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LIGAND BASED REDOX SERIES *

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CONTENTS

A. INTRODUCTION

The concept of redox series (sometimes called also redox chain or electron transfer series) has emerged in the literature only in about the last 15 years in connection with the study of redox properties of coordination compounds, even if, in thermodynamic aspects, it represents essentially only an extension of the work by Michaelis [1] on the semiquinone problem. Recent, mainly electrochemical, studies have shown, however, the generality of the concept of multistep redox processes and their importance for the general theory of redox processes as well as for catalysis of redox reactions, tailoring of redox agents [2], electrocatalysis and elucidation of biological electron-transfer systems.

Fundamental analysis of the available experimental material as well as the theoretical approach which have been undertaken in this laboratory uncovered several new aspects of the problem, especially those related to the structure–redox potential relationships and those of the influence of the

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* This article is an extended record of a lecture and does not comprise an exhaustive review of the topic.

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overall number of electrons in the system upon its donor–acceptor and redox properties in general [3]. The problem of the dependence of the substituent effect upon the oxidation state of the complex is of great general importance as only within a redox series can the influence of the substituent upon the various energy levels be studied [4].

A redox series is a set of compounds having identical composition, the members of which differ only in the overall number of electrons (n). For example, for a complex ML_m^z (m is the number of identical ligands, z is the charge of the complex) the set

$$ML_m^z - ML_m^{z-1} - ML_m^{z-2} - ML_m^{z-3} - \cdots$$

represents a redox series. Each redox series is characterized by the number of redox steps within the set (N, only sets with $N \geqslant 2$ are regarded as redox series; for $N = 1$ we have a redox couple), by the corresponding differences in n ($\Delta z = \Delta n$, in most cases $\Delta n = 1$) between neighbouring members of the series and by the values of the standard redox potentials (E_i^0) of the successive steps within the series. Furthermore, rate constants of the interconversion of neighbouring members and the intrinsic stability of individual members are of importance for description and understanding of the series.

Redox series of coordination compounds were first obtained chemically (e.g. the famous series of low-valent transition metal complexes with bipyridine prepared by Herzog and co-workers), however, the greatest progress has been achieved only when electrochemical techniques have been applied. Recently, new redox series are mostly discovered by using polarographic or voltametric techniques. Electrochemically a redox series is characterized by a sequence of redox steps (e.g. polarographic waves or voltametric peaks) which correspond in most cases to one-electron changes and are electrochemically reversible (i.e. fast electrode reaction). It can be shown, however, that electrochemical reversibility is *not* a necessary condition for a redox series. In many cases slow redox steps are observed along the series connected with an internal change of the structure within the same atomic framework (e.g. ring openings, bond length changes). On the other hand, chemical reversibility is essential as it indicates (and in most cases proves) that the subsequent members of the series can be interconverted by a simple change of electron number.

The aim of this article is to show some regularities in the patterns of redox series formed by transition metal complexes with ligands which are, in the uncomplexed form, capable of undergoing a redox reaction (redox active ligands).

B. REDOX SERIES WITH REDOX ACTIVE LIGANDS

Redox series are formed by most transition metals with a wide variety of ligands. As far as the mechanism of redox series formation is concerned, ligands function either as *stabilizers* of the redox series or as stabilizers and *carriers* of the tendency to form the redox series at the same time. In the first case the tendency to form the redox series is being carried by the properties of the central metal, by the presence of multiple metal–metal bond or of a metal cluster. Redox orbitals in complexes with this class of ligands (e.g. CN^-, CO) do not originate mostly from the ligand orbitals. Ligands stabilize the redox series by compensating the charge change via their σ- or π-orbitals.

The second, more common, situation arises when the redox orbitals used along the redox series originate from the ligand orbitals. Ligands of this class are mainly those which, in the free uncomplexed state, undergo redox reactions under the formation of stable products (radical anions or cations, dianions). In most cases these ligands are characterized by a well defined π-system to which the donor atoms are conjugated. However, not all ligands with well defined π-systems (e.g. benzene or cyclopentadienyl) do promote extensive redox series formation. The tendency of a ligand to function as the carrier of redox series is closely connected with the energy of its orbitals which might get involved in the redox process. Generally, the easier the reduction (or oxidation) of the free ligand is the more pronounced is the tendency of the ligand to become the carrier of the redox series. In a simplified way it can be stated that *redox active ligands* (with redox change localized in the π-system) *are usually carriers of redox series.*

The redox orbitals available in the complex for successive steps can thus originate from the ligand orbitals only (as in many porphyrin complexes in which the ligand is the only carrier) or from both the metal and ligand orbitals. The number of available redox orbitals in the complex determines the size of the redox series. For a complex ML_m, in which each free ligand exchanges N_L electrons (i.e. each ligand contributes $\frac{1}{2}N_L$ orbitals into the system of redox orbitals of the complex) and the central atom exchanges N_M electrons, the maximum possible size of the redox series (i.e. the number of redox steps) is given by [3]

$$N_{MAX} = N_M + mN_L \tag{1}$$

This equation is valid for all types of redox series.

Whereas the determination of N_L does not, in most cases, present any substantial problem [3], the discussion and prediction of N_M is not as simple. Even if theoretical derivation, based on the analysis of ionization potentials, could lead to the prediction of N_M values, some empirical rules, based mainly on the knowledge of electrochemical behaviour of the particular metal, seem at the present state of our knowledge to be more useful. For transition metal complexes only those processes are taken into consideration in which *d*-electrons are exchanged. Electron exchange is dependent upon the nature of the metal, and is usually confined to intervals between specific configurations, especially d^0–d^3, d^3–d^6, d^6–d^{10} (in this latter interval subgroups d^6–d^8 and d^8–d^{10} appear, however, not so distinctly as the main groups). Usually the number of metal based electrons does not exceed that corresponding to the metal atom.

