

# Infrared Intensity and ESCA Studies on the Polarity of the Nitrosyl Ligand in Some Transition Metal Pentacyanonitrosyl Complexes

BÖRJE FOLKESSON

Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund, 7, Sweden

The infrared absorption intensity of the N–O stretching vibration has been measured for the complexes  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}[\text{Mn}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$ ,  $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$ , and  $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$  in aqueous solution. It was found that the intensity ( $A_{\text{NO}}$ ) increases with decreasing frequency ( $\nu_{\text{NO}}$ ), which is in agreement with a model of  $d\pi-p\pi^*$  back donation. Thus, it was concluded that the degree of backbonding in the nitrosyl complexes increases in the order  $\text{Fe}(\text{II}) < \text{Mn}(\text{II}) < \text{Mn}(\text{I}) < \text{Cr}(\text{I}) < \text{Mo}(\text{0})$ .

Nitrogen  $1s$  and oxygen  $1s$  photoelectron spectra were recorded on the above mentioned nitrosyl complexes and also on  $\text{K}_3[\text{V}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ . It was found that both the nitrogen  $1s$  and oxygen  $1s$  electron binding energies for the nitrosyl group decrease with decreasing N–O stretching frequency in the complexes. Thus, when the degree of backbonding in the nitrosyl complexes increases, the effective charge on the nitrogen and oxygen atoms becomes more and more negative. It was found that the total charge on the nitrosyl group in the iron complex is positive (+0.35 a.u.), while the total charge on the nitrosyl group in the other complexes is negative. Most negative is the nitrosyl group in the vanadium complex (–0.41 a.u.).

From the dipole moment derivative,  $d\mu/dr$ , and the effective charges on the oxygen atoms, it was possible to get a value of the variation of charge with interatomic distance  $d|q|/dr$ . An estimation of  $d|q|/dr$  was also made from experimentally determined charges on the oxygen atoms and experimentally determined interatomic distances. It was found that both the calculation procedures gave the same value of  $d|q|/dr$ , viz. 0.6 a.u. This value agrees with the  $d|q|/dr$ -value earlier found for the N–N bond in dinitrogen complexes.

The bonding and electronic structures of transition metal nitrosyls have been frequently studied in recent years.<sup>1</sup> A comprehensive study

of the infrared spectra of metal nitrosyl complexes has been made by Lewis and Wilkinson and their coworkers.<sup>2,3</sup> They demonstrated that NO complexes absorb in the range from 1045  $\text{cm}^{-1}$  to about 1980  $\text{cm}^{-1}$ . Complexes which show NO absorption in the range 1200–1980  $\text{cm}^{-1}$  have been regarded as  $\text{NO}^+$  complexes, whereas NO compounds absorbing in the range 1045–1195  $\text{cm}^{-1}$  probably should be formulated as hyponitrito compounds.<sup>1</sup> In the present work a series of pentacyanonitrosyl complexes, in which the N–O stretching frequency varies in the range 1500–2000  $\text{cm}^{-1}$ , has been studied by IR and ESCA to get more detailed information about the charge distribution on the nitrosyl ligand. It is well known that the infrared intensity of a stretching vibration is related to the dipole moment derivative ( $d\mu/dQ$ ). This quantity has earlier<sup>4,5</sup> been found to give approximate information about charge distribution within coordination compounds. By means of ESCA<sup>6</sup> effective charges on atoms can be determined. From the combination of these two kinds of measurements the variation of charge with interatomic distance ( $d|q|/dr$ ) can also be determined, as has been done earlier<sup>5</sup> on dinitrogen complexes.

ESCA measurements on two pentacyanonitrosyl complexes, viz.  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  and  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$ , have been performed earlier<sup>7,8</sup> to attempt correlations of nitrogen  $1s$  binding energy with the character of the NO-group. It was found<sup>7,8</sup> that the  $\text{N}1s$  binding energy of the NO-group is higher in the iron complex than in the chromium complex. This means that the NO-group is more positive in the

iron complex that in the chromium complex. The N—O stretching frequency is higher in the iron complex than in the chromium complex, which indicates that the degree of  $d\pi-p\pi^*$  back donation of electrons from metal to NO-group increases from iron to chromium.

