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Optimization of Redox Potential Values—Approaches, Practical Importance, and Theoretical Obscurity

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This article deals with the state of the art in the field of predictions and optimizations of redox potential values for the couples of complexes and organometallics. The paper assesses how the dependence of the redox potential E^{o}(Ox/Red) on the electron affinity of Ox (the ionization energy of Red), on the differences in ΔG of solvation, and on the difference in ΔG accompanying the transformation of composition and structure of the reactant in its transition to the product is reflected in individual approaches dealing with the prediction of E^{o}(Ox/Red) values. Theoretical justification of generally used treatments is questioned.

Key Words: *metal complexes, redox potential, electrochemistry, ligand additivity*

1. INTRODUCTION

A substantial part of industrially, laboratory and biologically important chemical processes are redox reactions involving coordination compounds. There are several quantities related to redox properties of chemical species. The most frequently used charac-

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teristic, describing the ability of a species to undergo a redox reaction in solution, is the standard redox potential $E°$(Ox/Red) for reversible processes or the half-wave potential $E_{1/2}$(Ox/Red) in general. Chemists are in the habit of speaking in their professional slang of redox potential of one species (e.g., MnO_4^- anion is a strong oxidant having a redox potential of 1.51 V). It must be underlined, however, that when dealing with redox potential, the properties of both the oxidized and reduced forms (Ox and Red) of a redox couple are taken into account. This article is devoted to redox potential as an expression of the redox properties of coordination compounds.

2. FACTORS DETERMINING REDOX POTENTIAL VALUES

The electrochemical behaviour of metal complexes and organometallics in solution is a multivariable function of mutually related parameters; the following are to be mentioned among them[1]:

(a) the radius and the bonding ability of the central atom (particularly its spin-state, the energy and symmetry of its HOMO and LUMO);
(b) the electronic and steric properties of coordinated ligands (their σ- and π-bonding properties, electronic effects of their remote groups, skeleton rigidity);
(c) the structure of the chromophore (the influence of the central atom and ligands HOMO's and LUMO's interactions on the energy and symmetry of the redox orbitals);
(d) the properties of media (donor–acceptor and dielectric constants of the solvent, ionic strength, the presence of potential ligands).

Using thermodynamic language, the redox potential value $E°$(Ox/Red), where Ox and Red will denote the oxidized and reduced forms of a complex, is, in general, determined by various factors which can be grouped into three classes. Our attention will be focused on the processes in which the redox change is localized

on the central atom. For such systems the content of the three classes is as follows:

(1) the electron affinity of Ox for a process of the central atom reduction, or the ionization energy of Red when the central atom oxidation occurs;
(2) the difference in the Gibbs energy of solvation for the reactant and product (Ox and Red forms) of an electrochemical process, ΔG_{out};
(3) the changes in the Gibbs energy accompanying the transformation of the composition and structure of the reactant in its transition to the product, ΔG_{in}.

A quantitative evaluation of all the above contributions for a single Ox/Red couple is not a simple task. A more convenient way is to follow dependences within a homolytic series of compounds. In such families of similar complexes (having, e.g., the same oxidation number of the central atom, coordination number and shape of coordination polyhedra, spin-state) in the same solvent, some contributions can be taken as constant ones. For instance, ΔG_{out} can be assumed to be approximately constant within the series of $Cr^0(CO)L$ compounds at their electrochemical oxidation. In such an approach, a dependence of $E°$(Ox/Red) on only one parameter can be evaluated. This parameter can be, however, expressed by more variables (characterizing, e.g., σ-donor and π-acceptor properties of the ligands L and their relative position in the coordination sphere).

3. CRITICAL EVALUATION OF THE CURRENT APPROACHES

All the proposed methods for the calculation and prediction of redox potential values have been developed for complexes in which the redox process is localized (predominantly) on the central atom. The approaches stem from an assumption that the ligands as independent parts of the coordination sphere influence the properties of the central atom localized redox orbitals (HOMO and LUMO) and the sum of these influences is reflected in redox

potentials. This is why the approaches can be covered by the term "ligand additivity models."