As to which of these groups a given metal atom would belong can be judged from the preponderant configuration of the most frequent oxidation state of the metal in complexes with redox inactive ligands. This is, of course, very closely connected with the values of the ionization potential, I, of the free metal ion: most frequently those oxidation states are reached for which I_i is of the order 30–40 eV. This criterion would place titanium into the d^0–d^3 group, chromium into the d^3–d^6 group, cobalt into the d^6–$d^8(d^{10})$ group, etc. The groups specified above are, of course, not absolute limits of configurations of metal atoms from which members of redox series can be derived. However, the inspection of I-values of gaseous metals and the splitting of the *d*-levels due to complex formation support the general pattern according to which metals from Ti to Fe could mostly reach the d^6 configuration as the upper limit, metals from Co to Cu, the d^{10} configuration. Second and third row transition metal complexes exhibit usually a tendency to reach higher oxidation states—this is due to the fact that the values of higher ionization potentials of these metals are lower than those of

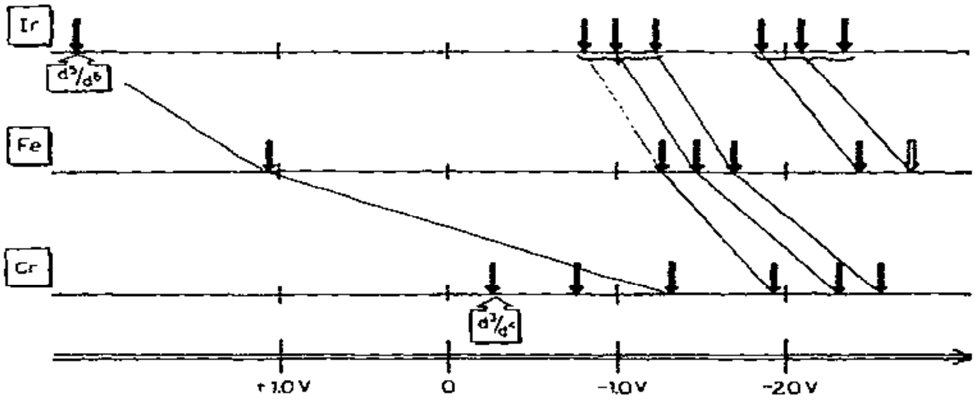


Fig. 1. Comparison of $E_{1/2}$ values for bipyridine complexes. Data taken from refs. 5–8. Open arrow denotes a not fully resolved electrode process. Lines connect formally isoelectronic species.

the first row elements. Further criteria for the estimation of N_M are given in ref. 3.

The rule expressed by eqn. (1) is generally valid in determining the maximum possible size of the redox series. However, other factors might influence the maximum accessible size of the series so that in many cases the actually observed size is smaller than that given by eqn. (1). On the other hand, rule (1) has proven its validity and usefulness in detecting the missing members of the set or in the explanation of the behaviour of the series.

Figure 1 compares the observed behaviour of three series of tris-bipyridine complexes. (Most of the data presented in the figures in this paper are based on references quoted. They have been, however, remeasured in this laboratory, whenever possible, to ensure identical scaling. From among the numerous series those formed by bipyridine and its analogues were chosen as examples throughout the paper.) The iridium series seems to be complete. The iridium atom in the +4 oxidation state has a d^5-configuration. The d^5–d^6 transition is that observed at about +2 V. The $d^6 - d^7$ energy difference for iridium is very large and the corresponding transition is unlikely to proceed in the accessible range of potentials. N_M thus equals 1. For bipyridine $N_L = 2$ so that, with $m = 3$, we get $N_{MAX} = 7$. As seen in Fig. 1 seven redox steps are observed experimentally in accordance with the prediction. For iron similar arguments hold and $N = 7$ should be observed. Experiments have shown only 6 redox steps. The ${}_6E_{1/2}$ value and the spacing of $E_{1/2}$s indicate that the missing step could be expected around −3 V, i.e. in the region extremely difficult for observation. However, other termination mechanisms cannot be excluded. For chromium with d^3 configuration in the +3 state N_M would be expected to be 3, i.e. up to d^6 configuration. With $N_L = 2$ and $m = 3$, N_{MAX} would be 9. Only six redox steps have been observed experimentally [6,9], with the most negative step at −2.5 V, i.e. about 0.3 V more negative than the E_1^0 for free bipyridine [6,10]. The analysis of the sequence of E^0-values indicates that not all the possible ligand-based redox steps are reached (see below, see also ref. 3). The validity of rule (1) is also shown in Figs. 4, 5, 6 and 9.

Series in which ligands are the essential carriers of the tendency to form redox series are generally of two types

(a) $N_M = 0, \quad m = 1$

i.e. the redox series is carried only by the ligand (e.g. many macrocyclic ligands)

(b) $N_M \neq 0, \quad m > 1$

i.e. complexes with redox active metal and two or more redox active ligands.

Whereas the former type of series is, as regards their interpretation, straightforward, the latter type needs a deeper analysis to get the full understanding of the factors governing the general pattern of E^0-values along the series.

Complexes of this type, i.e. ML_m^z, are formed by a variety of ligands, like β-diketones, *o*-quinone type ligands, heterocyclic ligands, etc. All these ligands are, as mentioned above, characterized by a well-defined π-system which might enter the interaction with the appropriate orbitals of the metal. This π-interaction of metal and ligand orbitals ranges continuously from weak to strong depending predominantly upon the relative energies of π-orbitals of the partners participating in the bonding. In the case of weak π-interaction it can be shown (see below) that the redox potentials along the redox series (${}_cE^0$) can be easily correlated to those of the free ligand (${}_LE^0$). On the other hand, strong interaction blurs the relation between the behaviour of the free ligand and that of the redox series. In the latter and, especially, intermediate cases, however, the change of π-interaction along the redox series has to be taken into consideration. Thus, e.g. the chromium bipyridine system, mentioned above, seems to show the behaviour typical for stronger interaction at the beginning of the series whereas the last three redox steps resemble closely those of iron or iridium systems in which weak π-interaction obviously operates.

As to whether strong or weak interaction influences the behaviour of the series can be deduced by quantum-chemical calculations [11]. However, comparison of theoretical considerations with experimental data leads to a simple way of prediction: if the central metal atom (with d^n, $n \leqslant 6$, configuration) in its +2 state, coordinated to redox inactive ligands, is a weak reducing agent with respect to the oxidized form of the ligand, the π-interaction can be expected to be weak and vice versa. Experimentally, if the M^{3+}/M^{2+} solvated couple is at least 2.5 V more positive than the first reduction step of the free ligand the observed behaviour is that predicted for the weak interaction, i.e. ${}_cE^0$ are related to ${}_LE^0$ ("well-behaved" series). If M^{3+}/M^{2+} hexacyanide couple is considered as the reference couple, the minimum difference has to be about 1.8 V.

There are complexes forming redox series with "inverted" position of ligand and solvated metal redox potentials, i.e. the free ligand reduction is more positive than the M^{3+}/M^{2+} couple. The exact formulation of these complexes has been subject to a debate in the literature. However, the analysis of the pattern of their redox series shows they mostly do follow the same rules as series discussed here (cf. ref. 3).

In following paragraphs of this paper the correlation of the ligand based redox steps in the "well-behaved" series with the redox properties of free ligands will be analyzed in more detail.

In a complex with two or more identical particles capable of undergoing identical redox reaction the problem of localization of a one-electron change is essential. In principle there are two possibilities for a complex of the ML_m^z-type.

(a) The electron is localized on to one ligand.

