COMPETITION OF LIGANDS WITH THE METAL OF COMPLEXES

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The study of chemical bonds in substituted metal carbonyls, derived from nickel carbonyl and the hexacarbonyls, has yielded several items of information on electronic phenomena induced by the substitutions[3,4,5,8]; indeed, these substitutions are such that the new ligands have donor–acceptor capacities different from that of CO, and that they bring about a lowering of molecular symmetry with respect to that of the mother molecule.

Simultaneous observation of the frequencies of vibrators C–O and M–C of the substitutes has led to the conclusion that the phenomenon of the lowering of frequencies C–O is closely tied to that of the raising of frequencies M–C. The C–O and M–C force constants have been calculated for the nickel carbonyl derivatives, confirming this relationship.

In addition, the curve of C–O force constants is linear in terms of the degree of substitution for a given ligand L. For all the ligands the slopes of these straight lines are a function of the effective electronegativity of groups A linked to ligand atom E of the ligands EA_3 (ref. 12) and they even vary linearly with Taft's polar substituent constants σ^* (ref. 1). Figures 1, 2 and 3 summarize these results.

Whereas it has been easy to explain the linearity of curve $\sigma^*(\nu_{C-O})$ as the conse-

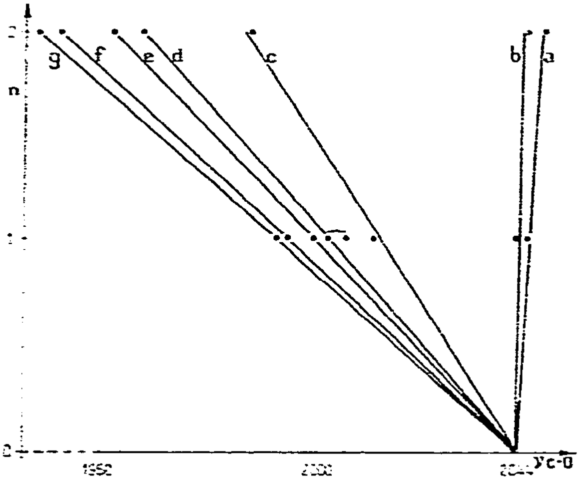

Fig. 1. F_2 Filiations of the stretching frequencies C–O of derivatives $Ni(CO)_{4-n}L_n$ (n = 0, 1, 2). a = PF_3; b = $P(CF_3)_3$; c = $P(C\equiv C-Ph)_3$; d = $Ph_2P-C\equiv C-C(CH_3)_2OH$; e = PPh_3; f = PMe_3, g = PEt_3.

quence of the essentially inductive[9] nature of the action of ligands on frequencies ν_{C-O}, the linearity of curve $k_{C-O} = f(n)$ (Fig. 2), k_{C-O} being the force constant of the C–O bond, has not yet been satisfactorily explained by the perfect electronic conductivity[12] of metal M and atom C in the L–M–C–O chain.

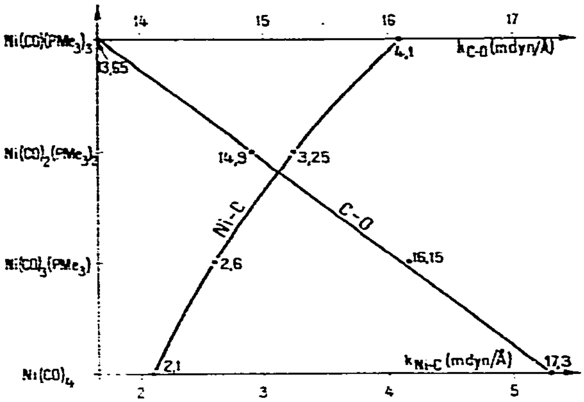

Fig. 2. Ni–C and C–O force constants of complexes $Ni(CO)_{4-n}(PMe_3)_n$ (n = 0, 1, 2, 3).