This investigation was started to further substantiate these observations on some more complexes of similar type and also to determine the charge on the oxygen atoms in the nitrosyl group.

## EXPERIMENTAL

### Preparation of nitrosyl complexes

$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ , which was commercially obtained, was of analytical grade.

$\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  was prepared according to the procedure given by Cotton *et al.*<sup>9</sup> from  $\text{K}_3[\text{Mn}(\text{CN})_5]$  and hydroxylamine in potassium cyanide solution. The salt first obtained,  $\text{Mn}_3[\text{Mn}(\text{CN})_5\text{NO}]_3$ , was converted to the potassium salt by the reaction with  $\text{K}_2\text{CO}_3$ . After repeated recrystallizations the compound was found pure. (Found: C 16.1; H 1.92; N 22.6. Calc. C 16.3; H 1.09; N 22.8).

$\text{Zn}[\text{Mn}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$  was prepared by oxidation<sup>9</sup> of  $[\text{Mn}(\text{CN})_5\text{NO}]^{3-}$  with nitric acid and precipitation of the salt with  $\text{Zn}^{2+}$ . The purity of the salt was checked by elemental analysis. It was found that the analysis values corresponded to a water content of the salt of 1 mol  $\text{H}_2\text{O}$ . (Found: C 21.0; H 1.18; N 28.5. Calc. C 20.1; H 0.67; N 28.2).

$\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$  was prepared according to Griffith *et al.*<sup>10</sup> (Found: C 18.3; H 0.51; N 25.2. Calc. C 17.3; H 0.58; N 24.2.)

$\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$  was prepared by Nast's method.<sup>11</sup> This purple pentacyanonitrosyl complex has been formulated in various ways, *viz.*

as a complex of molybdenum(0),  $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$ , either with<sup>11</sup> or without<sup>12</sup> water of hydration and as an eight-coordinated complex of molybdenum(II),  $\text{K}_4[\text{Mo}(\text{CN})_5(\text{OH})_2\text{NO}]$ .<sup>10</sup> In the work of Riley and Ho<sup>12</sup> it is pointed out that the complex partially decomposes in air and that this fact could be the reason for the earlier formulation<sup>10-11</sup> of the complex with water of hydration or as a hydroxy complex of molybdenum(II). Also an X-ray crystallographic investigation of the molybdenum complex by Svedung *et al.*<sup>13</sup> has shown that the complex should be formulated as  $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$ . The infrared spectrum of the compound used in the present investigation showed absorption in the 3300–3600  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  regions, which indicates the presence of water in the compound. The elemental analysis values are also in agreement with the formula  $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ . (Found: C 13.0; H 0.69; N 18.1. Calc. C 13.4; H 0.89; N 18.7). It is therefore reasonable to conclude that the compound investigated here is the partially hydrolysed pentacyanonitrosyl complex and consequently the formula with water of hydration has been used in the calculations of concentrations necessary for the infrared intensity calculations.

$\text{K}_3[\text{V}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  was prepared according to the method of Griffith *et al.*<sup>14</sup> from ammonium vanadate and hydroxylamine in alkaline potassium cyanide solution. The compound could, however, not be obtained analytically pure in spite of several recrystallizations. Consequently, the infrared intensity measurements have been omitted for this compound (*cf.* Table 1).

### Experimental techniques

The infrared spectra were recorded with a Perkin Elmer Spectrophotometer Model 521 equipped with a linear absorbance potentiometer. All spectra on the N—O stretching vibration were recorded with a wavenumber scale expansion, so that 1 cm on the chart corre-

Table 1. The results of the infrared intensity measurements on the nitrosyl complexes.