In this case an *m*-degenerate state would arise and the Jahn–Teller theorem would be violated. This means that the ligand which undergoes the redox change has to become different from the remaining ligands, e.g.

$$\begin{array}{lll} \mathrm{M}({}_a\mathrm{L}{}_b\mathrm{L}{}_c\mathrm{L}) & +e^- = & \mathrm{M}({}_a\mathrm{L}^-{}_b\mathrm{L}{}_c\mathrm{L}) \\ a=b=c & & a\neq b,c;\ b=c \end{array} \qquad (2)$$

There are of course three possibilities of localization (a, b, c) which necessarily result in three different Jahn–Teller states between which the system would oscillate.

Indirect spectroscopic evidence on the localization of the charge-change in CT spectra (see refs. 12–15) is not completely conclusive and not fully applicable to processes under discussion. The EPR measurements on $\mathrm{Co(bipy)(O_2C_6H_2(\mathit{t}\text{-}Bu)_2)_2}$ indicate, on the other hand, an intramolecular exchange of the electron between states with different localization of the redox change [16].

(b) The electron is delocalized over all identical ligands in a non-degenerate orbital arising from ligand–ligand interaction (or metal-mediated ligand–ligand interaction).

In this case the extra stabilization energy, analogous to the Jahn–Teller distortion stabilization, is gained by the delocalization of the charge over the entire ligand systems.

Which of the situations actually arises depends upon the relative stabilization via mechanism (a) or (b) and upon the possibility of the system to undergo Jahn–Teller distortion. Electrochemically these two possible localizations cannot be distinguished experimentally as the Jahn–Teller distortion with very rapid exchange between various states would result in an averaging of the system and thus in a picture identical with that obtained for a delocalized system. The changes in total energy under mechanism (a) and (b) are so subtle that present computational methods cannot give an unambiguous answer as to which situation is preferred.

The analysis of the redox series is, as will be seen later, influenced by this uncertainty only to a small degree as calculations indicate that the energy due to the electron interaction is the dominant factor in most cases under investigation.

C. REDOX BEHAVIOUR OF LIGATED MOLECULES

Most of the redox active ligands under consideration undergo a two- or generally $2k$- ($k = 1, 2, \ldots$) step electrode process. When, as is the most frequent case, the most oxidized form of the ligand is investigated, $2k$ reduction one-electron steps are observed. The first, leading to the formation of the radical anion $L^{\dot{-}}$, is usually fast, chemically as well as electrochemically reversible. The second reduction steps results in the formation of the dianion, L^{2-}, and is not necessarily electrochemically reversible (c.f., e.g. the reduction of bipyridine and its analogues [10]). A two step reduction of the free ligand can be described as

$$L \overset{_LE_1^0}{\Leftrightarrow} L^{\dot{-}} \overset{_LE_2^0}{\Leftrightarrow} L^{2-} \tag{3}$$

The difference $({}_LE_1^0 - {}_LE_2^0) = \Delta_L E^0$ is given mainly by the energy of spin-pairing in the redox orbital and difference in the free energy of solvation of the two couples. It has to be emphasized that this type of behaviour is observed only under strictly aprotic conditions, as most anion radicals, $L^{\dot{-}}$, react rapidly with hydrogen donors under formation of protonated species. This process is usually accompanied by a change of the mechanism of electrode process.

When the ligand is incorporated into a complex with weak metal–ligand π-interaction, MX_nL, its redox behaviour is qualitatively the same as that in the free state, a change in the values of standard redox potentials is, however, observed (see Fig. 2). In all cases studied *the standard redox potentials of a ligated molecule are more positive than those of the free molecule.* This shift towards more positive potentials is relatively constant, amounting to +0.4 to +0.7 V for a wide variety of metals and ligands. (It

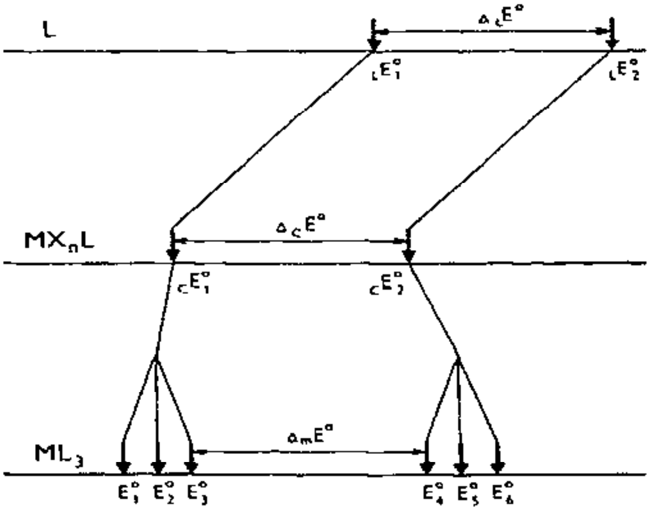


Fig. 2. Relation between the standard redox potentials of the free ligand (L), ligand coordinated to a metal (MX_nL) and a complex ML_m (for $m=3$).

has to be emphasized that this rule is applicable only for ligands of the type discussed, i.e. those bonded by a σ-bond with a specified donor atom. π-bonded ligands, e.g. η^6-benzoquinones, show mostly a shift towards more negative potentials (cf., e.g. ref. 17).) Only in ions with higher positive charge (+3 or +4) does this shift of ligand based redox potentials increase up to about 1 V.

Thermodynamic interpretation of this observation points to the conclusion that the reduced forms of the ligand, $L^{\overline{\cdot}}$ and L^{2-}, are more stabilized by ligation than the fully oxidized form L. This stabilization is caused for the most part by the central field of the metal atom which mostly carries a positive charge. Our model CNDO/2 calculations on diimine ligands [11] indicate a stabilization of 4.8 eV for the π-orbital and 5.3 eV for π-antibonding orbital per one unit of positive charge of the central field (cf. also ref. 18). σ-bonding between the ligand and metal also causes a stabilization of π-orbitals of the ligand due to the primary decrease of electron density on the donor atom and its compensation by electron shifts and inductive effects within the ligand molecule. This "σ-effect" seems to be of lesser importance but depends, however, strongly upon the nature of the ligand. Ligands with good ability to compensate the local charge change (e.g. those with extensive π-system and high polarizability) show generally a smaller σ-effect than those with localized π-bonds.