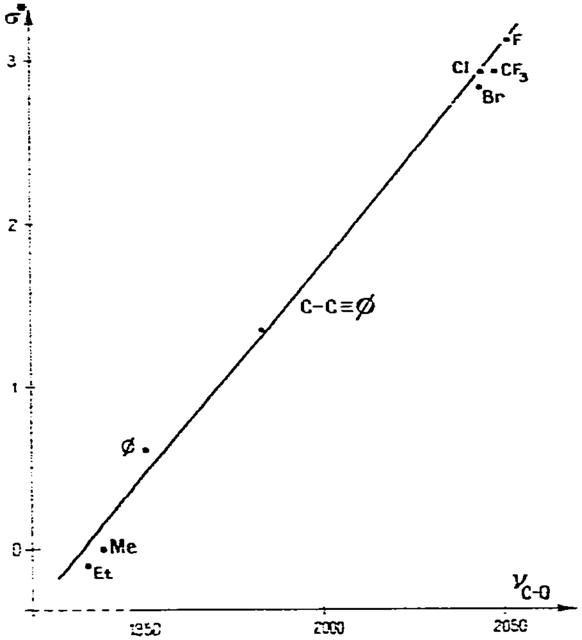

Fig. 3. Variations of the stretching frequencies ν_{C-O} of the $Ni(CO)_{4-n}L_n$ *vs.* the polar constants σ^* of groups XR of $L = P(XR)_3$.

If, as is generally implicitly admitted, a given ligand L is characterized by a fixed donor–acceptor capacity (σ–π), two ligands L opposed to two ligands CO in the di-substitute $Ni(CO)_2L_2$ should cause a variation in CO force constant equal to three times that caused by a single ligand opposed to three CO in the monosubstitute

$Ni(CO)_3L$. Similarly, the variation in the CO force constant in the tri-substitute $Ni(CO)L_3$ (three L for one CO) should be three times that of CO force constant in the di-substitute $Ni(CO)_2L_2$ (one L for one CO). It should therefore be possible to satisfy a relation which could be stated as follows: $\Delta k_{C-O} = m \cdot 3^{n-1}$ ($n = 1, 2, 3$; m: constant factor). $\Delta k_{C-O} = m, 3m, 9m$ for $n = 1, 2, 3$. This curve (B) is compared to the experimental curve (A) in Fig. 4.

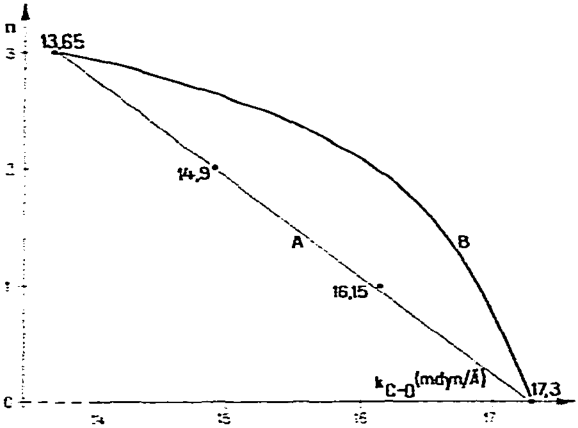

Fig. 4. Comparison of the experimental force constants curve (A) and curve (B) (see text) for complexes $Ni(CO)_{4-n}(PMe_3)_n$.

The disparity between these two curves is too great to proceed from inaccuracies in the calculations.

It is, then, necessary to reconsider the initial hypotheses and accept one of the two following restrictions:

a) either that atoms M and C are not perfect conductors: the higher the degree of substitution, the greater the negative charge retained by them;

b) or that the implicit rule whereby each ligand possesses a definite donor–acceptor capacity is not true.

It does not appear that the first above-mentioned restriction should be admitted. It violates Pauling's electro-neutrality principle but, above all, the phenomenon of an increase in the negative charge on atoms M and C, for a high value of n, should become attenuated when the ligand is increasingly less basic ($PMe_3 \rightarrow P(OMe)_3 \rightarrow PCl_3$). However, in each case the curve $k_{C-O}(n)$ is a straight line.

Finally, we think that it is necessary to reexamine in detail the rule of a donor–acceptor capacity fixed for a given ligand, using experimental data. These data are derived not only from spectroscopic measurements, as has been described, but also from the measurement of dipole moments on homogeneous series of metal carbonyl derivatives. The results obtained from measurement of dipole moments will be presented in another paper[16].