Nitrosyl complex	Dispersion medium	$\nu_{\text{NO}}$ $\text{cm}^{-1}$	$\epsilon$ $\text{M}^{-1} \text{cm}^{-1}$	$A_{\text{NO}} \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-2}$
○ $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	$\text{H}_2\text{O}$	1936	$1750 \pm 75$	$7.3 \pm 0.3$
● $\text{Zn}[\text{Mn}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$	KBr	1890	$425 \pm 40$	$6.3 \pm 0.6$
	$\text{H}_2\text{O}$	1800	$280 \pm 30$	
	$\text{H}_2\text{O}$	1880		$8.2^a$
□ $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	KBr	1730	$310 \pm 30$	$6.0 \pm 0.6$
	$\text{D}_2\text{O}$	1766	$1450 \pm 50$	$8.0 \pm 0.4$
■ $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$	$\text{D}_2\text{O}$	1682	$950 \pm 50$	$8.4 \pm 0.4$
▽ $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$	$\text{D}_2\text{O}$	1622	$500 \pm 50$	$8.7 \pm 0.8$
▼ $\text{K}_3[\text{V}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	$\text{D}_2\text{O}$	1545		

<sup>a</sup> *Cf.* the text.

sponded to  $12.5 \text{ cm}^{-1}$ . The measurements on the nitrosyl complexes were performed in aqueous solution but deuterium oxide was used when the N–O absorption coincided with the water absorption. Calibrated cells with  $\text{CaF}_2$ -windows and  $25 \mu$  platinum spacers were used. Some of the complexes (cf. Table 1) were examined in the solid state (KBr). For further details about the intensity measurements the reader is referred to Ref. 5.

The ESCA spectra were measured with an AEI ES 100 photoelectron spectrometer. All spectra were obtained with  $\text{AlK}\alpha$ -radiation ( $1486.6 \text{ eV}$ ). The electron binding energy  $E_b$  was obtained from the following expression:<sup>15</sup>

$$E_b = 1477.1 - E_{\text{kin}}$$

where  $E_{\text{kin}}$  is the measured kinetic energy of the electrons. The samples were mechanically spread out as a thin film on a platinum foil. Through this sample preparation technique no surface charging effects were obtained during the measurements. As before,<sup>15</sup> the Pt  $4f_{7/2}$  electron peak was used as reference peak.

## RESULTS AND DISCUSSION

The results of the intensity measurements on the nitrosyl complexes are given in Table 1. The complex  $\text{Zn}[\text{Mn}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$  was not soluble in water and therefore only measured in the solid state. It was found that the infrared spectrum of the compound in the solid state gave two bands assigned to the N–O stretching vibration. This situation has also been pointed out by Cotton *et al.*<sup>9</sup> The intensity of the two bands was measured and the total intensity given. It has earlier<sup>4,16</sup> been found that measurements of the same species in solution and in KBr immersion showed that the intensity was larger in the former by a factor of about 1.3. The intensity value for the zinc salt in solution has been estimated in accordance with these observations.<sup>4,16</sup> The compound  $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  has also been measured in KBr immersion and the intensity value was smaller than that in solution by a factor of 1.3. The molar absorption coefficients ( $\epsilon \text{ M}^{-1} \text{ cm}^{-1}$ ) at band maximum are included in Table 1. It can be seen that the  $\epsilon$ -values decrease within the series of complexes. The NO-absorption bands became, however, broader and the intensity was found to increase within the series. It can be seen from Table 1 that the intensity increases when  $\nu_{\text{NO}}$  decreases. In accordance with the reasoning in the previous studies<sup>4,5</sup> on dinitrogen complexes, a large infrared intensity means

a greater degree of  $d\pi-p\pi^*$  back donation of electrons from metal  $d$ -orbitals to antibonding  $\pi$ -orbitals of the ligand. The largest infrared intensity of the N–O stretching vibration has been found for the molybdenum compound. Thus, the degree of metal-ligand  $\pi$ -bonding should be greatest for this compound within the series of nitrosyl complexes. As mentioned above, the infrared intensity of the N–O stretching vibration in  $\text{K}_3[\text{V}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  could not be determined. The N–O stretching frequency in this compound was, however, determined and was found to be lower than in the other investigated nitrosyl complexes. Consequently, the degree of back donation of electrons should be pronounced in this complex as well. This fact has been confirmed through the ESCA measurements, which give evidence of a large negative charge on the NO-group (cf. Table 3).