An example of the influence of ligation upon the redox potential of the ligand is shown in Fig. 3. The series compared in Fig. 3 reflect for the most part only the influence of the metal–ligand bond upon the reduction of the ligand, as both the free ligand system and those of complexes are of the same

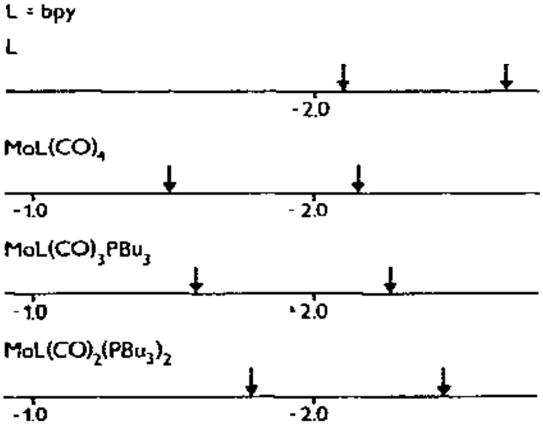


Fig. 3. Influence of metal–ligand bond upon the reduction of bipyridine ligand. Data taken from ref. 18 and rescaled using the author's data on free bipyridine and molybdenum-tetracarbonyl-bipyridine.

charge type so that the influence of change of solvation energy between various series can be expected to be small (only the difference in the size of the particles could play a role in determining the solvation energy). The examples quoted in Fig. 3 demonstrate the dependence of the bonded ligand reduction upon the remaining part of the coordination sphere, i.e. transmission of the electronic effects through the central metal atom. As the EPR-coupling constants [18] indicate, the electronic density on the molybdenum atom increases in the order

$$Mo(CO)_4bpy < Mo(CO)_3PBu_3bpy < Mo(CO)_2(PBu_3)_2bpy$$

The central field effect and thus the positive shift of the ligand reduction would be expected to decrease in the same order, in full agreement with the experiment and the general picture of the influence of ligation upon the redox potential of the molecule. The difference $\Delta_c E^0$ (see Fig. 2) is almost constant for all three molybdenum complexes and is about 0.1–0.15 V bigger than $\Delta_L E^0$, i.e. the value for the free ligand. This indicates a slight change in spin-pairing energy when going from the free to the ligated molecule, on one side, and an almost constant delocalization of the π-system in the three complexes compared, on the other side, confirming again that the main factor determining the shift of the ligand reduction is the influence of the central field due to the central atom.

This discussion can be summarized in the second rule governing the behaviour of redox series,

$${}_cE_i^0 > {}_LE_i^0 \tag{4}$$

i.e. the reduction potential of the ligated molecule is always more positive when compared with that of the uncomplexed molecule.

What has been deduced for the redox properties of one ligated molecule is necessarily valid also for complexes ML_m^z containing two or more identical redox active ligands at the same time. The value of the potential for the first reduction of such a metal bonded cluster of ligands is governed by the same factors as that of one coordinated molecule, i.e. E_1^0 (see Fig. 2) is always more positive than ${}_LE_1^0$ and in most cases slightly more positive than the value of ${}_cE_1^0$. The pattern of redox potentials of ML_m^z is influenced by two additional factors:

(i) Direct ligand–ligand interaction and metal-mediated ligand–ligand interaction

(ii) The interaction of electrons stepwise accepted by the ligand cluster.

These two factors cause each single reduction step of one ligand to split into m-reduction steps of the ligand cluster L_m. Generally a redox series ML_m^z in which each ligand can accept N_L electrons gives

N_L *sets of one-electron redox processes, each set being composed of* m *individual redox steps.*

This rule, which is generally valid, is demonstrated in a simplified form for $m = 3$ and $N_L = 2$ in Fig. 2.

Each im-step ($i = 1, 2, 3, \ldots$) corresponds to the formation of a complex with three identical ligands. Thus for $m = 3$ and $N_L = 2$ the third step corresponds to the formation of $M(L^{\overline{\cdot}})_3$ and the sixth step to the formation of $M(L^{2-})_3$ complex.

Examples of the validity of this most important rule describing the general pattern of redox series are given in Figs. 1, 4, 5 and 6.

The $Irbpy_3^{4+}$ redox series in Fig. 1 is an excellent example of the validity of the conclusions made. The case of $Febpy_3^{3+}$ was already discussed above —only the first triplet ($m = 3$!) is fully developed, the second is obviously complicated by other factors. Figure 4 compares $Febpy_3^{2+}$ with $Febpy_2(CN)_2$. In agreement with the last rule the set of three reduction steps in the tris-complex reduces to a set of two steps for $Febpy_2(CN)_2$. In the latter complex the E^0 values are shifted towards more negative potentials, obviously due to the decrease of the central field effect caused by the presence of negative ligands in the molecule. The second set in the bis-complex is represented by a two electron reduction accompanied by a partial decomposition of the complex after the acceptance of the third electron [19].

Figure 5 compares three types of ruthenium and iron complexes. In each case the set related to the first reduction of the ligand is in agreement with the above rule: the number of redox steps in the set always equals m (3 or 2). The second expected set is missing in the case of terpyridine complexes. Unless this is due to inconvenient experimental conditions, this result could be interpreted as being due to an enormous stabilization of the M $(terpy^{\overline{\cdot}})_2$. Complexes with TPTZ-ligand show two expected doublets of redox steps. However, for the ruthenium complex and for iron one and two more

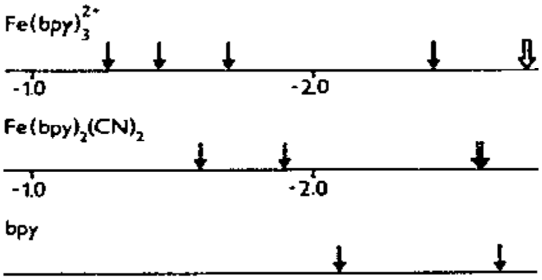
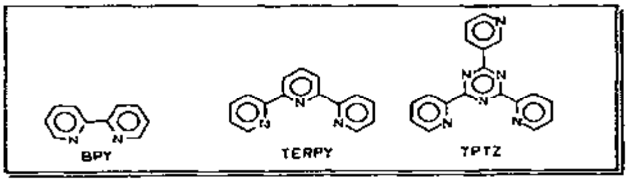


Fig. 4. Comparison of $E_{1/2}$ values for $Febpy_3^{2+}$ and $Febpy_2(CN)_2$ complexes. Data taken from refs. 19 and 20. Open arrow denotes a not fully resolved electrode process. Double arrow denotes a two electron reduction step.