STUDY OF THE DONOR-ACCEPTOR CAPACITIES OF THE LIGANDS L IN THE COMPLEXES $M(CO)_{c-n}L_n$

As the rule defining a fixed donor–acceptor capacity for a given ligand L is not in accordance with experience, we have attempted to predict the behaviour of n electron donor–acceptor L-ligands placed in the presence of ($c - n$) electron donor–acceptor L_0-ligands (c being the coordination number) through atoms presumed to be conductive, *i.e.*, which do not retain a charge.

It has already been shown that metal carbonyl derivatives appear to be highly conductive systems; we have thus been led to study the behaviour of these complexes from the behaviour of analogous electrical systems.

The study which follows is not limited to metal carbonyls—although for these substances the magnitude of electron transfer is particularly high—but extends to all the $M(L_0)_{c-n}L_n$ complexes in which one at least of the L or L_0 ligand types is both donor and acceptor.

In the metal carbonyl derivatives L represents ligands EA_3 or CNX (X = R or Ph), L_0 the ligands CO; the conductor atoms are the central metal M and the carbon atom of CO.

In the proposed representation L and L_0 are, prior to coordination, generally at different energy potentials; when $L = EA_3$ (E = N, P, As, Sb, Bi), L has a different potential to that of L_0. In the reasoning which follows, the potential of L will be assumed to be higher than that of L_c, but the same conclusions could be drawn, using the appropriate signs, if the reverse assumption had been made.

When coordination has been achieved—*i.e.*, when communication has been established between L and L_0 via M—these two types of ligands will tend to acquire the same potential, L by yielding electrons and L_0 by receiving these electrons; the potential of L decreases while that of L_0 increases until the potentials are equalized.

As the circuit L–M–L_0 does not include a reservoir of electrical charges on M (Pauling's electroneutrality principle), the electrons yielded by L are transferred in their entirety to L_0. As a result the coordination (closing of circuit L–M–L_c) gives rise to an electron flow through M in the direction $L \rightarrow L_0$; this flow can be measured either by the reduction in the charge of L or by the increase in the charge of L_0.

L and L_0, considered as energy reservoirs, can therefore be represented as electric accumulators (or as reversible cells). When the circuit is closed, L, which has a higher potential than L_0, discharges into L_0 through M until the potentials are equalized.

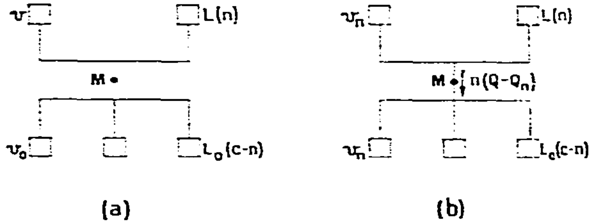

Fig. 5. Condition of accumulators L and L_0 before (*a*) and after (*b*) closing of circuit.

We shall examine the charge transfer phenomena in the general case of n ligands L and ($c - n$) ligands L_0; n stands for the degree of substitution and is an integral number $\leqslant c - 1$.

The reference potential is conventionally designated V_0.

The electron transfer values are governed by the respective capacities of the accumulators, the difference in potential between L and L_0—*i.e.*, ($v - v_c$)— and the ratio $n/(c - n)$.

The potential charge Q retained by each ligand L (Fig. 5a) is proportional to $(v - V_0)$:

$$Q = C(v - V_0)$$

C is the proportionality constant and is identical to the capacity of the accumulator.

Q represents the maximum amount of charge which L can deliver.

C is therefore the maximum quantity of the charge, referred to the unit value of the drop in potential, which L can deliver.

Similarly, the potential charge Q_0 retained by each ligand L_0 is:

$$Q_0 = C_0(v_0 - V_0)$$

Closing of the electrical circuit (Fig. 5b) causes the charge to flow from L to L_0 as shown by the equation:

$$n(Q - Q_n) = (c - n)(Q_0^n - Q_0)$$

Q_n represents the amount of charge remaining on the L ligands after the circuit has been closed.

Q_0^n represents the amount of charge borne by the L_0 ligands after the circuit has been closed.

