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Electrochemistry of coordination compounds — origin, development and outlook. A personal essay☆

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Molecular electrochemistry is a rather recently defined field of electrochemistry, the term itself being gradually coined in the last 20 years. By molecular electrochemistry [1] a complex study of molecules should be understood in which:

1. The complete electrochemical mechanism in electrochemical terms is elucidated — this description can be usually given in general terms, without any specification of chemical composition of the species involved.
2. Electrochemical terms are then translated into chemical species — individual intermediates and products are identified with specific chemical individuals. This step gives rise to the mechanism of electrode reaction described in terms of chemical species and is essentially connected with the identification, directly, as far as possible, of intermediates and products.
3. Explanation of the observed mechanism on the basis of molecular and submolecular structure of reacting molecules — this step is often very difficult when a single compound is being considered and the generalization can be made more easily for a series of structurally related compounds.

Molecular electrochemistry has evolved continuously with the background of development of electrochemistry itself. From rather primitive beginnings it became more sophisticated with the increasing knowledge and methodology of electrochemistry. Let me shortly summarize the contributions, which in my opinion, were most important for the development of molecular electrochemistry of coordination compounds.

☆ We are saddened to report that Antonín Vlček Snr. passed away on October 10th 1999 after this article had been completed but before it had been reviewed. Revisions and editing were completed by the Editor in consultation with his son, A. Vlček Jr.

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The electrochemical investigation of coordination compounds started early after the discovery of polarography in the first quarter of the last (20th) century. In the beginning, most studies were devoted to investigation of the equilibria of substitutionally labile complexes. This period was highlighted by the work of DeFord and Hume [2] resulting in the method of determination of consecutive stability constants from the shift of half-wave potentials of metals when deposited at the mercury electrode. Interest in these investigations slowly diminished, in the early 1950s with the studies of substitutionally inert complexes and, slightly later, of organometallic compounds. In the mid-1950s, an early attempt was made [3a], which may seem simple nowadays but was of great importance at that time, to correlate the electrochemical behavior of complexes with their structure. On the basis of these correlations, the formation of low-valent complexes as products of electrode reactions was predicted and their detection brought new insight to the mechanism of reduction of coordination compounds [3b]. Shortly after that, the first redox series was obtained [4]. Only two consecutive redox processes were known at the beginning of the 1950s — a student of Professor Heyrovský wrote a booklet on theoretical polarography and included a short chapter on four consecutive electrode reactions — Professor Heyrovský asked him to remove that chapter as nothing of this kind had been observed. A few months later the reduction of $[Cr(III)(bpy)_3]^{3+}$ was observed, limited at that time by experimental difficulties, to three waves only. However, in a short time the full redox series was described by Japanese colleagues [4].

The discovery of a relationship between spectral properties (transition energies) and electrochemical half-wave potentials [5] opened new fields of investigation, fully exploited only in the last decade in relation to the role of complexes in energy conversion and molecular electronic devices.

All new improvements in electrochemical instrumentation and in theoretical approaches were immediately used to study the electrochemical properties of coordination compounds. Thus a wealth of mechanisms was collected, however, they were not systematically analyzed from the point of view of the structure of the reacting species (rational prediction of mechanism based on the known structure). Studies of electrochemical mechanisms brought about the necessity to identify the intermediates and products of electrode reactions: spectroelectrochemical methods and later OTTLE (optically transparent thin layer electrode) and similar methods [6] to study the UV–vis, IR, Raman spectra as well as EPR spectra of intermediates and products were invented. Combined photochemical and electrochemical studies were made possible, detecting and following electrochemical intermediates and their reactions. It might be hoped that the sensitivity of spectroelectrochemical methods will be increased in such a way as to make the detection of short lived intermediates possible and thus to add more evidence to the mechanisms of electrode reactions written in chemical terms. Another possible approach is to add an agent, for example a spin trap, and thus induce a specific reaction of the intermediate, the products of which are easily detectable with one of the spectroelectrochemical methods. To reach shorter lifetimes of directly detected intermediates would be a great improvement for molecular electrochemistry and would allow characterization of very short-lived intermediates today deduced only from solving kinetic equations.