The model of Pickett and Pletcher[2] deals with the oxidation potential E° of substitutionally related transition metal carbonyls, $M(CO)_{6-n}L_n$. The model works with a three-parameter equation

$$E^\circ = A + n(\delta E^\circ/\delta n)_L + Q_y \qquad (1)$$

where the constant A depends on the solvent and reference potential, $(\delta E^\circ/\delta n)_L$ is the "ligand inductive parameter" which determines the E° change due to the replacement of one CO ligand by one monodentate L ligand, and Q is the charge parameter. The model assumes a correlation between E° values and HOMO energies for the series of carbonyls in which the MO's are strongly perturbated by the complex oxidation. Within such a series ΔG_{out} is supposed to be constant, and the shift in the oxidation potential ΔE° is independent of n. This model does not involve stereochemistry and cannot, therefore, explain some differences in E° for, e.g., *cis* and *trans* isomers of the complex with the same composition.

Bursten[3] was concerned with the energetics of three d_π orbitals of the central atom in d^1 and low-spin d^6 complexes with π-acid ligands (e.g., CO or RCN). His ligand additivity model for the systems $ML_nL'_{6-n}$ assumes a linear dependence of the energetic contribution of the ligands to the d_π-MO's on the number of each type of ligand (n) and on the number of the ligands interacting with the d_π orbitals (x_i). The orbital energy is independent of the chromophore stereochemistry in this model. The implication of the plot between the $E_{1/2}$ value for oxidation and the HOMO energy then leads to the following relationship:

$$E_{1/2} = A + Bn + Cx_{HOMO} \qquad (2)$$

where A, B, and C are empirical constants. The model offered successful results for obtaining $E_{1/2}$ values of unknown members of the given families of complexes of the several central atoms. The $E_{1/2}$ values also exhibited isomer dependency and the parameters A, B, and C should allow, potentially, the separation of

σ- and π-bonding effects. The Bursten model has been applied to complexes with octahedral geometry.

Applying a linear correlation of the oxidation potentials $E_{1/2}$ with the Hammett constant σ_H of the ligands L, Chatt[4] defined the ligand parameter, P_L:

$$P_L = E_{1/2}\{Cr(CO)_5L\} - E_{1/2}\{Cr(CO)_6\} \quad (3)$$

which reflects the net (σ and π) donor properties of the ligand L. It was concluded that the more negative the P_L value of the ligand L, the higher its σ-donor/π-acceptor ratio.

Lever[5,6] demonstrated a more general approach to the additivity of electrochemical potentials with respect to the ligand variation. His approach comprises the advantages of the previous attempts to rationalize and predict redox potential values and it can be assessed as the most comprehensive model for certain specific series of complexes.

For the Ru^{III}/Ru^{II} redox couples as an electrochemical standard, a ligand parameter E_L(L) has been defined as one-sixth of the redox potential for species RuL_6 in acetonitrile. At a wide range of electrochemically reversible or quasi-reversible complexes of ruthenium[5] and other metals[6] in organic as well as aqueous media it was shown that the experimental potential values fit a linear correlation

$$E^{\circ}_{exp} = S_M[\Sigma E_L(L)] + I_M \quad (4)$$

where S_M and I_M are constants for the specific M^n/M^{n-1} couple in the species $MX_xY_yZ_z$ of the given stereochemistry (hexacoordinated complexes) and spin-state. There is a linear relation between Pickett's ligand parameters[2] (see above) and Lever's E_L values.

Correlations for isomers may be done by adding new variables into Eq. (4), expressing the number of ligands which interact directly with the redox (HOMO) orbital. In analogy to the spectrochemical series a ligand sequence according to the E_L values was proposed. It allows us to predict both the redox potential values for new compounds with known composition and the structure of a complex of a given central atom based on its experimental redox potential value. In spite of its limitations (the model is applicable

to selected families of complexes, which is, however, a problem of all the models) its possibilities were clearly documented and it provides nearly true (experimental) redox potential values.

The approaches discussed up to now were focused on kinetically inert complexes preserving their composition and symmetry in both (oxidized and reduced) forms. Along with such compounds, there is a huge number of families of important complexes which do not meet the above characteristics. The differences will be exemplified on copper complexes which have become an object of our interest.

