Nitrosyl Complexes of Rhenium(II). Charge Distribution Study of Tetraethylammonium Salts of Penthalonitrosylrhenate(II) and of Its Monosubstituted Derivatives

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The charge distribution in $[Re(NO)X_5]^{--}$ and $[Re(NO)X_4L]^-$ (L = π acceptor ligand) is discussed in the light of the results from spectroscopic, spectromagnetic and polarographic techniques. The limits of the contributions from the different techniques and the possibility to compare the results are also considered.

Introduction

The electronic properties of d^5 metal ions, in field of ligands having different σ and π donor and acceptor abilities, were the subject of our recent paper [1]. Spectroscopic and spectromagnetic techniques were compared to characterize and to distinguish complexes with very similar electronic and structural properties. Now we wish to extend this type of investigation to $[Re(NO)X_5]^{--}$ (X = Cl⁻, Br⁻) and to their substituted products $[Re(NO)X_4\text{-}L]^-$ (L = pyridine; 2-methylpyridine; 3-Brpyridine; 3,5-dimethylpyridine; 3-Clpyridine; acetonitrile) in order to compare the possibilities of different techniques to study the charge distribution in these anions.

Experimental

Compounds were synthesized as previously described [2]. E.s.r. spectra were recorded on a Varian 4502-11 spectrometer, at liquid nitrogen temperature, and the g values were evaluated by standardization with diphenylpicrylhydrazyl. Electronic diffuse reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. Infrared spectra on a Perkin-Elmer 621 spectrophotometer in KBr (4000–200 cm⁻¹) and on a Perkin-Elmer

FIS 3 spectrophotometer in polytene (400–60 cm⁻¹). Raman spectra were recorded on a Coderg PHO instrument, equipped with Krypton and Argon lasers, with solid samples.

The spectroscopic and spectromagnetic measurements were carried out on the solid state, due to low solubility of all compounds.

Results and Discussion

Vibrational Properties

Vibrational properties were examined in the region of $\nu(NO)$, $\nu(M-X)$ stretching frequencies (Table I).

The frequencies related to $\nu(NO)$ vibrations are in the range characteristic of the NO⁺ group [3], in agreement with the observed oxidation state +2 of the rhenium and with the d^5 electronic configuration suggested by magnetic properties. Perturbations of $\nu(NO)$ due to change of the halogen from Cl⁻ to Br⁻ and to substitution of the halide *trans* to NO by a ligand L have been considered. As a matter of fact, on changing the halogen from chlorine to bromine, the frequency $\nu(NO)$ increases, although, on the basis of the electron affinity trend and by analogy with all known $[M(NO)X_5]^{--}$ dianions [4, 5], an opposite behaviour could be expected. However the electron affinity difference between halides could not be sufficient to explain the differences in the N–O bond strength.

The substitution of the halide *trans* to NO by a ligand L causes increase of the $\nu(NO)$ frequency; thus the *trans* ligand L increases the N–O bond strength. It can be suggested that the N–O bond strength depends on the weight of the electron transfer from the $d_\pi(Re)$ orbitals to the $\pi^*(NO)$ orbitals, so that the two variations previously described mean: i) the

TABLE I. Vibrational Spectra of $[(NEt_4)_2]$ $[Re(NO)X_5]$ and $[NEt_4]$ $[Re(NO)X_4L]$ Complexes.[a]