After the circuit has been closed, the potentials of L and L_0 are v_n and v_0^n respectively; these potentials should be equal:

$$nC(v - V_0 - v_n + V_0) = (c - n)C_0(v_0^n - V_0 - v_0 + V_0) \equiv (c - n)C_0(v_n - v_0)$$

$$\frac{v - v_n}{v_n - v_0} = \frac{c - n}{c} \cdot \frac{C_0}{C}$$

But:

$$(v - v_n) = (v - v_0) - (v_n - v_0)$$

Whence:

$$\frac{v_n - v_0}{v - v_0} = \frac{nC}{nC + (c - n)\,C_0}$$

This relationship defines in comparative terms the potentials v_n for the various substitutes of a given ligand in terms of the ratio C/C_0.

In the complexes we have studied, L_0 represents ligand CO; the charge transfer phenomena occur in the form of the transfer of a bonding doublet towards the non-bonding oxygen atmosphere. Similarly, in ligand L of type EA_3 or EA_2B (E = N, P, As, Sb, Bi) (A or B = R, Ph, NC_5H_{10}, OR, OPh, Cl, F, CF_3), the charge transfer phenomena are centered on transfer of the electron doublet of E to the metal atom. The type and content of the charge transfers are thus identical for L and L_0, and their capacities C and C_0 should therefore be the same.

It is not necessary that the same should hold true ($C = C_0$) for all the charge transfer systems occurring in the complexes.

Given these conditions, the preceding relationship is simplified for the complexes under consideration:

$$\frac{v_n - v_0}{v - v_0} = \frac{n}{c}$$

It can be stated as follows: the relative gain in potential of L_0 for the various substitutes of a given ligand on a given metal is proportional to the degree of substitution.

Since the two ligands L and L_0 have the same capacity, an analogy with hydraulics can be made whereby the cross-sections of energy reservoirs L and L_0 are the same.

Figure 6 shows *the case of tetra-coordinated complexes* ($c = 4$). A ligand L with a given potential v gives rise to the mono-substitute ($n = 1$) $M(L_0)_3L$, the di-substitute ($n = 2$) $M(L_0)_2L_2$ and the tri-substitute ($n = 3$) $M(L_0)L_3$.

When equilibrium is achieved, the potentials are:

$$(v_1 - v_0) = {}^1/_4(v - v_0)$$

$$(v_2 - v_0) = {}^1/_2(v - v_0)$$

$$(v_3 - v_0) = {}^3/_4(v - v_0)$$

The gain in potential of L_0 for each substitution from $n = 0$ to $n = 3$ is constant:

$$(v_n - v_{n-1}) = {}^1/_4(v - v_0)$$

We next propose to calculate the amount of negative charge flowing through M when, starting from $M(L_0)_4$, we replace an L_0 by an $L(q_1)$, or two L_0 by two $L(q_2)$, or three L_0 by three $L(q_3)$.

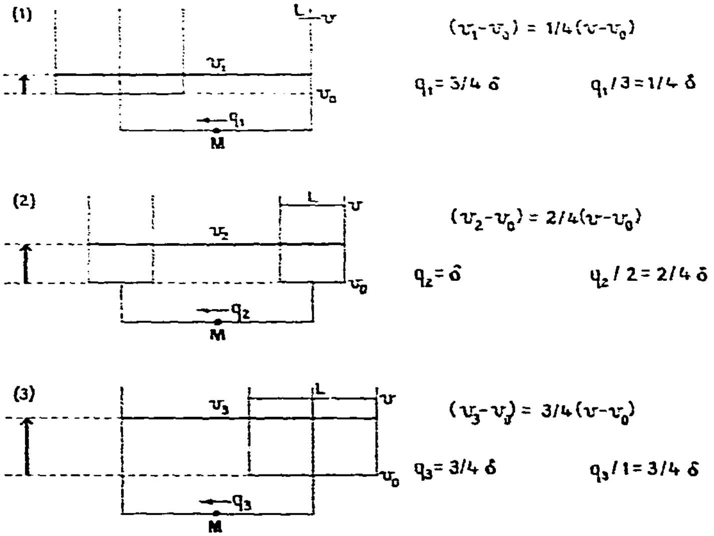

Fig. 6. Potentials of ligands L and L_0 in the tetra-coordinated complexes.