Copper(II) complexes, particularly those with unidentate ligands, usually prefer hexacoordination in solution with the chromophore having Jahn–Teller distorted tetragonal bipyramidal structure.[7] Copper(I) complexes, on the other hand, try to adopt tetrahedral structure. The redox processes Cu(II) ↔ Cu(I) are, therefore, coupled with changes in the complex composition and symmetry. The contribution of ΔG_{in} to the value of E° cannot be thus omitted or taken as a constant for various complexes even belonging to one family. In addition, the secondary coordination sphere is changed and ΔG_{out} can change substantially going from one complex to another.

The second problem arises from the presence of a polydentate open-chain or macrocyclic ligand coordinated to the copper central atom. Though within the mutual influence of ligand conceptions,[7] a fragmental approach may be used for the complexes with monodentate ligands; an integral approach should be applied to the complexes with polydentate ligands as such ligands can hardly be rationalized as a composite of individual, independent complex fractions. The properties of polydentate ligands (e.g., their rigidity and electronic configuration) are not a simple sum of the properties of their parts. In spite of this fact, methods based on evaluating individual contributions of the parts of polydentate ligands to the $E_{1/2}$ values for complexes provide predicted values which fit the experimental ones very well. In the published methods[1,8–10] the contributions to the $E_{1/2}$ values rather than direct calculation of ΔG_{in} and ΔG_{out} were offered.

The third difference concerns the relation of changes in the complex charge and the number of electrons accepted or released by the complex within an electrochemical process. For, e.g., ruthenium complexes[5] any oxidation of Ru(II) to Ru(III) is associ-

ated with a one-unit increase in the positive charge (decrease in the negative charge). The oxidation of Cu(I) to Cu(II) can be coupled to either an increase, or a decrease, or to no change in the complex charge due to a simultaneous occurrence of a substitution (addition, elimination) reaction involving charged ligands. This can be schematically expressed as follows:

$$[Cu^{I}(MC)]^{+} + 2X^{-} - e = [Cu^{II}(MC)X_2] \qquad (5)$$

where MC represents an electrically neutral tetradentate macrocyclic ligand and X^{-} are unidentate anionic ligands. A real occurrence of such simultaneous reactions depends on various factors (e.g., the rigidity and structure of polydentate ligands) and it can alter even for structurally similar (e.g., saturated and unsaturated) analogs.

Taking the above possible complications into account and parting from Addison's fundamental work,[9] we elaborate a method enabling us to predict the $E_{1/2}$ values for a one-electron reduction of Cu(II) complexes containing a polydentate ligand in the primary coordination sphere. Our procedure is based on the calculation of the $E_{1/2}$ values according to the equation

$$E_{1/2} = E^{\circ}(Cu^{2+}/Cu^{+}) + \sum_{i}\sum_{j}\Delta E_i \qquad (6)$$

where $E^{\circ}(Cu^{2+}/Cu^{+}) = 155$ mV vs. the standard hydrogen electrode (SHE) in aqueous medium, ΔE_i are contributions related to both the electronic and steric properties of the ligands, i is the ligand parameter and j its frequency.

Eighteen parameters (ΔE_i contributions) have been calculated following the treatment of published[10–15] redox potential values for 134 Cu(II) complexes with tetradentate, pentadentate, hexadentate macrocyclic and open-chain ligands (some of them measured in several solvents). Experimental values, $E_{1/2,exp}$, obtained in three media (water, methanol, and acetonitrile) have been involved after recalculation of the values to the SHE aqueous scale (further denoted as $E'_{1/2,exp}$). The ΔE_i contributions (Table I) have been obtained using a standard method of multiple linear regression analysis in its robust variant. The plot of $E'_{1/2,exp}$ and $E_{1/2,calc}$

TABLE I

Contributions ΔE_i of polydentate ligands to the half-wave reduction potential of Cu(II) complexes (Ref. 8).