Compound		A_1 ν_{NO}	A_1 ν_{ReX_4}	A_1 ν_{ReX} (axial)	B_1 ν_{ReX_4}	E ν_{ReX_4}
$[(NEt_4)_2]$ $[Re(NO)Cl_5]$	IR	1718 vs	330 m	270 sh	–	295 vs; 310 sh
	R	–	330 (10)	283 (0.5)	340 sh	–
$[(NEt_4)_2]$ $[Re(NO)Br_5]$	IR	1734 vs	–	180 m	–	210 vs; 220 sh
	R	–	212 (10)	179 (2)	190 (0.5)	–
$[NEt_4]$ $[Re(NO)Cl_4(CH_3CN)]$	IR	1765 vs	332 sh	–	290 sh	306 vs; 320 sh
	R	–	331 (10)	–	280 (1)	310 sh
$[NEt_4]$ $[Re(NO)Cl_4(Py)]$	IR	1753 vs	331 m	–	290 sh	304 vs; 310 sh
	R	–	332 (10)	–	290 (0.5)	310 (4)
$[NEt_4]$ $[Re(NO)Cl_4(3ClPy)]$	IR	1735 vs	330 m	–	288 sh	305 vs; 310 sh
	R	–	331 (10)	–	289 (1.6)	315 sh
$[NEt_4]$ $[Re(NO)Cl_4(2MePy)]$	IR	1755 vs	332 m	–	285 sh	306 vs; 317 sh
	R	–	330 (10)	–	286 (1.5)	–
$[NEt_4]$ $[Re(NO)Br_4(CH_3CN)]$	IR	1770 vs	200 m	–	–	230 vs; 226 m
	R	–	201 (10)	–	–	221 (4); 233 (2)
$[NEt_4]$ $[Re(NO)Br_4(Py)]$	IR	1762 vs	196 s	–	190 sh	234 vs; 220 s
	R	–	215 (10)	–	190 (5)	–
$[NEt_4]$ $[Re(NO)Br_4(3BrPy)]$	IR	1740 vs	218 sh	–	–	221 vs
	R	–	220 (10)	–	204 (1)	–
$[NEt_4]$ $[Re(NO)Br_4(3MePy)]$	IR	1758 vs	210 sh	–	184 w	225 vs
	R	–	213 (10)	–	188 (0.5)	220 (2)
$[NEt_4]$ $[Re(NO)Br_4(3,5Me_2Py)]$	IR	1755 vs	208 sh	–	–	221 vs
	R	–	210 (10)	–	180 (0.5)	220 (0.5)

[a]s = strong; m = medium; w = weak; vs = very strong; sh = shoulder.

electron affinity difference between halogens is not sufficient to explain the differences in back donation to NO; ii) the out-of-plane electron transfer from the metal to the ligand L successfully competes with the electron transfer from the metal to NO, both L and NO being π acceptor ligands. On this purpose the variations in ν(NO) are not a measure of the π acceptor properties of the ligand L, probably because the electron density on the rhenium is due to the properties of the ligands with π acceptor ability (aromatic system of L ligand) and to those of the donor ligands (in-plane halides and nitrogen of the ligand L).

The value of ν(NO) is related to the electronic charge delocalization on the complex, not just to the π acceptor power of the ligand L.

As a proof, the ratio $\Delta E/\Delta\nu$, calculated from the polarographic [6] and the vibrational data for [Re(NO)Br₅]⁻⁻ and [Re(NO)Br₄py]⁻, is 700 mV/100 cm⁻¹, as compared to the value of $\Delta E/\Delta\nu < 425$ mV/100 cm⁻¹ for NO and NO⁺ [7]; so the reduction potential is more sensitive to the change of ν(NO) in our complexes than in the free ligand NO and the redox orbital is considerably delocalized over the molecule.

At first the vibrational analysis in the Re–X frequency region has been carried out on [N(ethyl)₄] [Re(NO)Br₄(CH₃CN)] [8] and [N(ethyl)₄] [Re(NO)-

Cl₄py] [9], whose structural data are available. The first compound belongs to the $Pn2_1a(C^9_{2v})$ group, with four molecules in the unit cell and anion site symmetry C_1. The molecular symmetry of [Re(NO)-Br₄(CH₃CN)]⁻ is C_{4v} and four normal Re–Br stretching modes are expected: A_1(IR, R), B_1(R), E(IR, R).

The splitting of the E vibration, observed in the IR and Raman spectra, is due to site symmetry C_1, since no molecular interactions were observed.

