134. Reduction Potentials of Tetraaminecopper(II/I) Couples

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The difference in steric strain between the oxidized and the reduced forms of tetraaminecopper complexes is correlated with the corresponding reduction potentials. The experimentally determined data considered range from -0.54 to -0.04 V (*vs.* NHE) in aqueous solution and from -0.35 to -0.08 V (*vs.* NHE) in MeCN. The observed and/or computed geometries of the tetraaminecopper(II) complexes are distorted octahedral or square-pyramidal (4 + 2 or 4 + 1) with (distorted) square-planar CuN_4 chromophores ($Cu^{II}-N = 1.99-2.06$ Å; $Cu-O^{Ax}_{4+2} \approx 2.5$ Å; $Cu-O^{ax}_{4+1} \approx 2.3$ Å), those of the tetraaminecopper(I) complexes are (distorted) tetrahedral (four-coordinate; $Cu^{I}-N = 2.12-2.26$ Å; tetrahedral twist angle $\varnothing = 30-90°$). The reduction potentials of $Cu^{II/I}$ couples with primary-amine ligands and those with macrocyclic secondary-amine ligands were correlated separately with the corresponding strain energies, leading to slopes of 70 and 61 kJ mol^{-1} V^{-1}, with correlation coefficients of 0.89 and 0.91, respectively. The approximations of the model (entropy, solvation, electronic factors) and the limits of applicability are discussed in detail and in relation to other approaches to compute reduction potentials of transition-metal compounds.

Introduction. – The interpretation and prediction of redox properties of coordination compounds is a fundamental, demanding, and rather challenging task. The design of novel oxidants and reductants with specific potentials is only one of several aims. The dependence of molecular properties from molecular structures in general, and specifically that of the reduction potential, have been used to determine structures, based on observed molecular properties, *e.g.*, on reduction potentials. These methods are based on algorithms that relate structures with corresponding observables [1]. Also, the thermodynamic laws that describe the complex stabilities of the reduced and of the oxidized forms of a given coordination compound as a function of the corresponding reduction potential [2] have been used to develop powerful tools for the experimental determination of stability constants. Thus, a general and reliable method to calculate reduction potentials from computed structural data may also be used to calculate stability constants and hence to design new ligand systems with specific and high complex stabilities, *e.g.*, for metal-ion-selective complexation [1c].

A number of conceptually very different methods to compute reduction potentials have been described. Some of them ignore solvation and entropy effects, *i.e.*, they are only useful in a rather narrow application window. Ligand field parameters [2][3], hydrophobicity, specific H-bonding, ion pairing, solvation and entropy effects [4], and differences in the ligand-induced strain energy between the oxidized and the reduced forms of the complex [1][5] have been correlated with redox potentials. Traditionally, these methods have been applied to hexaaminecobalt(III/II) couples, and only a few other first transition-metal row systems have been investigated.

The most recent and rather general method to estimate reduction potentials is that of using ligand-specific electrochemical parameters, and an extensive number of ligand parameters and correlation functions for various metal ions and solvent systems have been reported [6]. However, that method seems to fail for redox couples with severe structural differences between the oxidized and the reduced forms of the couple [1c]. That is, systems with a strong correlation between reduction potentials and the differences in strain energies or ligand-field parameters fall outside the applicability of constant electrochemical ligand parameters. In these cases, the steric demand of the ligand sphere is a decisive factor for the thermodynamics of electron transfer. The large structural differences between copper(II) and copper(I) coordination polyhedra ($4 + 1$ or $4 + 2$ *vs.* tetrahedral; $\Delta(\mathrm{Cu-N}) \approx 0.2$ Å) makes tetraaminecopper(II/I) couples an ideal system to check this hypothesis.

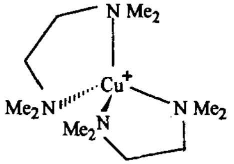
Theoretical Background. – Reduction potentials are related to the *Gibbs* energy of the electron-transfer reaction ($\Delta G^\circ = -nFE^\circ$). For transition-metal coordination compounds, ΔG° involves terms related to the ionization potential of the free metal ion, the complexation of the oxidized and the reduced free metal ion, and the solvation of the oxidized and the reduced metal complexes. The basis for using strain-energy differences $\Delta U_{\mathrm{strain}}$ between the oxidized and the reduced form of a redox couple to estimate reduction potentials is the assumption that some of these terms may be neglected. For a constant experimental setup (solvent and electrode) and a given class of compounds (constant metal center and type of ligands, *i.e.*, similar coordination polyhedra and donor groups), the environmental effects (solvation, ion-pairing), electronic factors (bonding energy), and the entropy contributions to ΔG° are assumed to vary, within the required accuracy, linearly with the strain energy ($\Delta G^\circ = f(\Delta U_{\mathrm{strain}})$, where f is a function that depends on steric factors) [1]. If this is a valid assumption, the reduction potentials E° are linearly dependent on the strain-energy differences $\Delta U_{\mathrm{strain}}$ between the oxidized and the reduced forms of the couples, *i.e.*, $E^\circ = f'(\Delta U_{\mathrm{strain}})$ ($f' = f/(-nF)$; for $f = 1$, the slope of the correlation line is 96.5 $\mathrm{kJ\,mol^{-1}\,V^{-1}}$, and the intercept is zero).