No.	Parameter	ΔE_i, mV (Significance, %)	Number of Data Processed
1.	-NH- aliphatic	−105 ± 10 (99.98)	149
2.	-N= aliphatic	−63 ± 15 (99.98)	70
3.	N(pyridine, quinoline)	−2 ± 5 (45)	56
4.	N(pyrrole)	−246 ± 19 (99.98)	6
5.	N(imidazole)	26 ± 26 (60)	4
6.	N(pyrazole)	106 ± 16 (99.98)	8
7.	O^-	−326 ± 30 (99.98)	14
8.	COO	−57 ± 17 (99.9)	30
9.	-S- (-SH)	140 ± 5 (99.98)	133
10.	macrocycle	−87 ± 43 (95)	32
11.	5-membered metallo-ring linked in chelate	−71 ± 16 (99.98)	46
12.	difference in atomicity from 14	70 ± 12 (99.98)	78
13.	conjugated system	352 ± 40 (99.98)	4
14.	octahedral geometry	−463 ± 46 (99.98)	6
15.	CH_3 group on N-donor	102 ± 17 (99.98)	15
16.	CH_3 group on S-donor	49 ± 18 (98)	6
17.	CH_3 group on α-carbon	−33 ± 10 (99.9)	69
18.	CH_3 group on β-carbon	61 ± 16 (99.9)	14

is expressed in Fig. 1. It follows from the data that the main factor influencing the values of redox potential for a given class of copper(II) complexes is the nature of the donor atoms. The highest tendency to undergo reduction exhibit the complexes with S-donor ligands, the lowest one those with N-donor and N,O-donor ligands.

The validity of our empirical model was checked for complexes whose experimental $E_{1/2}$ values were available to us after finishing and submitting our papers[1,8] for publication. These values were not, therefore, included in the computation procedure. Our procedure will be demonstrated on the calculation of the redox potential values $E_{1/2,calc}$ for two complexes (the other data are gathered in Table II). In the copper(II) complex with the macrocyclic ligand Me_8[14]aneN_4 (Fig. 2), three parameters are taken into account: No. 1 (aliphatic N), No. 10 (14-membered macrocycle) and No. 17 (CH_3-group on α-carbon). Using the corresponding

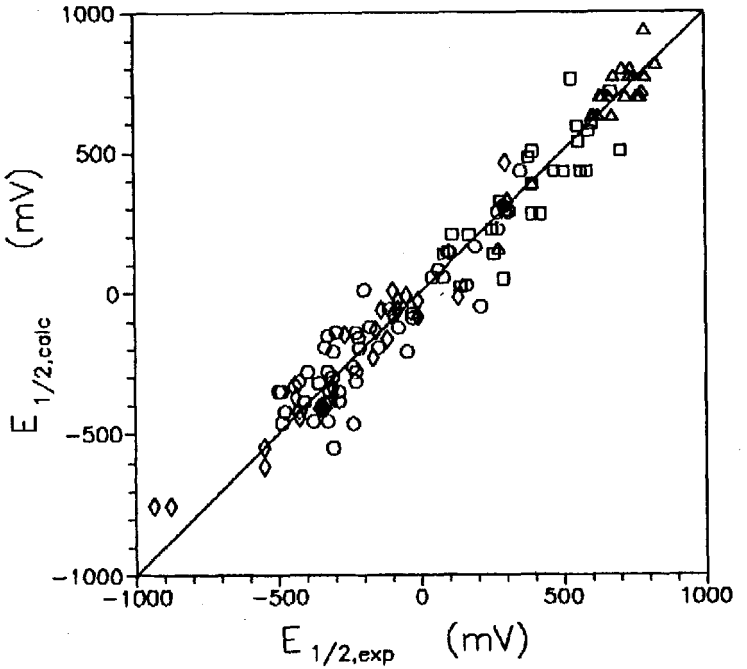


FIGURE 1 Plot of reduction potential values for copper(II) complexes with polydentate ligands calculated by the procedure (Ref. 8), $E_{1/2,calc}$, against corresponding experimental values $E'_{1/2,exp}$ in aqueous SHE scale. The circles are for N-donor ligands, squares for N,S-donor ligands, rhombuses for N,O-donor ligands, triangles for S-donor ligands.