$\text{N}1s$  and  $\text{O}1s$  photoelectron spectra were recorded on all the compounds. A representative example of a  $\text{N}1s$  electron spectrum for a pentacyanonitrosyl complex is given in Fig. 1. Two peaks show that the complex contains different nitrogen atoms. The  $\text{O}1s$  electron spectrum of the same complex is shown in Fig. 2. Besides the oxygen peak from the oxygen in the nitrosyl group there is also a broad peak with maximum

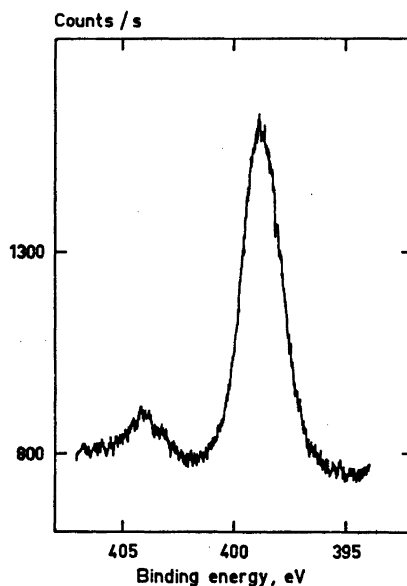


Fig. 1. Nitrogen  $1s$  electron spectrum of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ .

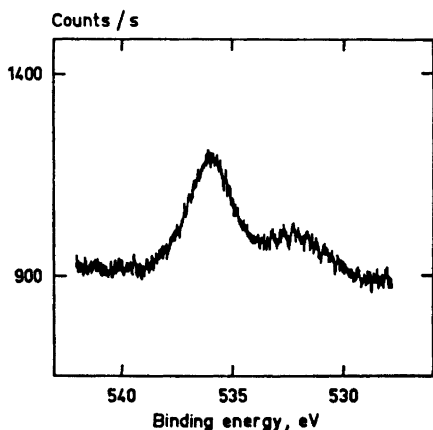


Fig. 2. Oxygen 1s electron spectrum of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ .

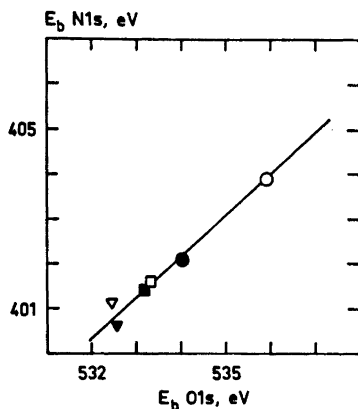


Fig. 3. The nitrogen 1s electron binding energy ( $E_b\text{N}1s$ ) as a function of the oxygen 1s electron binding energy ( $E_b\text{O}1s$ ) for the nitrosyl group in the various nitrosyl complexes. The same symbols as in Table 2 are used.

at a binding energy of about 532.5 eV. This broad peak probably can be assigned to adsorbed oxygen, as an oxygen peak at a binding energy of about 532 eV is always obtained in our ESCA measurements<sup>17</sup> with our present vacuum ( $\geq 10^{-7}$  torr). The measured N1s and O1s electron binding energies for the nitrosyl complexes are collected in Table 2. It can be seen that the N1s electron binding energy for the NO-group is greatest for the iron complex and smallest for the vanadium complex. The corresponding trend has been found for the O1s electron binding energy. In Fig. 3 the N1s electron binding energy is plotted against the O1s electron binding energy. A straight line with a slope of 1 is found, which shows that the change in the binding energy for the N1s and O1s electrons is the same from one complex to another. It must be pointed out that because of the oxygen peak from adsorbed oxygen the exact determination of the O1s electron binding energy for the nitrosyl oxygen in the molybdenum and vanadium complex is somewhat uncertain. Consequently, the error in the O1s electron binding energy is greater for these two complexes than for the other four complexes, in which the oxygen peak is well separated from the peak due to adsorbed oxygen. It is obvious from Table 2 that the N1s electron binding energy decreases with decreasing  $\nu_{\text{NO}}$  (and increasing infrared intensity). Thus, when the degree of  $d\pi-p\pi^*$  back donation of electrons from the metal to the NO-ligand increases (as is indicated by the decrease in  $\nu_{\text{NO}}$ ), the charge on the nitrogen atom becomes more and more negative. The same conclusion can be drawn about the charge on the oxygen atom in the NO-ligand.

