement of charge, *i.e.* a . Because of the high polarizability of the central group, however, we regard this displacement as small and put $da/dR=0$, which gives eqn. (8).

$$\frac{d|\mu|}{dR} = |q| + |R| \frac{d|q|}{dR} \quad (8)$$

From previous work we have found that for a single bond $d|q|/dR \approx 0.1 - 0.2$ a.u./Å (HgCl_2),³⁴ for a double bond ($(\text{V}=\text{O})^{2+}$, Ref. 35) $d|q|/dR=0.8$

± 0.15 a.u./Å. A calculation from eqn. (8) on CO_2 – with typical formal double bonds – based on the IR intensity given by Robinson³³ and the charge estimated by McLean *et al.*³⁶ and Horani *et al.*³⁷ results in $d|q|/dR=0.90$ a.u./Å.

On the other hand, formally triplebonded species such as CO and CN^- yield $d|q|/dR=0.50$ and 0.30 a.u./Å respectively. (In these latter calculations we have used for CO the IR intensity data given by Gribov and Smirnov³⁸ and the population analysis of Forsén and Roos.³⁹ For CN^- we have used the IR intensity data of Lykvist and Larsson⁴⁰ and the charge analysis by Hendrickson *et al.*⁴¹)

In passing it can be worth while to observe that in contrast to what was previously thought³⁴ $d|q|/dR$ does not seem to be a monotonous function of the bond order but rather shows a maximum for double bonds.

Returning now to the $\text{M}-\text{N}_1 \equiv \text{N}_2$ group, the $\text{M}-\text{N}_2$ distance covers about one single and one triple bond. Because of the pronounced back donation, weakening the $\text{N}\equiv\text{N}$ bond, strengthening the $\text{M}-\text{N}$ bond, it can be described almost as a “double bond” $\text{M}=\text{N}=\text{N}$. As a crude approximation one would like to suggest $d|q|/dR$ to have the value of a typical double bond with some admixture of that of a typical triple bond in describing the present vibration. As the first-mentioned quantity ranges between 0.9 and 0.8 a.u./Å, the latter one between 0.5 and 0.3, a value of 0.75 a.u./Å could possibly be representative. Insertion of this into eqn. (8) gives the values of q reported in Table 8. The actual number of these quantities must not, however, be taken as an indication of whether the *exo* or *endo* nitrogen atom is the most negative one as it is obviously highly dependent on the choice of $d|q|/dR$. The discussion above intends to point out that it is at most the order of magnitude of q_{N} that can be arrived at.

Table 8. Estimation of the charge on the *exo*-nitrogen atom in some *trans*-bis[dinitrogen] complexes using eqn. (8). $d|q|/dR$ is assumed to be 0.75 a.u./Å, *cf.* the text. $R_{\text{M}-\text{N}_1-\text{N}_2}$ is estimated from the data on *trans*- $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ ⁴² and the application of Badger's rule⁴³ to the frequencies ν_{NN} given in Table 2.

	$A_{\text{NN}} \times 10^{-4}$ $\text{M}^{-1}\text{cm}^{-2}$	$\frac{\partial \mu}{\partial R}$ a.u.	$R_{\text{M}-\text{N}_1-\text{N}_2}$ Å	$\frac{dq}{dR}$ a.u./Å	q_{N_2} a.u.
<i>trans</i> - $\text{W}(\text{N}_2)_2(\text{PMePh}_2)_4$	10.3	2.70	3.14	0.75	0.35
<i>trans</i> - $\text{W}(\text{N}_2)_2(\text{dppe})_2$	11.1	2.80	3.14	0.75	0.45
<i>trans</i> - $\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4$	8.5	2.45	3.14	0.75	0.09
<i>trans</i> - $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$			3.132 ⁴²		

CONCLUSIONS

The present investigation has aimed at a demonstration of the principle of internal calibration in ESCA work on solid samples. The use of the A_{CH} parameter to define a suitable value of C_{1s} has made it possible to utilize the calibration lines established previously.¹⁶⁻¹⁹ In this way quite reasonable values of q_N , q_{Cl} and q_P have been obtained. Indeed with few extra assumptions a mapping of the charge distribution of the complexes has been made possible. It must be stressed, however, that continued and improved work in this field demands an increase in the accuracy of the IR-intensity measurements.

It has further been demonstrated that the conclusions reached earlier³ on the direction of the polarity of the $M-N\equiv N$ bonds were based on ESCA data with insufficient calibration. With the proper calibration, now used, the variation of q_N within each $N\equiv N$ group is found to be quite small. It is therefore not possible to derive the position of the most negative N-atom from a combination of ESCA and IR measurements.

With the internal calibration that we now use another feature of these complexes is more easily observed: The difference between q_{N1} and q_{N2} varies not very much and certainly not within a series of one and the same metal. $\Delta q_N = |q_{N1} - q_{N2}|$ is found to be 0.27 (Re), 0.23 (W) and 0.21 (Mo).

Furthermore, the data presented in Table 6 indicate that the electronic structure (charge distribution) is not significantly different for the mono-tertiary phosphine complexes and the diphosphine ones. The difference in reactivity found by Chatt and coworkers⁴⁴ must then be explained in other terms. As was pointed out in our preliminary note⁴⁵ on this investigation, it seems that our study supports the mechanism suggested,⁴⁴ viz. that the substitution of phosphine ligands for stronger electron donating ligands is required for a complete reduction of the N_2 unit.

Implicit in that explanation⁴⁴ is that the electron donating, new ligand would increase the negative charge density on the metal atom and thereby increase the electron population of the antibonding π orbitals of the $N\equiv N$ group. However, looking at the data in our Table 6, one finds that a decrease of the central metal atom's charge from +0.3 to 0 will affect the charge on the nitrogen group very little. Therefore, either one has to reconsider the argument of Chatt and coworkers⁴⁴ or one must

conclude that the influence of q_N on the reactivity of the N_2 group is small if of any importance at all.

Acknowledgements. The award of a Fellowship (to A.M.) by the International Seminar, University of Uppsala is gratefully acknowledged. A. M. also thanks the University of Dacca for research leave. The authors are also thankful to Drs. C. A. Andersson and B. Rebenstorf of the catalysis research group, University of Lund, for technical suggestions and to Mrs. Ingrid Back for valuable practical assistance. The cost of the ESCA instrument has been covered by grants from *Riksbankens Jubileumsfond* (The Bank of Sweden Tercentenary Fund) and *Styrelsen för Teknisk Utveckling* (The Swedish Board for Technical Development). We appreciate the kind gift of samples of the *cis* complexes by Prof. J. Chatt and Dr. R. L. Richards at the ARC Unit of Nitrogen Fixation, University of Sussex, Brighton.

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Received February 26, 1980.