Use of channel electrodes (and similar devices) [6c] made it possible to easily study the reactions of intermediates of electrochemical and/or photochemical processes in flow-through systems. Attempts to measure redox potentials of electronically excited systems directly could be approached either by fiber optic steady state excitation close to the electrode surface or by excitation in a fast-flow system using, e.g. channel electrodes. The comparison with data obtained from ground state potentials and emission energy would be of great interest and prove the validity of assumptions made in deducing the fundamental equations relating these quantities.

Fast-flow systems might be used in the study of very unstable compounds. Two jet streams containing reagents from which the desired species is formed very rapidly are directed into the electrochemical detection system. If the flow does not fluctuate, the electrochemical signal of a very unstable species might be obtained. Rather recently, electrochemical methods combined with an on-line electrospray mass spectrometer add to the set of methods used for the study of products of electrode reactions [6d].

A fundamental contribution to the study of coordination compounds is represented by the use of solvents with a very broad potential window. On the cathodic side such a solvent, e.g. tetrahydrofuran, makes it possible to reach, at low temperatures, potentials more negative than -3.5 V (versus SCE) and thus study extremely strong reducing agents or use the electrode as such an agent. A real breakthrough was the introduction of liquid sulfur dioxide as a solvent [7]. At low temperature, potentials up to $+4$ V are easily obtained and oxidations of coordinated ligands and central metal atoms are studied. Oxidation of coordination compounds at very positive potentials is a relatively new field of study, applied up to now to only a few groups of complexes. It will be important to enlarge the number of systems where oxidation under these extreme conditions is investigated. Some problems, which have general importance for the definition of oxidation state, may be solved in this way. These include the distinction between oxidation of the central metal atom or ligand, or between localized and collective oxidation of the system or of its part. The localization of the oxidation in the ligated molecule is also open to discussion — does a lone pair get oxidized or is the electron removed from the π-system? At present only sulfur dioxide is used as a solvent for these studies. A search for other solvent (or solvents) might result in finding a solvent of similar properties but more easily handled and more environmentally friendly.

Following the success of preparative chemistry, most new classes of compounds have been studied electrochemically and electrochemistry contributed substantially to the elucidation of their structure. Thus, fullerenes and their metal derivatives [8] have been studied extensively. Most of them show multiple redox changes localized on one redox center and the interaction of successive electrons can thus be studied. A similar situation is obtained in the study of large metal (carbonyl) clusters, e.g. made of Pt, Pd, Ni, Mo and other atoms with CO groups and some other ligands, like S or phosphines, attached to the surface of the cluster. In this case, the inner structure of the cluster seems to influence the overall redox behavior, not only the number of electron steps but also the rate of electron exchange [9].

A vast number of new compounds have been investigated from the advent of the supramolecular chemistry [10]. There are three main aspects studied electrochemically with supramolecular compounds: (i) studies, rather nonsystematic from the electrochemical point of view, of electrochemical behavior of new compounds as a component of their general physicochemical description; (ii) investigation of the interaction of supramolecular systems with metallic ions in the solution which in most cases depends fundamentally on the oxidation state of the host. Even if the observed changes in redox potentials are sometimes rather small the observed changes form a good basis for molecular recognition. (iii) the most promising aspect is represented by studies of supramolecular species with multiple redox centers, identical or different, and mutual interactions between these redox centers. For simpler polycentered complexes (e.g. polynuclear ruthenium complexes), the mapping of interactions of various redox centers in supramolecular assemblies is possible. However, in big assemblies, like dendrimers having up to 64 individual redox centers, the study of interaction of individual redox centers is not possible as the electrode reaction proceeds in one step. This indicates none, or very weak, interaction between redox centers even through space. Sometimes the high multiplicity of redox centers makes it impossible to distinguish the individual interactions. The multiredox-centered species are studied from the point of view of electron reservoirs (or electron sinks), of electron or energy transfer units and of intramolecular excited state quenching. All these processes might serve potentially for information transfer, storage or switching of such a process. One of the future points of interest might be to study reactive radicals encapsulated by the supramolecule and thus shielded from the interaction with the components of the solution.