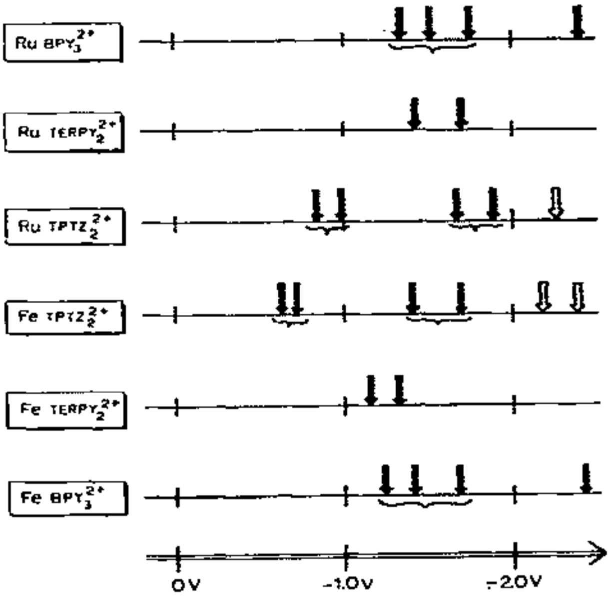


Fig. 5. Comparison of $E_{1/2}$ values for iron and ruthenium diimine complexes. Data taken from refs. 21–23.

reduction steps, respectively, even if not fully identified, have been described [21]. This observation can be explained only by assigning $N_L > 2$ to the TPTZ complex. Even if for the free ligand $N_L = 2$ was observed, its structure does not exclude the possibility of $N_L > 2$. For the free ligand the third reduction step is obviously too negative to be observed and its existence appears only in the complex due to its shift towards more positive potentials caused by the coordination. Both the tris-bipyridine complexes show the first three-step set and the beginning of the expected second set. The existence of the second set of redox processes is clearly manifested in the reduction of substituted ruthenium complexes shown in Fig. 6. The essential factor contributing to the appearance of the full redox series of substituted bipyridine complexes is the influence of the substituents upon the redox potentials, which are shifted towards positive potentials due to the influence of the

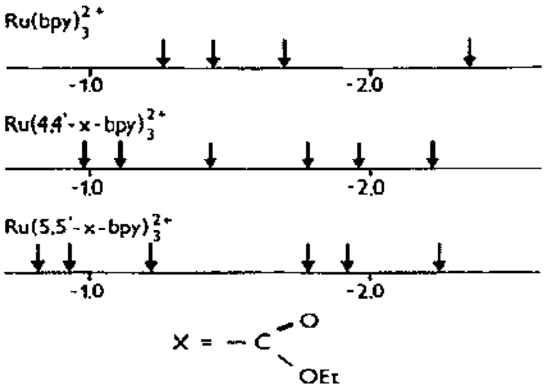


Fig. 6. Comparison of $E_{1/2}$ values for substituted ruthenium tris-bipyridine complexes. Data taken from ref. 24.

substituents. Simple extrapolation of the data of 5,5-disubstituted complexes would indicate the missing steps of the unsubstituted ruthenium-tris-bipyridine complex to still be placed in the accessible range of potential. Comparison of $\Delta E_{1/2}$ for the series shown in Fig. 6 shows that they depend upon the substituent as well as overall number of electrons so that simple extrapolation is misleading. This finding is in full agreement with the theoretical analysis of the dependence of the substituent effect upon the energy and type of the redox orbitals [4] along the redox series.

D. SOLVATION ENERGY ALONG THE REDOX SERIES

Along each redox series the overall charge of the individual members, z, changes in a broad range and differs from that of the free ligand. This means that when comparing the behaviour of free and ligated molecules as well as the differences of redox potentials along the redox series, the change of solvation energy has to be taken into account.

For the redox potential of ith redox couple, $ML_m^z - ML_m^{z-1}$, the following equation can be written

$$FE_i^0 = I_i - \Delta_i G_S^0 + T\Delta_i S_c^0 + \text{const} \tag{5}$$

I_i is the gas phase adiabatic ionization potential of the reduced form of complex particle (i.e. of ML_m^{z-1}) (alternatively, I_i can be replaced by $I_i' - \Delta H_c$, where I_i' is the gas phase ionization potential of the free ligand and ΔH_c represents the difference of the stabilization energy of the ligand in the reduced and oxidized form of the complex in the gas phase—cf. ref. 3).

$\Delta_i G_S^0$ represents the difference of the real free energy of solvation between the reduced and oxidized form.

$\Delta_i S_c^0$ is the change of entropy accompanying the ionization process in the gas phase.

Const represents an additional term depending on the particular reference state of the electrochemical system.

For the difference of two subsequent redox potentials the expression holds

$$F\Delta_{i,j}E^0 = F\left(E_i^0 - E_j^0\right) = \Delta_{i,j}I + \Delta_{j,i}G_S^0 \tag{6}$$

In deriving eqn. (6) it is assumed that the value $\Delta_{i,j}S_c$ is negligible, an assumption which seems to be fully substantiated for big molecules and processes in which the change of the overall number of electrons does not induce a substantial redistribution of charge density within the molecule.

Hush [27] using the Born approximation has shown that

$$\Delta_{j,i}G_S = -2\Delta_1 G_S \tag{7}$$

where $\Delta_1 G_S$ is the Born difference in solvation energy for the couple $-1/0$ (or $+1/0$, with appropriate change of sign).

Insertion of (7) into (6) points to the conclusion that under this approximation the value of $\Delta_{j,i}G_S$ is independent of charge type and is constant throughout the whole redox series. This means that the difference of redox potentials is equal to that of the ionization potentials diminished by a certain constant. Figure 7 shows, schematically, the relation between the gas phase ionization potentials and redox potentials. It is seen that, due to the solvation energy, the $\Delta_i E^0$-values are lower than $\Delta_i I$-values. However, using

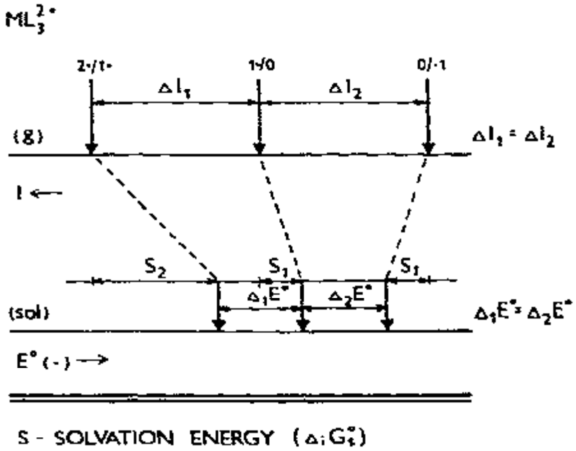


Fig. 7. Schematic representation of the relation of the gas phase ionization potentials (I) and redox potentials (E^0). $\Delta_i I$ values chosen arbitrarily, $\Delta_i G_S$ values are those calculated for iron-tris-bipyridine complex using Born's approximation according to ref. 26.

approximation (7), the $\Delta_i E^0$ follow $\Delta_i I$ and generally

$$\Delta_i E^0 = \Delta_i I + \text{const} \tag{8}$$

Equation (8) indicates that variations in ionization potentials are reflected in variations in redox potentials and thus the discussion of structural factors valid for gas phase molecules can be applied to the discussion of behaviour in solution assuming provision is made for the solvation energy.