These quantities will be referred to the charge that ligand L would be likely to release to reach a potential of v_0; namely δ (for the hypothetical case in which $c \rightarrow \infty$). They can be calculated as charges lost by the L or gained by the L_0 ligands; we immediately obtain:

$$q_1 = (Q - Q_1) = 3(Q_0^1 - Q_0) = 3 \times {}^1\!/_4\,\delta = {}^3\!/_4\,\delta$$

$$q_2 = 2(Q - Q_2) = 2(Q_0^2 - Q_0) = 2 \times {}^1\!/_2\,\delta = \delta$$

$$q_3 = 3(Q - Q_3) = (Q_0^3 - Q_0) = 1 \times {}^3\!/_4\,\delta = {}^3\!/_4\,\delta$$

Thus the function $q(n)$ reaches a maximum for $n = 2$. The significance of this maximum is clear: in passing from a di-substitute to a tri-substitute, the electrons flow from L_0 towards L, the reverse of what takes place in the transition from a non-substitute to a mono-, then from the mono- to the di-substitute. This phenomenon can be easily visualized: assuming[13,14] that the intermediate form of the transition from a mono- to a di-substitute is a tri-coordinated form, $M(L_0)_2L$, in which the two L_0 must bear the charge formerly borne by the three L_0, that is ${}^3\!/_4\,\delta$, each L_0 of the $M(L_0)_2L$ therefore bears ${}^3\!/_8\,\delta$. The addition of an L-ligand to $M(L_0)_2L$ to obtain $M(L_0)_2L_2$ creates a flow of electrons ($L \rightarrow L_0$) so that ultimately each L_0 ligand bears ${}^1\!/_2\,\delta$.

In the transition from the di- to the tri-substitute, the single L_0 of the intermediate form $M(L_0)L_2$ bears a charge δ; to reach a point of balance for $M(L_0)L_3$ (${}^3\!/_4\,\delta$ on L_0), it is necessary that the electron flow occurs from L_0 towards L.

Quantities q_n concern the electron flow through M. We can immediately deduce the amounts of the charges $q_n/(c - n)$ received by a single ligand L_0: these quantities define the electron state of the L_0 ligands in the various substituted derivatives:

mono-substitute	$q_1 = {}^3\!/_4\,\delta$	$q_1/3 = {}^1\!/_4\,\delta$
di-substitute	$q_2 = \delta$	$q_2/2 = {}^1\!/_2\,\delta$
tri-substitute	$q_3 = {}^3\!/_4\,\delta$	$q_3/1 = {}^3\!/_4\,\delta$

It is apparent that the electron states vary proportionally to the degree of substitution:

$$\frac{q_n}{c - n} = \frac{n}{c} \cdot \delta$$

For the hexacoordinated complexes ($c = 6$), the situation of the various substitutes is quite analogous. Figure 7 represents the appropriate diagrams for the five substitutes; the notation δ′ has been used in place of δ to show that δ′ is not necessarily equal to δ.

The electrical analogy of complexes constituted by a set of ligands L *and* L_0, *which are accumulators of energy, interconnected through a perfectly conductive metal* M, *finally leads to the conclusion that ligands* L *and* L_0 *have donor–acceptor capacities which vary with the energy state of the complex to which they are bonded.* For example (Fig. 6) in the mono-substitute $M(L_0)_3L$, ligand L drops from potential v to potential v_1, whereas