A powerful tool in investigations of complicated mechanisms is represented by digital simulation methods [11] capable of solving processes at various types of electrodes and various regimes of transport to the electrode surface. This invaluable and powerful method has to be used, however, with great caution. Too many parameters introduced into the simulation make the results less decisive. The differences between simulated curves for different mechanisms might become almost indistinguishable, by far exceeding the accuracy of experimental data. One has to remember an old saying, originating from chemical kinetics ‘With ten parameters to choose you can describe even an elephant’.

Much work has been done using coordination compounds and organometallics as homogeneous electrocatalysts [12] of, mainly, redox reactions. The compounds used as catalysts are either in solution or confined to the electrode surface. The true homogeneous electrochemical catalysis is that in which the catalyst, or its precursor, is regenerated by the electrode reaction, i.e. substoichiometric amounts of the catalytically active species are used with a high turnover in the second cycle coupled with the electrode reaction. Very effective are those molecules that are able to transfer electrons both directly and via atom transfer. The most important studies are those dealing with the catalysis of electrode reduction of oxygen [2b] (one of the most important electrochemical reactions), nitrogen [12c], or carbon dioxide [12d,e]. Use is made, however not exclusively, of porphyrin or polypyridine complexes of transition metals as catalysts. In many cases, the catalytically active complexes are used in the form of a modified electrode with the catalyst attached directly to the electrode surface. The future of electrocatalysis lies not so much in the improvement of electrochemical methods — it lies essentially on the side of design of new catalysts: for the catalysis of reduction of oxygen, nitrogen and carbon dioxide multielectron and multicoordination-site catalysts are needed. The design of such a catalyst is not an easy task, as at the same time the compound must meet some electrochemical requirements (such as appropriate reduction potential of all steps, fast electron transfer to the electrode, easy intramolecular electron transfer, stability of intermediates and, possibly, electrochemical reactivity of intermediate with the substrate attached to the catalyst). It is hoped that the search for such catalysts will attract the continuous attention not only of electrochemists but also of synthetic molecular engineers.

There are also some very valuable sacrificial processes in which the catalyst or reactant is generated at the electrode in stoichiometric quantities. Sacrificial electrodes [13] of less common metals were used to synthesize series' of organometallic compounds. The potential use of all these processes, catalytic and sacrificial, is enormous, however, their widespread use is hindered by the inherent difficulty of electrochemistry in preparative processes — the surface of the electrode, to which these processes are confined, has to be very large to produce economically interesting amounts of products. At present, these processes find, if any, applications as laboratory procedures, large scale electrolysis being rather rare.

Modified electrodes, especially those with complexes attached to the electrode surface by self-adsorption or polymerization or by direct binding by chemical means, are studied, not only for electrocatalytic purposes, but also as electrochemical sensors for the determination of various components of solutions or gases. However, the ultimate goal of these studies, to construct an array of differently modified electrodes for the simultaneous determination of several components is still far away, though some electrode arrays have been investigated.

The potential use of modified electrodes, especially with coordination compounds attached to the surface, is enormous. Layers formed of, among others, polymerized polypyridine complexes with metals in mixed valence states, generated electrochemically, proved to be very useful in studies of the electron transfer mechanism [14] in solid state electrochemistry and form one of the fundamental bases for their use in molecular electronics.

For effective use in molecular electronics, the species attached to the surface have to be spatially oriented to enable vectorial electron transfer. This is usually achieved by co-adsorption with a closely related electroinactive molecule. This results in a rather low concentration of the electroactive complex at the electrode surface and, thus, a low surface efficiency for the process. Electrodes modified by electrochemically and/or photochemically active coordination compounds, are used in studies of processes occurring in molecular electronic devices. In these devices, the redox properties of the components of molecular layers, their different spectroelectrochemical behavior, or the differences in conformational properties or in coordination ability of different oxidation states are exploited [15]. Molecular wires based on coordination compounds with long-chain ligands were also constructed [16]. They should make it possible to connect the molecular operating units with the macro environment. Coordination compounds are unique in these applications due to their variable redox, spectrochemical and coordination properties. The development of electrochemical molecular electronics is closely connected with the use of coordination or organometallic compounds.