The compound [N(ethyl)₄] [Re(NO)Cl₄py], belongs to the C2/c (C^6_{2h}) group, with eight molecules in the cell and anion site symmetry C_1. However pyridine, whose plane lies parallel to the X–Re–X axis direction, lowers the molecular symmetry to C_{2v} and the splitting of the E vibration could be related to this effect. In this light, the π electron system of pyridine or its hydrogen atoms can strongly interact with the in-plane halide and remove the axial symmetry. The spectra of the other anions [Re(NO)-X₄L]⁻ show smaller axial symmetry perturbation, with respect to the acetonitrile and pyridine derivatives, and the splitting of the E vibration is only deducible from the shoulder coupled to the stronger absorption. Moreover the occasionally IR visible B_1 band indicates that the effects of a symmetry lower than C_{4v} are already present. Probably the greater steric hindrance of ligands other than the two discussed minimizes the effect of the site symmetry
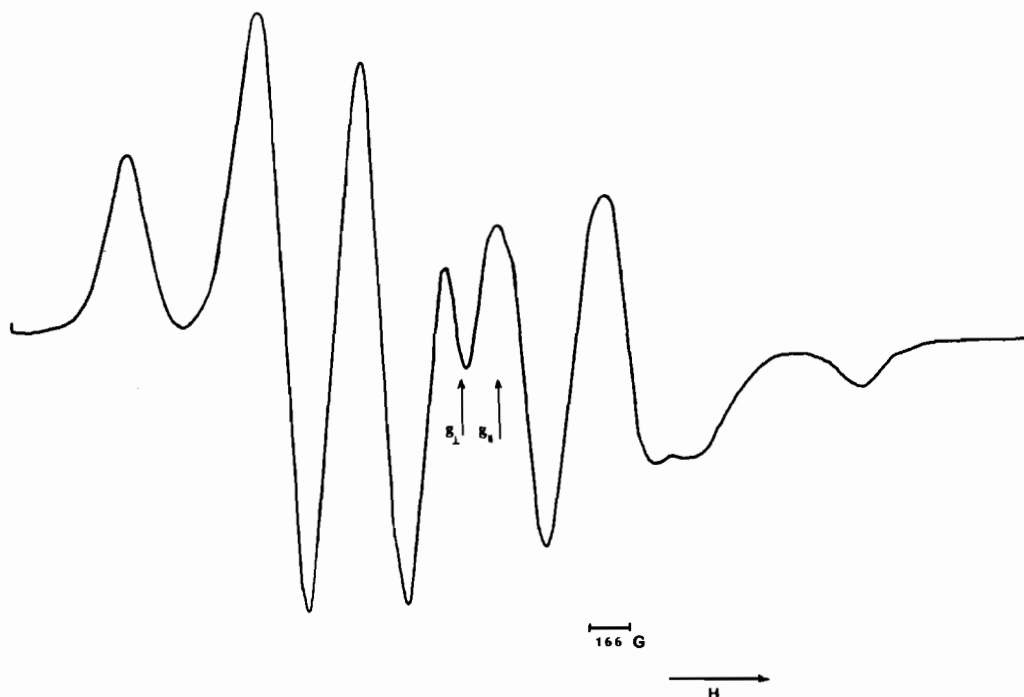
Figure 1. E.s.r. spectrum of $[NEt_4]_2 [Re(NO)Br_5]$.

and of the electronic perturbations which remove axial symmetry.

Penthalonitrosyl dianions $[Re(NO)X_5]^{--}$ should show Re–X stretching vibrations $2A_1(IR, R)$, $B_1(R)$, $E(IR, R)$ for true C_{4v} molecular symmetry. One additional band appears in the low infrared region and can be assigned to the A_1 vibration of Re–X bond *trans* to NO (See Table I).

Electronic and Magnetic Properties

Penthalonitrosyl complexes of rhenium(II) and their substituted derivatives are paramagnetic low spin compounds, with magnetic moment values in the range 1.6–1.8 B.M. at room temperature [2]. The d^5 low spin electronic configuration is the most probable for rhenium.

Polycrystalline samples of $[Re(NO)X_5]^{--}$ dianions give, at liquid nitrogen temperature, well resolved e.s.r. spectra (Fig. 1) showing also hyperfine interaction with rhenium nucleus. The shape of lines indicates axial symmetry, in agreement with the results of the vibrational analysis, and the e.s.r. spectra can be explained by the C_{4v} point group symmetry. In this light, calculations were performed to decide the ground state electronic configuration and to propose the most probable order of the rhenium d orbitals in a ligand field of this kind. Perturbations due to spin–orbit coupling and tetragonal distortion have been considered in the hole formalism which regards the t_{2g}^5 configuration as a one hole configuration [10]. The expression of the Hamiltonian operator is

$$H = -\zeta ls - \delta(l_z^2 - 2)$$

The eigenfunctions of the perturbation matrix are three Kramer's doublets, with general expression

$$\phi_1 = A \,|\zeta_1^\pm\rangle \pm B \,|\pm 1^\pm\rangle$$

where A and B are mixing coefficients between the orbitals $|2, 1\rangle$ $|2, -1\rangle$ and $\zeta_1 = 1/\sqrt{2}$ ($|2, 2\rangle$ $- |2, -2\rangle$).