Table 2. Nitrogen 1s and oxygen 1s electron binding energies in the various pentacyanonitrosyl complexes. All binding energy values are referred to a binding energy for Pt  $4f_{7/2}$  electrons of 71.1 eV.

Nitrosyl complex	$E_b\text{N}1s(\text{CN})$ eV	$E_b\text{N}1s(\text{NO})$ eV	$E_b\text{O}1s$ eV	$\nu_{\text{NO}}$ $\text{cm}^{-1}$
○ $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	398.7	403.9	535.9	1936
● $\text{Zn}[\text{Mn}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$	398.3	402.1	534.0	1880
□ $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	398.3	401.6	533.3	1766
■ $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]\cdot \text{H}_2\text{O}$	399.0	401.4	533.2	1682
▽ $\text{K}_4[\text{Mo}(\text{CN})_5\text{NO}]$	398.8	401.1	532.5	1622
▼ $\text{K}_3[\text{V}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$	398.8	400.6	532.6	1545

While the N1s electron binding energy for the NO-ligand varies from one complex to another the N1s electron binding energy for the cyanide ligand is practically constant within the series of pentacyanonitrosyl complexes, as can be seen from Table 2. This means that the degree of  $\pi$ -bonding within the M–C–N group is changed very little compared to the more pronounced change in the degree of  $\pi$ -bonding within the M–N–O group. Such a conclusion can also be drawn from the variations in the C–N stretching frequency and the N–O stretching frequency (*cf.*, *e.g.*, Ref. 1).

The charge on the nitrogen atom in the NO-group in the various nitrosyl complexes has been estimated with the aid of the correlation between N1s binding energy and calculated charge, which has been determined earlier (Fig. 5 in Ref. 15). The result is given in Table 3. It can be seen that the nitrogen atom in the NO-group in the iron complex has a positive charge, while the nitrogen atom in the NO-group in the other complexes is negatively charged. It is more difficult to obtain the charge on the oxygen atom, since surprisingly few ESCA data and charge calculations on oxygen compounds exist. However, it seems clear from the figures given by Siegbahn *et al.*<sup>18</sup> that a crude correlation between O1s binding energy and calculated charge ( $q_o$ ), disregarding the potential fields from neighbouring atoms, should result in a slope ( $dE_b/dq_o$ ) of about 12 eV/a.u. In a recent paper by Larsson *et al.*<sup>19</sup> oxygen atom charges have been estimated for two values of O1s electron binding energy from a combination of IR data with ESCA data on some oxinato complexes. The values reported<sup>19</sup> are  $q_o = -0.37$  a.u. corresponding to an O1s electron binding energy of 530.0 eV and  $q_o = -0.27$  a.u. corresponding to

531.5 eV. From ESCA measurements on vanadium compounds<sup>20</sup> the charge on the vanadium atom in  $V_2O_5$  has been estimated to +1.01 a.u. The charge on the oxygen atom can thus easily be calculated to –0.40 a.u. This value corresponds to an O1s electron binding energy<sup>20</sup> of 529.6 eV. Furthermore, from ESCA measurements on solid carbon suboxide<sup>21</sup> one can get an oxygen atom charge of –0.28 a.u. corresponding to an O1s electron binding energy of 531 eV, if the binding energy is referred to a C1s electron binding energy of 285 eV. From the above mentioned corresponding values of O1s electron binding energy and oxygen atom charge a correlation has been constructed. This is presented in Fig. 4. The slope of the straight line is about 11.5 eV/a.u., which is in accordance with the crude correlation found by Siegbahn *et al.*<sup>18</sup> From Fig. 4 and the measured O1s electron binding energies the charge on the oxygen atom in the NO-group in the nitrosyl complexes has been determined. It can be seen from Table 3 that the oxygen atom charge in the iron complex is positive, while the charge on the oxygen atom in the other nitrosyl complexes is negative.