Theoretical considerations point to the conclusion that future devices will be composed of several layers, or chains, of different electrochemically and/or spectroelectrochemically active compounds and that the information, in most cases in the form of a transfer of electron or energy, will proceed in a vectorial way along the energy gradient in the system. There have been several schemes proposed for how such devices might function. After their simple inspection, it must be concluded that many of them are, at best, just rather crude pictures of the possible function of such devices. Namely, it is tacitly assumed that there is no spontaneous electron flow in a system composed of a donor part at one end, and an acceptor part at the other end, which are connected by an isolating unit capable of electron transfer only in the excited state. This is, of course, not true. Whenever a system contains a donor and an acceptor part, such as electrodes spanning a potential drop across the system, a continuous flow of electrons follows, even if small; electron excitation only enlarges this flow. Furthermore, it is assumed (or forgotten?) that electron transfer is directed to a specific molecule and, especially, that the electron stays in the first layer of molecules. This again does not happen, the electron after the transfer might penetrate more layers at different positions of the surface so that a smeared signal would reach the other end of the system. The ultimate solution of this problem is the application of results of single-molecule electrochemistry using supramolecular chains addressed individually.

Electrodes of extremely small dimensions were first developed for biological research. Electrochemists paid more attention to these electrodes in connection with two different ideas: one was the use of high-speed scans (Wightman); and the second, explored successfully only recently, was the idea to observe the stochastic nature of the electrode reaction (Fleischman). However, at the end of the 1970s and beginning of the 1980s, the experimental equipment was not adequate and as early attempts had shown other very promising fields for the application of microelectrodes, the original idea was laid aside. Microelectrodes (radius 10^{-1}–10^{-3} cm) or ultramicroelectrodes [17] (10^{-3}–10^{-7} cm), due to their very small surface, have very small currents (mA–pA) and thus a very small ohmic drop. Hence, with ultramicroelectrodes, it is possible to work in low dielectric constant solvents with small concentrations of supporting electrolyte, or even without it. The geometry of the ultramicroelectrode leads to special diffusion conditions, enhancing the transport to the electrode and making it possible to attain a steady-state regime of transport to the electrode surface. All these specific properties of ultramicroelectrodes make it possible to use very high scan rates (up to 10^6 V s^{-1}) and thus to study very fast follow-up reactions, up to a nanosecond time scale! The conditions of electrochemical studies are thus very close to the regime of homogeneous reactions. Therefore, catalytic systems can be investigated by electrochemical methods under real conditions. Under these conditions, several follow-up reactions of complexes can be studied, for example, conversion of isomers. High rates of voltage scan made it also possible to study electrode reactions cleanly without the follow-up reactions of products. It is thus possible to determine the reversible redox potentials of couples with one extremely unstable form.

Electrodes of even smaller dimension, so called nanodes (radius of about 1 nm, i.e. 10 Å), have been constructed [18] and used mainly to measure rates of very rapid electrode reactions. With ultramicroelectrodes the rates of electron transfer are apparently higher than when measured at 'normal' electrodes. With nanodes the rates are even bigger, the Nernstian form of the curve being, however, preserved. These observations, if confirmed for larger sets of species, might indicate that the electrode reaction is not a simple one but consists of several individual processes.

With the advent of nanodes, the possibility arose to study extremely small volumes of solution and led to the construction of the scanning electrochemical microscope and to electrochemistry of single molecules [19]. These very pretentious experiments are limited to few laboratories only, but the results are promising. Most experiments of this kind, involving, for example, single-molecule electrochemistry, electrochemical scanning microscopy, as well as chemiluminiscence generated under these conditions, do not deal with an isolated single molecule but with a limited small set of molecules. However, even with this arrangement it was possible to observe the sequence of individual electron transfer steps [20] and thus to follow the stochastic nature of an electrode process. Most studies were, up to now, carried out on model substances, mainly substituted ferrocenes. With these experiments we meet the limits of classical thermodynamics and chemical kinetics which are based on the, frequently forgotten, condition of independence of individual quantities on the number of particles, being derived for infinite space and very large assemblies of particles. It thus might be necessary to reconsider the limits of the theory and their applications to small sets of particles.