By first order interaction of the ground Kramer's doublet with the magnetic operator

$$H = (l + 2s)H$$

we obtain the expressions of the principal g components

$$g_\parallel = 2(A^2 - B^2 - kB^2)$$

$$g_\perp = 2(A^2 + \sqrt{2}\, kAB)$$

The assignment of the ground-state configuration is clearly related to an unequivocal determination of the mixing coefficients and to a sure assignment of the g components. The value of the Stevens constant k may be obtained from the normalization of the coefficients. In the absence of single crystal analysis, the assignment of the principal g components for axially symmetrical $Re(NO)X_5^{--}$ dianions was carried out on the basis of the intensity differences (see Table II). Moreover four combinations are possible depending on the sign of the experimental g values. The choice has been carried out as follows:

TABLE II. Assignment of E.s.r. Parameters and Related Electronic Energy Levels.

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{a}$	$A_{\perp}^{a}$	A	B	η	ΔE_1	ΔE_2
$[(NEt_4)_2[Re(NO)Cl_5]$	1.842	2.025	626	328	0.6964	0.7176	0.023	1.02ζ	1.29ζ
	(−1.842)	(2.025)							
$[(NEt_4)_2[Re(NO)Br_5]$	1.980	2.086	600	295	0.5874	0.8093	0.013	1.48ζ	1.51ζ
	(−1.980)	(2.086)							

$^{a}cm^{-1}$ 10^4. In parentheses calculated values.

a) Four different sign combinations of $g_{\parallel}$ and $g_{\perp}$ have been considered and four different combinations of coefficients A and B were obtained, together with an equal number of k values.

b) The combinations which did not well reproduce the experimental g values or which gave k values much differing from unity have been ruled out. In this way only one assignment can be considered (Table II).

c) Knowledge of the coefficients A and B, which are known functions of the spin–orbit coupling constant (ζ) and of the tetragonal distortion parameter (δ), allows the calculation of δ as a function of the spin–orbit coupling constant ($\eta = \delta/\zeta$ in Table II); as a consequence it allows the diagonalization of the spin–orbit coupling and tetragonal perturbation matrix and the determination of the energy levels of our system as a function of the spin–orbit coupling constant (ΔE_1 and ΔE_2 in Table II).

The d-orbital order associated with the proposed assignment of the g components is in agreement with that proposed by Casey and Murmann [11] for $[Re(NO)Cl_5]^{--}$ and by Manhoran and Gray [12] for $[M(NO)CN_5]^{n-}$, with schematic representation:

$$2\delta \underline{\hspace{4cm}} \zeta_1$$
$$0 \cdots\cdots\cdots\cdots\cdots$$
$$-\delta \underline{\hspace{4cm}} |2, 1 > |2, -1>$$
$$2\delta = \langle \zeta_1 | -\delta(l_z^2 - 2) | \zeta_1 \rangle \qquad -\delta = \langle \pm 1 | -\delta(l_z^2 - 2) | \pm 1 \rangle$$

The ground state configuration, obtained by diagonalization of tetragonal distortion and spin–orbit perturbation matrix is

$$\phi_1 = AE''(^2B_2) + B\,E''(^2E)$$

where the eigenfunctions $^2B_2$ and ^2E, classified as E'' in the double group, respectively belong to e^4b_2 and e^3b^2 configurations. First and second excited states are

$$\phi_2 = AE''(^2E) - BE''(^2B_2)$$

$$\phi_3 = E'(^2E)$$

and lie at energy values ΔE_1 and ΔE_2 from the ground doublet state (see Table II). The unpaired electron is thus mainly in the e type d_π orbitals of the metal ion.

It is our opinion that one electron energy levels and states should not be coincident in this case. Indeed the spin–orbit coupling is first in the perturbation order, as confirmed by the low value of the η parameter, and has a determining effect on the composition of the ground state.

The hyperfine interaction with the rhenium nucleus has not been taken into account in the present paper, because the necessary structural data [13] on $[Re(NO)X_5]^{--}$ are not available. In the case of the substitution products $[Re(NO)X_4L]^-$ (L = py, CH_3CN), whose structures are known [8, 9], the spectrum does not show any hyperfine interaction. This effect may be due to a large change in the spin lattice relaxation times, which, in the case of the transition metal ions, is mainly related to large changes in the spin–orbit coupling constant [14]. An increasing spin–orbit coupling constant could be related to the increasing positive charge of the metal ion, shown by the polarographic measurements [6], on substitution of halide trans to NO with the ligand L.

The electronic spectra of penthalonitrosyl complexes and of their substituted derivatives (Table III, Fig. 2) show high intensity bands in the region 14000–17000 cm^{-1} and lower intensity bands in the region 3700–6600 cm^{-1}.