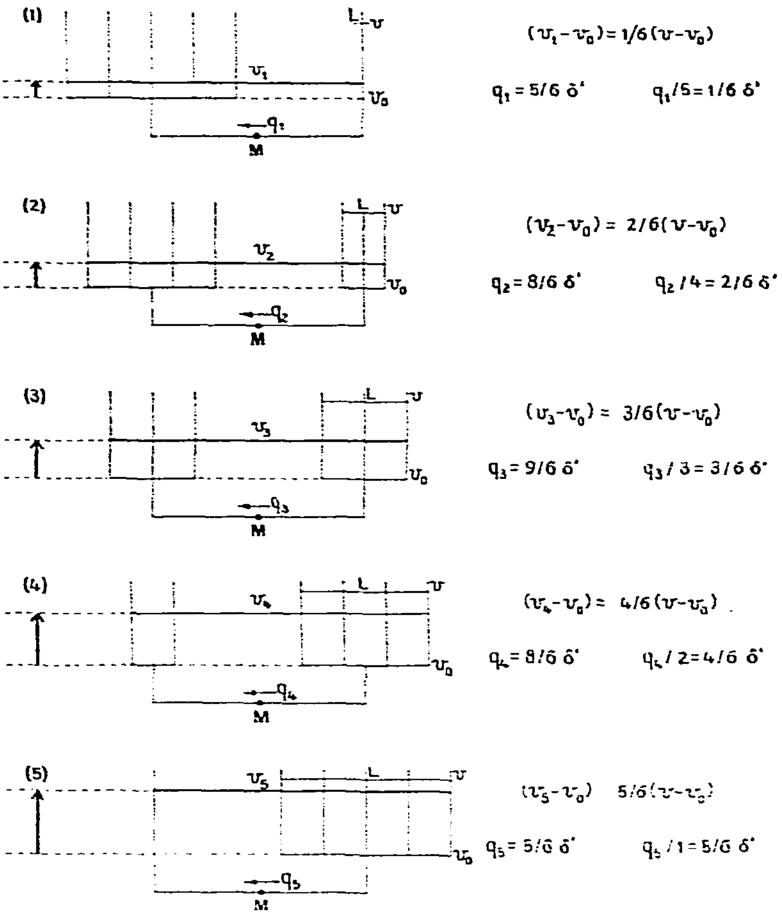

Fig. 7. Potentials of ligands L and L_0 in the hexa-coordinated complexes.

the L_0 ligands change from v_0 to v_1; in the di-substitute $M(L_0)_2L_2$, the potential of the L's drops from v to v_2, while that of the L_0's changes from v_0 to v_2. In the first case the L ligands have behaved as ligands with donor–acceptor capacities of $(v - v_1)$; in the second case, as ligands with donor–acceptor capacities of $(v - v_2)$, smaller than $(v - v_1)$.

In sum, the same ligand L behaves in different ways in the mono-, di- and tri-substitutes. This also holds true for the L_0 ligands, with donor–acceptor capacities represented respectively by $(v_1 - v_0)$, $(v_2 - v_0)$ and $(v_3 - v_0)$.

This mode of representation has the essential advantage of showing that a linear variation can be expected in the amounts of charge $q_n/(c - n) = (n/c)\delta$ acquired by each of the ligands L_0. In the case of $L_0 = CO$, this law should result in a linear variation in the CO force constants in terms of the degree of substitution, a variation which agrees with the results of the experiment (Fig. 2).

We shall now examine some of the consequences to be expected concerning the complexes $M(L_0)_{c-n}L_n$, derived from the proposed representation.

a) We can study the donor–acceptor capacities proper to homologous ligands, for example PA_3, in which A varies from Et to F, by observing the variations $q_p/(c - p)$ for a given degree of substitution $n = p$ and for a coordination number c. We then see that the donor–acceptor capacities proper to the ligands are proportional to the differences in potential $(v - v_0)$, which vary with each ligand. The conclusions previously presented regarding the classification of ligands and their mode of action on the complex do not therefore call for modification, as they were obtained by an analysis in conformity with the proposed scheme.

b) The direction of the electron flow through the metal M is shown by the relative values of q_n. It has already been seen that the flow changes direction starting from the substitute $n = c/2$. It is unlikely that such an effect can be demonstrated by a spectrographic method; a kinetic study appears more suitable. It could show a sudden change in the specific rate or in the activation energy of the substitution at the level of the substitute of $n = c/2$.

c) No specificity of the metal atom M having been introduced in the calculation other than the distinction $\delta - \delta'$, it should be possible to observe certain simple relationships between the slope of straight lines $k_{C-O}(n)$ furnished by a given ligand on atoms M of different coordination numbers. The energy state of L_0 being defined by $q_n/(c - n) = (n/c)\delta$, if we study the variations of $q_n/(c - n)$ of complexes with the same degree of substitution (constant n) with a given ligand on different atoms M (variable c), we see that $q_n/(c - n)$ is proportional to δ/c.