One of the main goals of the theory is to calculate the value of redox potentials. Already the oldest theories of electrode reactions (from the early twenties, connected with attempts to calculate the absolute electrode potential of a couple) assumed that there is a linear relation between the thermodynamic electrode potential and the ionization potential of the reduced form of the couple. Simple theory predicts a one-to-one relation. This has not been confirmed and the failure is being attributed to the difference between the vertical gas-phase ionization potential, used in these calculations, and the corresponding solvated species ionization potential. This requires one to estimate or calculate the ionization potential including atomic relaxation energy, relaxation energy connected with change of electronic structure and the accompanying solvation energy changes. This task is rather difficult as it aims, among other things, to calculate the open shell configuration of one of the components of the redox couple. Most calculations failed due to the inadequacy of the open shell calculation. This difficulty is usually evaded by calculating the HOMO energy of the oxidized form and by adding rough estimates of solvation energy and inner relaxation energy. For small values of relaxation energies and solvation energy changes this use of Koopman's theorem might be an acceptable approximation (the proper choice of parameters helps the agreement between theory and experiment!). For systems in which the redox change causes bigger inner changes this approach is unacceptable. Furthermore, most of the calculations deal with isolated molecules (gas phase) and the solvation is mostly added, if at all, only as an empirical parameter. Some reasonable conclusions can be obtained from calculation of HOMO energies for a set of structurally related series of compounds and analysis of the relationships of these values to the redox potentials. This approach is acceptable only if it might be assumed that the relaxation energy is very small or related to the HOMO energy and the solvation energy influence is more or less constant within the series.

Facing these problems, relationships with other physicochemical quantities, for which the structural dependence is known, were used to rationalize the structural dependence of redox potentials. Most frequently a plot of redox potential against spectroscopic quantities was used. (Actually, the plot of half-wave potentials against transition energies of cobalt and rhodium complexes was one of the very first attempts of this kind [5a]). Usually, however, the sets of data inspected were rather small and unambiguous conclusions could rarely be drawn. Mostly these studies finish with the statement that the redox potential is proportional to some other quantity, however, with some specific deviations.

A comparison of sets of data for a sufficiently large structurally related series of compounds seems, at the moment, to be the best approach to solve the structural dependence of electrochemical behavior. Let me, as an example of this approach, briefly discuss our recent investigation of dependencies of two electrochemical quantities with an attempt to draw some general conclusions from the structural dependence observed. The plot of E_{ox} versus E_{red} for a very large series [Ru(polypyridyl)$_2$(X)(Y)] gives a straight line [21] with rather small deviations therefore indicating that the influence of X and Y upon reduction and oxidation of the complexes stems from the same reasons. It has been long established that the E_{red} reflects the redox potential of a free polypyridine [22]. Therefore, E_{red} can be used as a parameter characterizing the free ligand. Indeed, the first reduction potential of a large series of tris-polypyridine complexes is linearly proportional to the first reduction potential E_{free} of the free ligand with a slope very close to 1 and a relatively small scatter of the experimental points. A similar plot of E_{red} against the E_{ox} for Ru(II)–tris-polypyridine complexes also gives, rather unexpectedly, a straight line with the slope of 1.16 ($R = 0.96$) [23]. There is some scatter of points along the line, in most cases, however, not exceeding 150 mV. This scatter is, in principle, to be expected as the values plotted were measured in various laboratories, against various reference electrodes and not exactly under identical conditions. This 'experimental' scatter can be estimated to be ± 80 mV. Moreover, there are few points that are reported as irreversible in the reduction process and which deviate considerably from the line, however, still keeping the general trend of the dependence. Furthermore, some data, reported as reversible, do not fit the depen-