In our opinion the sharp bands in the region 3700–6600 cm^{-1} should be due to vibronic transitions, because they appear to be identical in the electronic spectra of all the compounds here described. Meanwhile the bands due to the electronic transitions $\phi_1 \rightarrow \phi_2$, $\phi_1 \rightarrow \phi_3$ could be assigned to the broad envelope in the 3700–4500 cm^{-1}. Transitions $\phi_1 \rightarrow \phi_2 = \Delta E_1$ and $\phi_1 \rightarrow \phi_3 = \Delta E_2$ have been calculated by a spin–orbit coupling constant value of ~2800 cm^{-1}, because this value reproduces the two transitions expected between the states ϕ_1, ϕ_2, ϕ_3, through the values of ΔE_1 and ΔE_2 derived from the e.s.r. data. The value of the spin–orbit coupling constant satisfactorily reproduces the value calculated and plotted for an approximate +2 charge on the rhenium [13]. The electronic transitions $\phi_1 \rightarrow \phi_2$ and $\phi_1 \rightarrow \phi_3$ do not vary in our series of products.

The absorptions at 14000–17000 cm^{-1} could be assigned to $d_\pi \rightarrow \pi^*(NO)$ transitions, in agreement
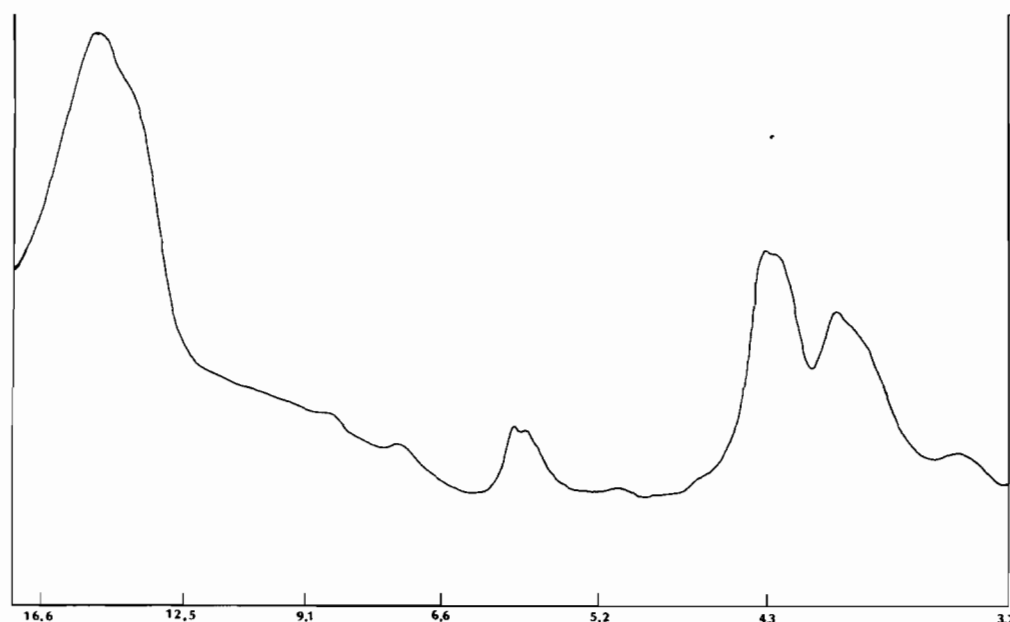
Figure 2. Electronic diffuse reflectance spectrum of [NEt$_4$]$_2$[Re(NO)Br$_5$].

TABLE III. Electronic Bands[a] in [(NEt$_4$)$_2$] [Re(NO)X$_5$] and [NEt$_4$] [Re(NO)X$_4$L] Complexes.

Compound	$d_\pi \rightarrow \pi^*$(NO)
[(NEt$_4$)$_2$] [Re(NO)Cl$_5$]	16.0 ; 15.04 sh
[(NEt$_4$)$_2$] [Re(NO)Br$_5$]	15.04; 14.1 sh
[NEt$_4$] [Re(NO)Cl$_4$(CH$_3$CN]	16.13; 15.4 sh
[NEt$_4$] [Re(NO)Cl$_4$(Py)]	16.1 ; 15.4 sh
[NEt$_4$] [Re(NO)Cl$_4$(3ClPy)]	16.66; 15.6 sh
[NEt$_4$] [Re(NO)Cl$_4$(2MePy)]	16.53; 15.60 sh
[NEt$_4$] [Re(NO)Br$_4$(CH$_3$CN)]	15.04; 14.30 sh
[NEt$_4$] [Re(NO)Br$_4$(Py)]	15.27; 14.30 sh
[NEt$_4$] [Re(NO)Br$_4$(3BrPy)]	15.62; 14.50 sh
[NEt$_4$] [Re(NO)Br$_4$(3MePy)]	15.15; 14.38 sh
[NEt$_4$] [Re(NO)Br$_4$(3,5Me$_2$Py)]	15.27; 14.38 sh