The constant in eqn. (8) should be identical with the value given by eqn. (7). Our calculations [11], based on more sophisticated models of solvation (see, e.g. refs. 25 and 26), show that the Hush's approximation given by eqn. (7) is valid to about ±3% assuming the charge density along the series changes continuously. Any discontinuous change of electron density localization along the redox series leads to the change of the constant in eqn. (8). In the series discussed here the electron density usually changes smoothly with increasing change of the overall number of electrons so that eqn. (8) is applicable.

Calculations [11] show, however, that the value of the constant in eqn. (8) depends not only upon the size but also upon the type of charge density distribution which depends upon the nature of the ligand and in some cases also upon the substituent. This means that it is, in principle, possible to compare the $\Delta_i E^0$ values only for the same type of ligand with the provision that the introduction of a polar substituent might influence the value of solvation energy.

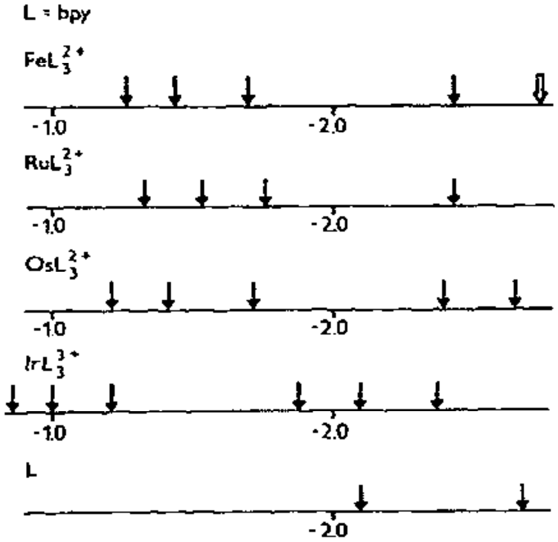


Fig. 8. Comparison of $E_{1/2}$ values for tris-bipyridine complexes of iron, ruthenium, osmium and iridium. Data taken from refs. 5, 21 and 28.

Calculations the author has carried out on iron–tris–bipyridine systems lead to the value of the constant in eqn. (8) of about 2.4 eV using approximation [26] and 2.15 eV using approximation [25]. This value seems to be more general and applicable to the other tris–bipyridine complexes. Figure 8 shows that differences in redox potentials depend only slightly upon the nature of the central atom or overall charge of the complex, thus confirming the general conclusion.

The experiments generally point to the conclusion that the change in solvation energy does not play as big a role as would be predicted from the theory. The data shown in Fig. 8 and Fig. 9 demonstrate this conclusion. The absolute values for iron, ruthenium and osmium complexes, and especially the differences, $\Delta_i E^0$, vary only slightly with the nature of the central atom. For the iridium redox series all the values of redox potentials would be expected to be shifted towards more negative potentials as the increase of the overall positive charge by one unit would be expected to stabilize all the oxidized forms (approximate value obtained by calculations would indicate the increase of ΔG_S value for the first step of Irbpy_3^{3+} by about 2.6 eV as compared for the same reduction step of complexes of charge-type +2). Experimentally a shift of about +0.4 V is found for Irbpy^{3+} as compared with Febpy^{2+}. This finding points to the conclusion that the central field effect overcomes the solvation effect. However, data shown in Fig. 9, as well as those reported in refs. 29 and 30, seem to show that calculations overestimate the change of solvation energy with the overall charge. E^0 as well as $\Delta_i E^0$ obtained in various solvents differ only slightly for the same redox series, a result which again supports the same conclusion [32]. One of the factors which might play an important role is the ion-pair formation or

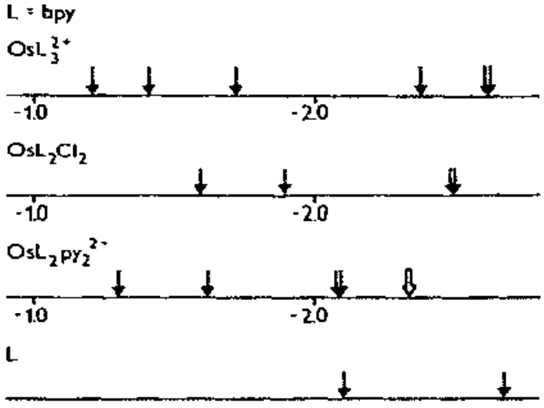


Fig. 9. Comparison of $E_{1/2}$ values for osmium-bipyridine complexes of different charge type and composition of coordination sphere. Data taken from refs. 21, 28 and 29.

screening of the charge by the ionic atmosphere, mainly effective in solvents with low dielectric constant. Detailed experimental evidence on the influence of these processes upon the values of redox potentials is missing.

Data on some highly charged substituted bipyridine complexes, even if not fully analysed, are also in agreement with all the other experimental evidence on the change of real solvation energy with the charge of the particle [31].

The above discussion on the influence of solvation energy upon the values of redox potentials along the redox series indicates:

(i) Equation (8) is valid supposing a continuous change of charge density along the series takes place.

(ii) The value of the constant in eqn. (8) depends upon the nature of the ligand and might be changed by introducing a substituent into the molecule.

(iii) The absolute value of the constant in eqn. (8) is 2–2.5 eV for the complexes studied.

(iv) The dependence of ΔG_S upon the formal charge of the particle seems to be overestimated by most theoretical approaches, or the effective charge of the particle in solution is less than the formal charge.

E. PATTERN OF THE REDOX SERIES

The above analysis shows that the discussion of the redox potentials and especially that of their differences can be based on the discussion of the ionization potentials of isolated molecules.

For the ligand based redox processes being dealt with, the redox orbital originates, for the main part, from the ligand redox orbital. In the cluster of m ligands (with $N_L = 2$) there are m redox orbitals originally of identical

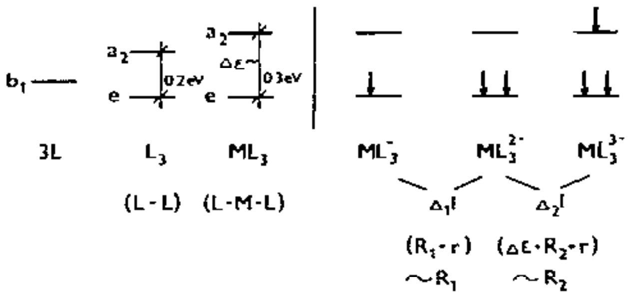


Fig. 10. Schematic representation of redox orbital-multiplet in ML_3 and simplified picture of the formation of ML_3^{3-}. R_i, electron repulsion energy; r, relaxation energy; $\Delta\epsilon$, difference in orbital energy in delocalized model $r \rightarrow 0$. For systems with two and three electrons only one possible electronic configuration is shown in each case.

energy and properties. The direct ligand–ligand interaction separates these orbitals into a rather narrow multiplet of *m*-energetically different orbitals. Figure 10 shows such a multiplet for a complex ML_3, L being the bipyridine ligand. (Splitting of three b_1 orbitals into a set of $a_2 + e$ is shown. However, the real structure of the complex is such that the *e*-set is further split due to the distortion of configuration.) The calculated difference between the orbital energies (using the SCCC–MO method) of the newly formed multiplet is about 0.2 eV in the case of ligand–ligand interaction only and 0.3 eV for ligand–ligand interaction mediated by the *p*-orbital of the central metal atom [11]. At first sight it is tempting to correlate these energy differences with the observed differences in E^0s. However, remembering eqn. (6) and noting that the $\Delta_{j,i}G_S$ term is of the order of about 2 eV, it is seen that the ligand–ligand interaction plays only a minor part in determining the magnitude of $\Delta_i E^0$.