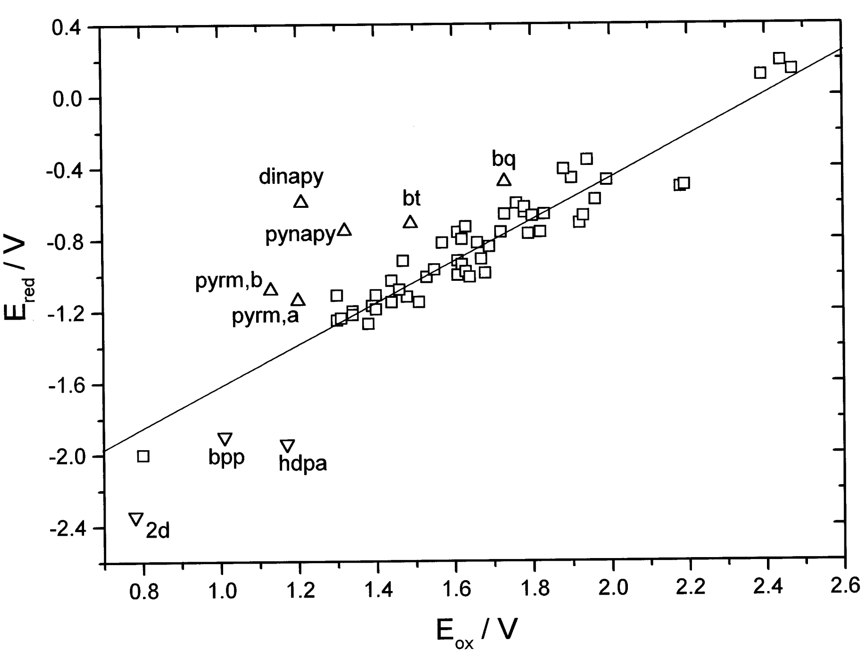

Fig. 1. A plot of reduction potentials E_{red} vs. oxidation potentials E_{ox} for a series of Ru(II) tris-polypyridyl complexes. Data against NHE taken from Ref. [24]. □ = well behaved points; △ = deviating points, reversible processes; ▽ = reduction reported irreversible, only some representative points included. Abbreviations used: bt = 2,2′-bi-2-thiazoline; bq = 2,2′-biquinoline; dinapy = 5,6-dihydrodipyrido[3,2-b:2′,3′-*j*][1,10]phenanthroline; hdpa = di-2-pyridyl amine; pynapy = 2-(2-pyridyl)-1,8-naphthridine; bpp = 2,6-bis(*N*-pyrazolylpyridine), see Ref. [25]; 2d: see Ref. [26], pyrm,a and pyrm,b: see Ref. [27].

dence discussed. Nevertheless, they still show approximately the same general trend, see Fig. 1.

The first reduction potential of polypyridine complexes is related to the energy of the lowest π^* orbitals of the ligands, whereas the oxidation process is generally believed to be metal-localized, i.e. each of the orbitals should be influenced by other structural factors. However, the above plot indicates unambiguously that both the reduction and oxidation potential are influenced by the nature of the ligand in approximately the same way. This means that the HOMO and LUMO of the complex are under the influence of the same structural factors.

The reduction potential is, as mentioned above, related to the reduction potential of the free ligand. The dependence of the oxidation potential on the nature of the ligand can be understood by taking into account the interaction of the metal t_{2g} orbitals with the occupied ligand π orbitals. In the Ru(II)-oxidation state there is a small, but definite interaction between t_{2g} and π orbitals resulting in the HOMO orbital of a weakly antibonding character with respect to Ru–N(polypyridyl) bonds. This orbital is in Ru(II) complexes predominantly localized on the central atom. By removing one electron from this orbital the situation changes in that the

t_{2g} orbital of the central atom is more stabilized by the extra positive charge than the π system of the ligand. Consequently the t_{2g} and π orbitals are energetically closer and their interaction increases. The relative position of t_{2g} and π orbitals and, thus, the extent of their interaction, depend on the nature of the ligand: If the ligand orbitals are higher in energy ('donor' type), the t_{2g} and π orbitals will be energetically close, the antibonding interaction relatively large and, thus, the HOMO of higher energy. Consequently the oxidation potential will be relatively negative. On the other hand, if the ligand orbitals are low in energy ('acceptor' type), the π orbital is well below the t_{2g} orbitals, the antibonding interaction is small and, thus, the antibonding contribution to the energy of HOMO is also small. This results in a lower energy of HOMO and thus in a relatively positive oxidation potential. The experimental data point to a proportionality between the LUMO and HOMO energies which indicates also that the energies of the π and π* orbitals of the ligands are mutually dependent or their difference is nearly constant.