The total charge on the NO-group has thus been found to be positive (+0.35 a.u.) in the iron complex, while in the other complexes the total charge on the NO-group is negative. The negative charge on the NO-group increases throughout the series of complexes. Thus, in the vanadium complex the charge on the NO-group is –0.41 a.u. There is, consequently, an increase of the electron density over the NO-ligand caused by  $d\pi-p\pi^*$  back donation of electrons from metal  $d$ -orbitals to antibonding  $\pi$ -orbitals of NO. This result confirms and strengthens the result from the infrared intensity measurements.

Table 3. Experimentally obtained charges on the nitrogen and oxygen atoms in the nitrosyl group together with calculated values of  $|d\mu/dr|$  and  $d|q|/dr$  for the various nitrosyl complexes.

Nitrosyl complex	$q_N$ a.u.	$q_O$ a.u.	$ d\mu/dr $ a.u.	$r_{M-O}$ Å	$d q /dr$ a.u.
○ $Na_3[Fe(CN)_5NO]2H_2O$	+0.22	+0.13	3.35	2.76 <sup>23</sup>	0.58
● $Zn[Mn(CN)_5NO]H_2O$	–0.04	–0.03			
□ $K_3[Mn(CN)_5NO]2H_2O$	–0.11	–0.09	3.50	2.87 <sup>24</sup>	0.59
■ $K_3[Cr(CN)_5NO]H_2O$	–0.14	–0.10	3.58	3.01 <sup>25</sup>	0.58
▽ $K_4[Mo(CN)_5NO]$	–0.18	–0.16	3.69	3.18 <sup>13</sup>	0.56
▼ $K_3[V(CN)_5NO]2H_2O$	–0.26	–0.15		2.95 <sup>26</sup>	

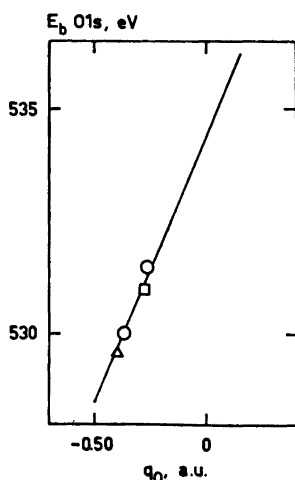


Fig. 4. Plot of oxygen 1s electron binding energies ( $E_b$  O1s) against calculated charge on oxygen atoms. (○) Ref. 19; (△) V<sub>2</sub>O<sub>5</sub> Ref. 20; (□) C<sub>2</sub>O<sub>2</sub>(s) Ref. 21.

From the measured infrared intensities of the N–O stretching vibration it is possible to get approximate information about the polarity of the N–O bond. In this case the fixed charge model has been applied. The complexes are considered as two-atomic molecules, *viz.* consisting of, *e.g.*, Fe(CN)<sub>5</sub>, N and O. For a two-atomic molecule, the absorption intensity is related to the dipole moment of the molecule by the formula<sup>22</sup>

$$A = \frac{\pi N}{3c^2 \times 10^8 \times \mu_{\text{red}}} \left( \frac{d\mu}{dr} \right)^2 \quad (1)$$