ΔE_i contributions (Table I) for four N-donor atoms and eight CH_3 groups we obtained the $E_{1/2,calc}$ value as follows:

$$E_{1/2,calc} = E°(Cu^{2+}/Cu^{+}) + 4\Delta E_1 + \Delta E_{10} + 8\Delta E_{17}$$

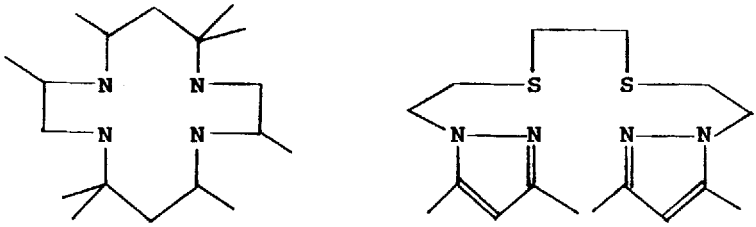
$$= 155 + 4(-105) + (-87) + 8(-33) = -616 \text{ mV} \quad (7)$$

which is in good agreement with the experimental value $E_{1/2,exp} = -556$ mV in the aqueous SHE scale.[16] Similarly, for the Cu(II) complex with the open-chain ligand abbreviated "bddo"[17] (Fig. 2), the parameters No. 6 (N-pyrazole), No. 9 (S-donor), No. 12 (difference in the ring atomicity from 14), and No. 17 (CH_3-group

TABLE II

Reduction potentials: experimental in water or acetonitrile (AN), $E_{1/2,exp}$, experimental recalculated into the aqueous SHE scale, $E'_{1/2,exp}$, and calculated according to the procedure (Ref. 8), $E_{1/2,calc}$, for copper(II) complexes (data in mV vs. SHE)

Complex Cu(II), (solvent)	$E_{1/2,exp}$	$E'_{1/2,exp}$	$E_{1/2,calc}$	Ref.
[Cu[15]aneNS$_4$] (AN)	740	570	520	8
[Cu(biquinen)]$^{2+}$ (AN)	220	170	170	8
[Cu(biqudien)]$^{2+}$ (AN)	−60	−40	−10	8
[Cu(Me$_8$[14]aneN$_4$)]$^{2+}$ (H$_2$O)	−556	−556	−616	16
[Cu(Me$_2$[14]dieneN$_4$)]$^{2+}$ (H$_2$O)	−496	−496	−334	16
[Cu(C-mesoMe$_2$[14]aneN$_4$)]$^{2+}$ (H$_2$O)	−536	−536	−418	16
[Cu(bddo)(H$_2$O)]$^{2+}$ (AN)	999	769	731	17
[Cu(N$_4$tripod)] (AN)	607	467	464	18
[Cu{N$_4$(CH$_2$)$_6$NH}]$^{2+}$ (H$_2$O)	−26	−26	−76	27
[Cu{N$_4$(CH$_2$)$_6$NCH$_3$}]$^{2+}$ (H$_2$O)	39	39	26	27
[Cu{N$_4$(CH$_2$)$_5$NH}]$^{2+}$ (H$_2$O)	81	81	151	27



a b

FIGURE 2 Schematic structure of the ligands Me$_8$[14]aneN$_4$ (a) and bddo (b).

on α-carbon) with the frequency of each parameter $j = 2$ contribute to the $E_{1/2,calc}$ value:

$$E_{1/2,calc} = E^{o}(Cu^{2+}/Cu^{+}) + 2\{\Delta E_6 + \Delta E_g + \Delta E_{12} + \Delta E_{17}\}$$

$$= 155 + 2\{106 + 140 + 70 - 33\} = 731 \text{ mV}. \quad (8)$$

The value of $E_{1/2,exp} = 755$ mV vs. SCE in acetonitrile (which corresponds to the value 769 mV in water vs. SHE) documents that an excellent agreement of experimental and calculated values

was reached for the given Cu(II) complex, and that this redox potential (declared by the authors as "unusually high") is of the expected value.