The above explanation covers the main feature of the proportionality of both redox potentials. There are, however, additional contributions that are not simply dependent on the nature of the ligands and the variation of which is responsible for the scatter of data in Fig. 1. The solvation effects might play a role, even if relatively small as only the difference enters the expression for the redox potential. In addition, the difference in structural rearrangement on reduction or oxidation between complexes with different ligands also contributes to the variation of redox potentials. The complexes which are reported to possess irreversible reduction processes are those in which the LUMO is not a fully conjugated orbital and where the change in charge results in a greater change of structure during the electron transfer. On the other hand, some complexes whose redox processes are reversible can differ considerably in their π and π* orbital energy separation. Another factor is the steric effect of a substitution on atoms close to the N-donor atom (e.g. 6,6′-substitution in bipyridines and analogous molecules).

This explanation of the observed plot is only the first step in the overall analysis of the structural dependence covering the most probable contributions to the observed experimental observation. The final confirmation will only be given after reliable calculations are made and, especially, after all the deviations are reasonably explained. (Explanation of deviations is in most cases a proof of the theory!).

The complete solution of one single system represents a great contribution but cannot serve any predictive purposes. Predictive power can be obtained only from analysis of a large series and it is necessary that the wealth of data existing in the literature, on structurally related series, will be critically collected and analyzed with the help of reasonable theory. The theory of the relationships between redox potential and structure has been studied for a long time. The main problem is to find readily accessible calculations for ionization potential, including correct open-shell calculations. Modern quantum chemical techniques like DFT, which are applicable even to relatively large molecules show great promise in this respect. It might not be necessary to calculate each species in the series but the general trend of the quantity has to follow correctly from the calculation.

Recent results of measurements of rates of fast electrode reactions are very promising, reaching into regions denoted as 'reversible'. However, data are few and not obtained in any systematic way. When more measurements, especially on structural series, are available it will be of a great interest to correlate them with the theory. Of great importance would be the measurement of the rate of consecutive redox processes in redox series. Such measurements might open new, today not yet fully formulated questions, such as how (if at all) does the rate of electron transfer to the identical molecule depend upon the number of electrons already present in the system. The answer might be obtained by studying systems whose structure changes minimally with the number of electrons, such as big metal clusters.

These future trends are a rather simple extrapolation of the present state and can be more or less deduced from today's results (some might have been already published without the knowledge of the author). The true prognosis, that is prediction of really new discoveries is actually impossible: absolutely new phenomena cannot be predicted- they are just discovered. We might, however, try to make a 'superextrapolation' and predict some thinkable uses of a single-molecule electrochemistry. It has been shown that the response from a single molecule is measurable-with difficulty, but measurable. Let us assume a single large molecule having more redox active sites, for example A-L-B, the redox potential of the site B being more negative than that of A, attached to an electrode surface. Under the experimental conditions of single-molecule electrochemistry, it might be possible to address different redox sites separately, for example by the tip of a nanode. The electron transfer to the site B could thus be enforced. Such an experiment might make it possible to follow not only the redox potential but also intramolecular changes in the molecule returning to its reduced ground state. Note that the reduction of site B attached to the molecular fragment A-L- cannot be seen under normal conditions but only using single-molecule electrochemistry. Other possibilities for the application of single-molecule electrochemistry of coordination compounds are directed towards molecular electronics: It might be possible to construct an assembly of ultra-small electrodes with a single vectorial supramolecule having several functions which would serve for storage of information, transfer of signals and triggering the whole process. This can be achieved either by an electric impulse, by a photochemical impulse, or by combination of both. Another possibility lies in the change of a steric arrangement or in coordination, again triggered by a photochemical or electric impulse.

It is obvious that the future molecular electronic devices will operate on a molecular level since only this can reach the necessary density of information. Molecular electrochemistry can well be an important approach to meet this goal.

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