The derivatives of $Ni(CO)_4$, $Fe(CO)_5$, $Mo(CO)_6$ should then present values of $q_n/(c - n)$—*i.e.*, k_{C-O}—proportional to $\delta/4$, $\delta''/5$, $\delta'/6$ respectively [δ'' is related to $Fe(CO)_5$]. For a given degree of substitution and a given ligand, we should observe:

$$(\Delta k_{C-O})_{Ni}/(\Delta k_{C-O})_{Fe}/(\Delta k_{C-O})_{Mo} = (6/5/4)\,(\delta/\delta''/\delta')$$

We have been careful to suppose that $\delta \neq \delta' \neq \delta''$. It is possible that the differences between these values are minor, in which case we could verify the above relationship, although up to now the calculations of k_{C-O} have been made for only the nickel carbonyl derivatives.

However, δ, δ', δ'' could differ widely from each other: these values, which correspond to the maximum transfer of L towards M, are partly determined by the overlapping of the bonding orbitals of L and M. However, we know this to be a function of the hybridation type of M: Pauling[2] has defined comparative "bond strengths" of metal atoms, which differ in the same metal when tetrahedrally or octahedrally coordinated. It therefore seems reasonable to maintain a distinction between δ, δ' and δ''. As this distinction is of a qualitative nature only, it is no longer possible to verify the relationship predicted above.

d) As yet no hypotheses have been formulated on the contents of bonds M–L; it has only been stated that the potential of L-ligands drops, by coordination, from v to v_n. There has been repeated discussion of the π-bonding of the M–L bonds[6,7,9,10,11,13,15,17,18]. The drop in potential from v to v_n accounts for only the over-all phenomenon; the σ and π contributions could be revealed only by spectrographic study of the M–L bonds. Experimental results obtained on the M–L bonds up to now known are not sufficient to justify drawing a conclusion.

CONCLUSION

To explain the experimental facts observed in a certain class of complexes, it is assumed that, generally speaking, the ligands cannot be characterized by definite donor–acceptor capacities. The donor-acceptor capicity of a ligand is governed by two main factors: the donor–acceptor capacity peculiar to the ligand, which depends on its chemical structure; and the electron state of the complex to which the ligand is bonded.

The proposed mode of representation is shown for complexes derived from metal carbonyls, in which the very large variations registered in the force constants of C–O and M–C bonds when the ligand and the degree of substitution vary, allow an accurate study to be made.

The ligands L and L_0 of complexes $M(L_0)_{c-n}L_n$, initially at different potentials, tend to equalize their potentials, with one of the ligands receiving the electrons released by the other. It is possible to calculate the relative charge transfers—or, what amounts to the same thing, the relative donor–acceptor capacities—for each of the substitutes with a given ligand on a given metal: these vary in proportion to the degree of substitution. As these transfers determine the energy state of the acceptor ligand CO, it should be possible to observe that the variation of the C–O force constants in terms of the degree of substitution is linear. This has been confirmed experimentally.

It should be possible to bring out the behaviour of ligands with varying donor–acceptor capacities—which underlies the described interpretation—in complexes $M(L_0)_{c-n}L_n$, in which at least one of the ligands behaves both as an acceptor and as a donor, but generally with a much feebler intensity than those observed in cases where $L_0 = CO$.

Finally, the proposed representation makes it possible to explain the values of the dipole moments of substituted metal carbonyls[16].

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SUMMARY

The study of force constants in the chemical bonds of numerous complexes of a special class leads to the conclusion that coordinated ligands cannot, generally speaking, be characterized by definite donor–acceptor capacities. These are dependent both on the donor–acceptor capacities peculiar to the ligands, which depend on their chemical structure, and on the over-all electron state of the part of the complex to which they are bonded.

RÉSUMÉ

L'étude des constantes de force des liaisons de nombreux complexes d'une classe particulière conduit à admettre que, d'une façon générale, les ligands coordinés ne peuvent être caractérisés par des pouvoirs donneur–accepteur définis. Ceux-ci sont

déterminés à la fois par les pouvoirs donneur–accepteur propres des ligands, dépendant de leur structure chimique, et par l'état électronique global de la partie du complexe à laquelle ils sont liés.

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