The main contribution to the energy differences between successive members of the redox series in the gas phase, $\Delta_i I$, is given by the electronic repulsion energy (R_i, see Fig. 10) and possible electronic or atomic relaxation energy. In the delocalized model the latter contribution does not play an essential role so that $\Delta_i I$ is given mainly by the electronic repulsion energy arising from the successive filling up of the multiplet of redox orbitals by electrons. The calculation of the electronic repulsion energy for ML_3^{2-} and ML_3^{3-} systems is not quite as simple as several configurations (not shown in Fig. 10) and configuration interactions have to be taken into account.

Experiments show, in all cases analyzed, that

$$\Delta_1 E^0 \ll \Delta_2 E^0$$

(the same is valid for the second multiplet of redox steps, see, e.g. Fig. 6). Supposing that the electronic repulsion energy is the main factor contributing to the energy difference between various members of the redox series, it has to be concluded that

$$R_1 < R_2$$

i.e. the repulsion energy accompanying the acceptance of the second electron is smaller than that accompanying the acceptance of the third electron. This experimental finding is in general accordance with the simple theoretical considerations on the electronic repulsion energy, however, the accuracy of calculations is small enough to make any unambiguous comparison of calculated and experimental data possible.

The product resulting in the last process of the first multiplet of redox steps is a complex formed by the cluster of semireduced ligands, i.e. in the case of ML_3-series $M(L^{\bar{\cdot}})_3^{\bar{\cdot}}$ is formed. Even if in most cases the spin multiplicity of these compounds is not known, theoretical considerations predict a high spin configuration, i.e. $\mathrm{M(L^{\mp})_3^{\mp}}$ is expected to be formed by the cluster of three radical ions $\mathrm{L^{\mp}}$ with parallel spins. Only in cases with great energetic splitting of the multiplet of redox orbitals or in those where the central metal atom has unpaired electrons, electron pairing would be expected. In these cases the corresponding $\Delta_j E^0$ values would be, however, larger (cf. ref. 3) than those observed for the complexes under discussion.

The next reduction of $\mathrm{M(L^{\mp})_3^{\mp}}$ complex involves, necessarily, spin pairing, a change in configuration which can be described in a simplified way as

$$(e+a_2)^3 \rightarrow (e+a_2)^4 \tag{9}$$

The energy difference between these two configurations is given mainly by the spin-pairing energy which is higher than the differences between configurations $(e+a_2)^a$ arising for $a \leqslant 3$, which are determined mainly by electron repulsion energy, as has been shown above. This larger energy difference in the transition depicted by eqn. (9), described as $\Delta_m E^0$ in Fig. 2, gives rise to the separation of the individual sets of redox steps (see Fig. 2). Process (9) is essentially analogous to that of the free ligand reduction for which the second reduction step corresponds to the change in configuration

$$b_1(\pi^*)^1 \rightarrow b_2(\pi^*)^2 \tag{10}$$

The experimentally observed values $\Delta_m E^0$ and $\Delta_\mathrm{L} E^0$ are in all cases very similar, generally

$$\Delta_m E^0 \geqslant \Delta_\mathrm{L} E^0 \tag{11}$$

This result might suggest a similar process both in the free ligand and in the cluster of ligands. In highly delocalized redox orbitals in the cluster of ligands spin-pairing energy would be expected to be less than that for the isolated ligand. On the other hand, the localized model would predict $\Delta_m E^0$ to be equal or larger than the value $\Delta_\mathrm{L} E^0$ for the free ligand. The experimentally observed differences between $\Delta_m E^0$ and $\Delta_\mathrm{L} E^0$ are significant but not high enough to make an unambiguous distinction between the two models of delocalization possible, especially if it is taken into account that the value $\Delta_{j,i} G_\mathrm{S}$ for the free ligand and the complex is necessarily different, this difference being of about the order of the experimentally determined values of $(\Delta_m E^0 - \Delta_\mathrm{L} E^0)$. With all this uncertainty in mind, it can be nevertheless concluded that the reduction of the ligand cluster, $(\mathrm{L})_m$, follows the same general pattern as that of the free ligand, i.e.

First the multiplet of m-redox orbitals is filled with m-electrons, giving rise to a set of m-redox steps. The succeeding redox processes correspond to a complete filling up of the multiplet of the redox orbitals with further m-electrons, giving rise to the second set of m-redox steps.

For $N_\mathrm{L} > 2$ each ligand contributes two (or more) redox orbitals which give rise to two (or more) multiplets of redox orbitals in the ligand cluster. The centre of gravity of these multiplets would be separated, approximately, by the energy corresponding to the difference of orbital energy of the two redox orbitals in the free ligand. $N_L > 2$ is observed, however, only rarely for free ligands and only for molecules with redox orbitals with rather close orbital energies so that the $\Delta_i I$, and thus the corresponding $\Delta_i E^0$, are of the order comparable to those observed for successive filling up of the ligand cluster (cf., e.g. the reduction of porphins or the recently described reduction of a polycyclic hydrocarbon [33]). This similarity between the pattern of redox potentials of the ligand cluster and that of the molecules with $N_L > 2$ substantiates the general idea that the ligand cluster can be looked on as a sort of macrocyclic ligand.

It has been shown that the half-filling of the multiplet of the redox orbitals is separated by a larger energy gap from the next set of redox steps. Each complex in which the multiplet of redox orbitals is unoccupied, half-filled or fully occupied by electrons, i.e. complexes arising from coordination with clusters $(\mathrm{L})_m$, $(\mathrm{L}^{\mp})_m$ or $(\mathrm{L}^{2-})_m$, exert a relative stability [3] with respect to other members of the series. This relative stability, reflected in the general pattern of the redox series by its separation into distinct multiplets of redox steps, can be compared with that observed for atomic systems with half-, or fully filled subshells. For clusters $(\mathrm{L}^{\mp})_m$ an extra-stabilization arises due to exchange and delocalization effects of the unpaired electrons [3].