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. If it is assumed that the charges on the molecular fragments are  $+q$  and  $-q$  (atomic units), the dipole moment is

$$\mu = r|q| \quad (2)$$

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

$$\left| \frac{d\mu}{dr} \right| = |q| \quad (3)$$

If, on the other hand, there is a variation of charge with interatomic distance, a term relat-

ing to this, *viz.*  $d|q|/dr$ , is easily derived from eqn. (2), *i.e.*

$$\left| \frac{d\mu}{dr} \right| = |q| + r \frac{d|q|}{dr} \quad (4)$$

Calculated values of  $|d\mu/dr|$  from eqn. (1) are given in Table 3. Calculations have been performed only for those complexes for which it has been possible to measure the infrared intensity of the N–O stretching vibration in aqueous solution. The  $|d\mu/dr|$ -values are relatively high, so it is reasonable to suppose that the charge varies with the interatomic distance. As the charge on the oxygen atom is determined with ESCA (Table 3) and interatomic distances are known from X-ray crystallographic measurements,<sup>13,23–26</sup>  $d|q|/dr$  can be determined from eqn. (4). In the calculation of  $d|q|/dr$  the M–O (M–N+N–O) distance has been used and not the N–O distance, since  $r$  in eqn. (4) means the distance between two charge centers and it is quite reasonable that the charge center on the big molecular fragment is placed closer to the metal atom than to the nitrogen atom. The M–O distances from the literature<sup>13,23–26</sup> are included in Table 3. The calculated values of  $d|q|/dr$  are given in Table 3. It can be seen that  $d|q|/dr$  has about the same value for all the nitrosyl complexes. Thus, as  $|q_0|$  is small and practically constant, the change in  $|d\mu/dr|$ , which one observes, depends on the change in the interatomic distance ( $r_{\text{M-O}}$ ).

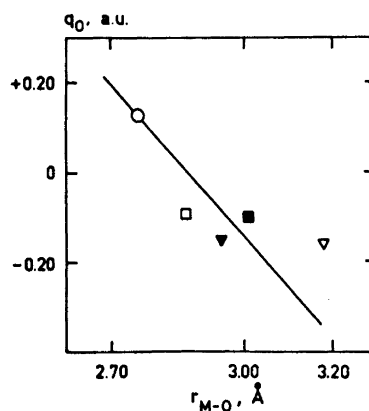


Fig. 5. The charge on the oxygen atom ( $q_0$ ) in the various nitrosyl complexes plotted against experimentally determined M–O distances. The same symbols as in Table 3 are used.

A more direct way to obtain a value of the charge parameter  $d|q|/dr$  is from experimentally determined charges on the oxygen atoms and experimentally determined interatomic distances.<sup>13,23-26</sup> In Fig. 5 the charge on the oxygen atom ( $q_o$ ) has been plotted against the M—O distance. From the slope of the straight line  $d|q|/dr$  has been estimated to  $0.6 \pm 0.2$  a.u., a value in good agreement with the  $d|q|/dr$ -values calculated from infrared intensity data (cf. Table 3).

#### CONCLUDING REMARKS

The results of the present investigation and the previous studies<sup>5,15</sup> on dinitrogen complexes show that it is possible to get more detailed information from ESCA data about the charge distribution on the M—X≡Y group than from infrared intensity measurements. Through the combination of infrared intensity data with experimentally determined charges on atoms, it has been possible to determine the variation of charge with interatomic distance ( $d|q|/dr$ ). 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. The calculated value of  $d|q|/dr$  for the nitrosyl complexes is about the same as the  $d|q|/dr$ -value earlier found<sup>5</sup> for the N—N bond in the dinitrogen complexes of rhenium and iridium. Consequently, a  $d|q|/dr$ -value of about 0.6 a.u. may be characteristic for the bond type that exists in the M—X≡Y group.

A further similarity between nitrosyl complexes and dinitrogen complexes is found if one regards the charge distribution on the dinitrogen ligand and the nitrosyl ligand. In the previous work<sup>5</sup> it was found that the inner nitrogen atom in the group M—N—N was the most negative one. In the present investigation it has been found that the nitrogen atom in the nitrosyl group is more negative than the oxygen atom (cf. Table 3). This is valid for all the complexes except for the iron complex, in which the nitrogen atom is more positive than the oxygen atom. This means that the degree of  $\pi$ -bonding in the iron complex is very small compared to the degree of  $\pi$ -bonding in the other complexes.