Our approach covers a sort of complex other than those of Lever and the other above-discussed models. It is suitable only for copper complexes with polydentate ligands. Its preliminary application to a tripodate complex[18] (Table II) suggests it could also be extended for complexes with this kind of ligand. Some of the 18 parameters obtained up to now might be unified in the future, and some new ones may appear. The approach does not work with ligands containing strong electron donating or withdrawing peripheral groups (e.g., CF_3, NO_2, NH_2). The effects of such groups is under investigation,[19,20] and after the research is concluded, new parameters might be added to those in Table I.

4. CORRELATIONS BETWEEN ELECTROCHEMICAL AND OTHER DATA

Electronic configuration and bonds in complexes are investigated by several experimental techniques. It is, therefore, natural that there have been attempts to search for relations between the results provided by various methods.

A common basis for the ligand additivity approaches is the concept that the redox potentials are additive with respect to ligand substitution due to the independent-like influence of all the ligands on the redox orbital (HOMO or LUMO) energy. At first glance, HOMO energies (which are in direct relation to the core, experimentally easily obtainable, orbital energies[21]) can be related to the charge localized on the central atom (redox site) and this charge can be evaluated from ECSA measurements. Independent characterization of ligands in a review[3] according to the values of the binding energy shifts (ΔE ECSA) and the values of the redox potential shifts (ΔE°) was done without attempting to mutually correlate both values. For some monodentate ligands a correlation of the ESCA shifts, ΔE ESCA with Lever's parameters E_L and Bursten's parameters E_B, is, for the sake of lucidity, shown in Fig. 3.

A more careful look into the problem documents that the mutual

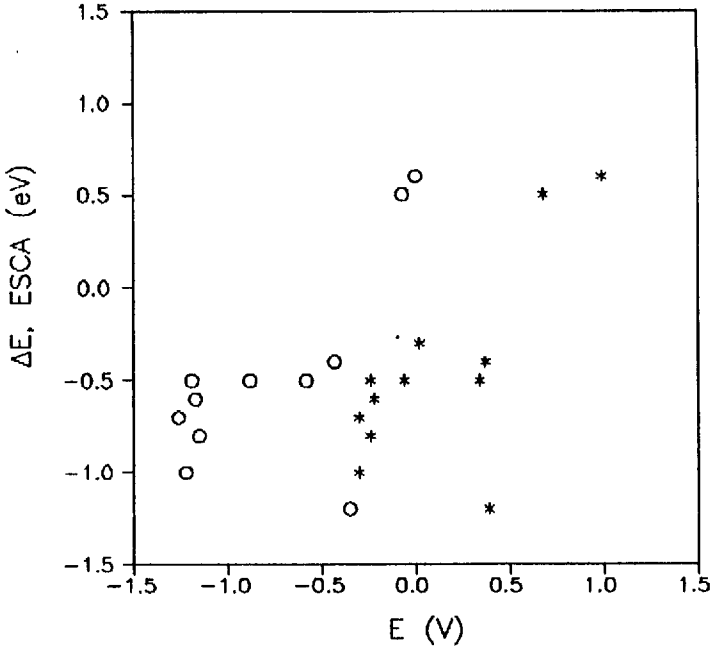


FIGURE 3 Plot of core electron binding energy shifts, ΔE ESCA (Ref. 3), against Lever's E_L (Ref. 5) (circles) and Bursten's E_B (Ref. 3) (asterisks) redox potential parameters.

correlation of these parameters should not be used for the prediction of E° values based on ESCA values. In addition to the differences arising from different phases (ESCA measurements of solid compounds, E° values obtained for complexes in solution, difficult precise evaluation of the medium effects in both cases), the fundamental difference emerges from the fact that the HOMO energy of a complex depends both on the charge localized on the redox site and on the LF splitting. The latter statement can be understood on d^6 and d^7 low-spin systems. Possessing the same charge (average d-orbital energy), the higher the LF splitting, the lower the HOMO energy for d^6 complexes but the higher the HOMO energy for d^7 complexes. The differences in the HOMO energies will be reflected in E° values, not, however, in ESCA values.