[a]10^3 cm^{-1}; sh = shoulder.

with the position of π^*(NO) orbitals proposed by Gray [12]. These bands vary in the series of our products, either on varying the halide, or on substituting the halide *trans* to NO by the ligand L. The shift to higher frequencies from bromine to chlorine derivatives is in accordance with the lower π donor ability of chlorine [15] and, within the series of the derivatives of the same halide, the shift to higher frequency is a consequence of the greater π acceptor ability of ligand L with respect to halide.

Conclusions

The most significant results from the different techniques may be summarized as:

a) suggestion of a metal ground state which accounts for magnetic, electronic and redox [6] properties;

b) increase in spin–orbit coupling constant upon substitution of the halide *trans* to NO by a π acceptor ligand;

c) decrease in metal to NO out-of-plane back donation, upon substitution of halide *trans* to NO with a π acceptor ligand and consequent increase in N–O bond order.

The half wave potentials, derived from the polarographic reduction, show lower negative values upon substituting the halide *trans* to NO by a π acceptor ligand L [6].

The redox properties are therefore sensitive to the out-of-plane electron transfer from the d_π orbitals of the metal to the π^* orbitals of the ligand L and, as a consequence, the $|2, 1> |2, -1> d_\pi$ orbitals of the metal give considerable contribution to the molecular redox orbital. The magnetic properties show that the same d_π orbitals of rhenium contain the unpaired electron. So the electronic configuration that, on the basis of the magnetic resonance properties, has the major role in the ground state, agrees with that determining the polarographic reduction. An increase in spin–orbit coupling constant is generally related to displacement of the negative charge from the metal and, in this case, is due to the π acceptor properties of the ligand L. By considering that the variations of the half wave potential, within derivatives of the same halide, show that the metal in anions [Re(NO)X$_4$L]$^-$ carries more positive charge than in [Re(NO)X$_5$]$^{--}$, the charge variations derived from e.s.r. and polarographic measurements are in

agreement. Electronic and vibrational data show that the groups NO and L are competitive π acceptors from the metal; so the presence of a back donation from the d_π rhenium orbitals to the π^* orbitals of the ligand L necessarily corresponds to an increase in the frequency of the transition $d_\pi \rightarrow \pi^*(NO)$ and in $\nu(NO)$ value for derivatives of the same halide. On the other hand, on passing from bromine to chlorine derivatives, the higher electronic frequency of the $d_\pi \rightarrow \pi^*(NO)$ transition is in agreement with the greater electron affinity of chlorine, whereas $\nu(NO)$ does not reproduce the trend of the change in inductive effect.

The same anomalous behaviour has been observed in $[Re(NO)X_5]^{--}$ dianions, in contrast to that of penthalonitrosyl dianions of d^6 transition metal ions [4, 5]. So we suggest that rhenium(II), like other d^5 systems [1], is generally less available than the d^6 systems to electron exchange with π ligands. If the ligand *trans* to NO is pyridine or an analogous compound, the electronic situation is more apt to transfer the effects of π acception to NO group than the effects of the inductive changes. Accordingly the values of the half wave potential [6] are in opposition to the changes in inductive effects.

At this point, it may be observed that the use of different techniques allows correlation of the different effects we have indicated under *a, b, c*, but correlation can be required only in those cases where charge modifications are due to an identical mechanism. The out-of-plane electron transfer from $d_\pi(Re)$ to $\pi^*(L)$ is a modification process common to all derivatives of the same halide and the results of all spectroscopies which depend on it are in agreement within the series; upon changing the halide modifications of inductive origin are implied and the results of the electronic and vibrational spectroscopies differ from those of the redox studies.

The separation of the results deriving from different techniques is not absolute, since each one is sensitive mostly to one effect, and to a lesser degree to others. For this reason the broadening of e.s.r. spectra does not quantify the π acceptor power of ligand L, nor does the increase in $\nu(NO)$ exactly reflect the trend of the π acceptor properties of the ligand *trans* to NO. The charge distribution in the molecule is never completely separable into the effects from which it derives, nor can these effects always be correlated.

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