On the basis of the similarities which have

been found between dinitrogen complexes and nitrosyl complexes when considering the charge distribution and the charge parameter  $d|q|/dr$ , it could be of interest also to investigate carbonyl complexes. Carbonyl complexes are isoelectronic with corresponding dinitrogen complexes and are consequently suitable to investigate in this connection. Probably, it can be expected that they will give results which are well comparable with those found for dinitrogen complexes and nitrosyl complexes.

When this manuscript was close to completion it was learned that an ESCA investigation on almost the same nitrosyl complexes had been performed at the University of Gothenburg (Dr. N.-G. Vannerberg). It must be emphasized that these two investigations have been carried out completely independently. The ESCA spectra obtained in both these investigations were essentially identical.

The financial support for this work from the Swedish Board for Technical Development and the Bank of Sweden Tercentenary Fund is gratefully acknowledged. The author wishes to thank Dr. R. Larsson for his kind interest and valuable discussions. The author is also indebted to Mrs. Karin Trankéll for her assistance in the infrared spectroscopic measurements.

#### REFERENCES

1. Johnson, B. F. G. and McCleverty, J. H. *Progr. Inorg. Chem.* 7 (1966) 277.
2. Lewis, J., Irving, R. J. and Wilkinson, G. *J. Inorg. Nucl. Chem.* 7 (1958) 32.
3. Griffith, W. P., Lewis, J. and Wilkinson, G. *J. Inorg. Nucl. Chem.* 7 (1958) 38.
4. Folkesson, B. *Acta Chem. Scand.* 26 (1972) 4008.
5. Folkesson, B. *Acta Chem. Scand.* 27 (1973) 276.
6. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S.-E., Lindgren, I. and Lindberg, B. *ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almqvist & Wiksell, Uppsala 1967.
7. Hendrickson, D. N., Hollander, J. M. and Jolly, W. L. *Inorg. Chem.* 8 (1969) 2642.
8. Finn, P. and Jolly, W. L. *Inorg. Chem.* 11 (1972) 893.
9. Cotton, F. A., Monchamp, R. R., Henry, R. J. M. and Young, R. C. *J. Inorg. Nucl. Chem.* 10 (1959) 28.
10. Griffith, W. P., Lewis, J. and Wilkinson, G. *J. Chem. Soc. A* (1959) 872.
11. Hieber, W., Nast, R. and Gehring, G. *Z. Anorg. Chem.* 256 (1948) 169.

12. Riley, R. F. and Ho, L. *J. Inorg. Nucl. Chem.* **24** (1962) 1121.
13. Svedung, D. H. and Vannerberg, N.-G. *Acta Chem. Scand.* **22** (1968) 1551.
14. Griffith, W. P., Lewis, J. and Wilkinson, G. *J. Chem. Soc. A* (1959) 1632.
15. Folkesson, B. *Acta Chem. Scand.* **27** (1973) 287.
16. Larsson, R. and Mieziš, A. *Acta Chem. Scand.* **23** (1969) 37.
17. Schön, G. and Lundin, S. T. *J. Electron Spectrosc.* **1** (1972/73) 105.
18. Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Hedén, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Manne, R. and Baer, Y. *ESCA Applied to Free Molecules*, North Holland, Amsterdam 1969.
19. Larsson, R. and Larsson, L. *Chem. Scr.* **5** (1974) 195.
20. Larsson, R., Folkesson, B. and Schön, G. *Chem. Scr.* **3** (1973) 88.
21. Gelius, U., Allan, C. J., Allison, D. A., Siegbahn, H. and Siegbahn, K. *Chem. Phys. Lett.* **11** (1971) 224.
22. Barrow, G. M. *Introduction to Molecular Spectroscopy*, McGraw, New York 1962.
23. Manoharan, P. T. and Hamilton, W. C. *Inorg. Chem.* **2** (1963) 1043.
24. Tullberg, A. and Vannerberg, N.-G. *Acta Chem. Scand.* **21** (1967) 1462.
25. Vannerberg, N.-G. *Acta Chem. Scand.* **20** (1966) 1571.
26. Jagner, S. and Vannerberg, N.-G. *Acta Chem. Scand.* **24** (1970) 1988.

Received January 23, 1974.