Effects of the phase and LF splitting (together with usually non-

negligible uncertainties in the discussed values) may be a reason for the poor correlation of ΔE ESCA and ΔE° values for ligands (moreover, one must keep in mind the problems connected with the obscurity in ΔG_{in} and ΔG_{out} contributions to the E° values).

The reversible oxidation potentials, E°, and the force constants of the carbonyl stretching frequencies, k(CO), were measured[22] for a series of complexes $MeCpMn(CO)_2L$, where L are unidentate N, O, P, or C-donor ligands. The extensive scatter of the E° vs. k(CO) values indicates that k(CO) are not suitable for the prediction of E° values, particularly when a broader series of donors is considered.

Morris[23] directed his work to the reverse problem, i.e., exploitation of oxidation potentials in predicting the stability and acidity (pK_a values) of dihydrogen compounds $[M(H_2)L_5]$, where M are d^6 central atoms. It was found that the potentials for the oxidation of $[M(N_2)L_5]$ and $[MHL_5]$ can be taken as a measure of the relative stability and pK_a values of dihydrogen compounds.

An excellent correlation between the experimental reduction potentials of Co(III) macrobicyclic cage complexes, Co(X-sar), and various substituent constants σ of the remote groups X of the bicyclic ligands was unveiled by Sargeson *et al.*[24,25] The authors introduce a new substituent constant, σ_E, related to the shift in the potential, $\Delta E_{1/2}$, due to the presence of a substituent X (compared to the potential of the complex with unsubstituted ligand) as follows (at 20°C):

$$\Delta E_{1/2} = \sigma_E/17.2. \tag{9}$$

Thus the knowledge of the σ_E values (which correlate with Hammett and other substituent parameters) can be used in predicting and tuning the redox potential values within the given class of cobalt compounds.

Relationships between the electronic properties of the central atom (particularly the symmetry of its redox orbital), remote groups of tetradentate open-chain ligands and the redox properties of some cobalt, copper, and nickel complexes were found and rationalized.[26] They were not used, however, for prediction or purposeful modification of the redox properties of the complexes.

5. CONCLUDING REMARKS

Turning back to the title of this article, an opinion on three points (approaches, practical importance, theoretical justification) should be expressed.

Whatever the approach for the prediction of redox potential values, there is a common feature: the treated complexes are imaginarily divided into fragments which, behaving as independent individuals, influence the central atom. All the approaches are applied to the complexes and organometallics having their central atom as a redox center. Electronic affects (symmetry and energy of HOMO and LUMO and their connection to the possibility to participate in σ and π interactions) are taken into account as the main factor determining the redox potential value. The steric factors, chiefly for complexes with monodentate or non-bulky bidentate ligands are understood as being of minor or negligible importance. In complexes with polydentate ligands (copper complexes), steric factors and the skeletal rigidity of the ligands also seem to play an important role in their redox properties.

There are wide blank areas containing complexes with ligand-localized redox orbitals. The study of electrochemical properties of such complexes from the viewpoint of the predictability of their E° values is still a challenge for chemists dealing with redox chemistry.

The practical importance of the discussed subject lies in the following possibilities:

(1) to predict the E° values for any redox couple within a structurally similar family of compounds based on known (tabulated) values of ligand parameters;
(2) to assess the E° value for a given redox couple within a structurally similar family of complexes of a certain central atom based on the composition and structure of the primary coordination sphere;
(3) to formulate the composition and structure of complexes with the aim that they adopt the required redox properties. In this sense nature can serve as an example (e.g., redox potential determined consecutive processes in photosynthesis).

Something is rotten (it has nothing to do with Denmark!) in the theoretical justification of the discussed approaches. The core of doubt lies in the fact that no complex, or multiatom particle in general, is a simple sum of its parts (e.g., no chemist can seriously regard the porphyrin ring as being a composite of four equivalent, independently behaving fragments). From this point of view each of the discussed models has its hidden or apparent scientific weakness. Lever[5] adumbrated the necessity of "rethinking of our chemical bonding models and concepts". Such a necessity is not, of course, conditioned by the ligand additivity approaches only. The problem is more general and can be, as one of the fundamental questions of science, formulated as follows: are we justified to exploit incorrect approaches to fulfil and reach advantageous goals?

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