F. TERMINATION OF REDOX SERIES

As has already been mentioned not all the series reach the maximum possible number of redox steps. Excluding those experiments which were not aimed to study the complete series or those which failed for experimental reasons (purity of solvent, improper base electrolyte or unsuitable electrode arrangement) to reach sufficiently negative or positive potentials, two main termination mechanisms can be distinguished:

Interaction with the medium

Intrinsic instability

Interaction with the components of the medium includes, first, substitution reactions in which one of the components of the medium replaces one or more reduced (fully or partly) ligands and, second, redox reactions in which the low valent species is reoxidized predominantly by the solvent or some hydrogen donor present in the solution. Reduced members of redox series are electron rich compounds capable of reacting with many electrophiles which might be present in the solution. A rather frequent reaction is abstraction of hydrogen under formation of hydride or reaction with quaternary ammonium cations used as base electrolytes. All these reactions

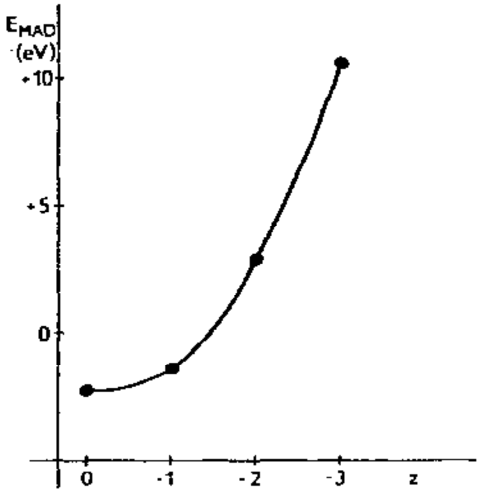


Fig. 11. Model calculation of Madelung energy for ML_6^z complex. L, linear triatomic ligand; charge on the metal atom constant (0.5 unit), increase of charge delocalized continuously along the ligand system, 0.056 units per atom per 1 unit of overall charge.

are extremely interesting from the chemical point of view and furnish information on charge localization in the individual members of the series [34]. However, by proper choice of experimental conditions all these reactions can be eliminated and the intrinsic stability of various members of the redox series can be followed. The most powerful experimental approach to achieve these conditions is to study the process in strictly aprotic conditions (e.g. in anhydrous tetrahydrofuran) at low temperature using fast scan polarization of the electrode (50 V s^{-1} or more). These experimental conditions in most cases prevent any induced reactions following the electron transfer steps proper and in some cases even slow reactions arising from the internal instability of the members of the series.

The increasing negative charge (or in some other series, positive charge) causes a decrease of the overall stability of the members of the redox series with increasing number of electrons in the system. Figure 11 shows a model calculation of the electrostatic repulsion energy of the system with increasing negative overall charge z. This decrease of stability has thermodynamic consequences either manifested by the decrease of stability or resulting in the intrinsic instability and thus in the decomposition of the species, irrespective of the medium or stabilization effect of solvation.

Thermodynamically a decrease of the stability of the reduced form results, which is manifested in the shift of the corresponding redox potential towards more negative potentials. This factor plays a role only for the most negative redox steps. There are systems for which the most negative step, corresponding to the total reduction of the cluster, is more negative than the second reduction step of the free ligand (cf. some of the tris-bipyridine complexes or reduction of iron-tris(4,7-diphenyl-1,10 phenanthroline) complex [36]). In other cases this thermodynamic decrease of the stability of the reduced form may account for such a negative shift of redox potentials of the last reduction steps of the ligand cluster that they cannot be observed experimentally. This fact explains the failure to observe full redox series in some of the examples quoted above.

The kinetically based intrinsic instability resulting from high negative overall charge is manifested by the decomposition of the later members of the series. Rarely is a complete decomposition observed. In most cases a readjustment of atomic configuration appears. In complexes of the type ML_m usually the loss of one *partly* reduced ligand ($\mathrm{L}^{\dot{-}}$) is observed from such a member of the series which can, by this process, attain a stable configuration of the ligand cluster with diminished number of ligands in the cluster

$$\mathrm{M}(\mathrm{L}^{-(2m-1)})_m \rightarrow \mathrm{M}(\mathrm{L}^{-2(m-1)})_{m-1} + \mathrm{L}^{\dot{-}} \tag{12}$$

An example of this mechanism is depicted in Fig. 12. This tendency to reach the stable configuration of ligand cluster is one of the dominant factors governing the mechanism of decomposition of members of redox series. Rarely, if at all, as published experiments are not quite conclusive, is the loss of one *fully* reduced ligand from the ligand cluster observed.

The decomposition and even the thermodynamic decrease of stability of reduced forms is diminished by introducing such substituents into the ligands which enhance the compensation mechanism, i.e. the distribution of the extra charge onto the ligands via the system of σ- and π-bonds [37].

Complexes of the $\mathrm{ML}_m\mathrm{X}_n$ type decompose generally in such a way that

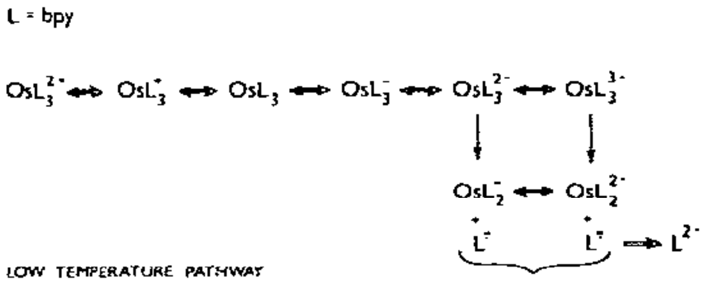


Fig. 12. Reduction mechanism of osmium–tris–bipyridine redox series as deduced from data in ref. 28. Horizontal double arrow denotes one-electron transfer step, vertical arrow denotes a chemical reaction.

ligands X are lost, the system attaining the configuration of metal complex bonded to a stable ligand cluster even if with smaller coordination number. This splitting of ligands X does not substantially depend upon their charge and nature (systems with X being a redox-forming ligand of different type than L have not been studied in sufficient detail) and seems to be always preferred to that of L or $L^{\mp}$.

G. CONCLUSION

In the above review only some aspects of redox series have been discussed. The analysis has been limited to "well behaved" redox series formed by redox active ligands and a relation between the behaviour of free ligand and that of the complex has been stressed using the concept of ligand-clusters and the concept of compensation principle [37]. The regularities shown have, however, a more general validity and can be applied to other types of redox series starting with the analysis of the origin and interaction of redox orbitals within the complex. The concept of rigid redox orbital is not valid in most cases and has to be replaced by the *concept of the multiplet of redox orbitals.* developed above, with inclusion of orbital relaxation which plays an important role in many redox series [35].

Other aspects, such as the change of the substitution effect or reactivity along the redox series and, especially, the problem of the change of the rate of electron transfer along the redox series, will be dealt with in another paper.

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