The slope f' of such a regression curve for a series of coordination compounds is a function of the relative contribution of the strain-energy difference $\Delta U_{\mathrm{strain}}$ with respect to the neglected terms. Thus, it is expected that the accuracy of estimated reduction potentials based on force-field calculations decreases with decreasing structural changes accompanying the reduction process, while the accuracy of estimated potentials based on approaches that neglect structural factors, such as the method that uses electrochemical parameters, increase in parallel. The slope for hexaaminecobalt(III/II) couples with Co–N bond length differences of *ca.* 0.2 Å is, depending on the type of amine ligand, $(45-65\ \mathrm{kJ\,mol^{-1}\,V^{-1}})^{-1}$, compared to the theoretical value of $(96.5\ \mathrm{kJmol^{-1}V^{-1}})^{-1}$, with an intercept between 0.7 V and 1.1 V [1c].

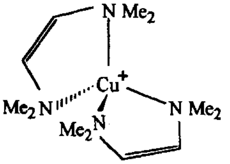
Apart from the general approximations discussed above, there are two additional problems with $\mathrm{Cu^{II/I}}$ couples: *i*) the structure of $\mathrm{Cu^{II}}$ with variable coordination numbers (4, 5, and 6), and *ii*) the structure of $\mathrm{Cu^{I}}$ with a coordination number that generally is different from that of the oxidized form (4 *vs.* 5 or 6). The axial ligands of tetraaminecopper(II) complexes, *i.e.*, solvent molecules or counter ions, are only loosely bound to the metal center (shallow bonding-potential curve) and do, therefore, not contribute significantly to the total strain energy of the complex. Also, the axial ligands of five-coordinate

Cu^{II} compounds have shorter bonds to the metal center than the two axial ligands of six-coordinate compounds (*ca.* 2.3 Å (one interaction) *vs.* *ca.* 2.5 Å (two interactions)). Thus, the decreasing number of bonding interactions is compensated by an increasing strength. The analysis of the data (see below) indicates that the small differences in bonding energy and steric strain may be compensated by corresponding differences in entropy and solvation effects. This is fortuitous but not unexpected for the tetraamine systems considered here (note that this may not be a generally applicable assumption, but preliminary experiments indicate that tetrathia and mixed thia/aza systems lead to similar conclusions [7]). The reduction of a tetraaminecopper(II) to the Cu^{I} complex occurs in two steps: electron transfer to a six- or five-coordinate species and loss of the axial ligands. Our approximation of computing the structures and strain energies of the four-coordinate Cu^{I} products is based on the assumption that the distances of the putative axial ligands to Cu^{I} are so long that they do not contribute to the structure and strain of the reduced product.

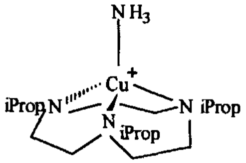
Modeling Procedures and Experimental Details. – *Force-Field Calculations.* MOMEC97 [8] with a published force field [9] was used to compute the optimized structures and the corresponding minimized strain energies. Parameters not published before are given in *Table 1* (note that the parameterization of the ligand backbone for Cu^{I} is different from that of ligands coordinated to 2+, 3+, and 4+ metal centers, and it is the same as for metal-free ligand systems [9c]). The parameters were fitted to structures **1**–**4**, and the observed and computed bond distances of the Cu^{I} chromophores are reported in *Table 2*.



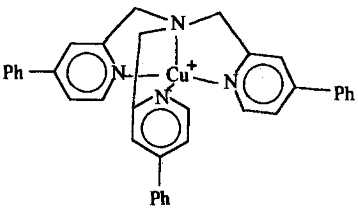
1[10a]



2[10b]



3[10c]



4[10d]

Electrochemistry. Electrochemical measurements were made with a *BAS100B* system, using $1 \cdot 10^{-3}$ M solns. of the Cu^{II} compounds in H_2O, with LiCl (0.1M) as electrolyte. A standard three-electrode cell was used, consisting of a HMD working electrode, Pt-wire counter and saturated-calomel reference electrodes.

Results and Discussion. – Twenty-six tetraaminecopper(II/I) couples are considered in this study (*Tables 3* and *4*). Theoretically, each conformer of a given $Cu^{II/I}$ couple must lead to a different reduction potential (square scheme). However, similar strain-energy differences of pairs of conformers lead to small differences of the corresponding reduction potentials, and these are generally not resolved experimentally; with large strain-en-

Table 1. *New Force-Field Parameters*

Bond[a])	Force constant [mdyn Å^{-1}]	r_0 [Å]
$Cu^{I}-N_{amine}$	0.450	2.125
$Cu^{I}-N_{imine}$	0.450	2.040
$C_{alkene}-C_{alkene}$	6.000	1.290
$C_{alkene}-H$	5.000	0.970
$N_{amine}-C_{alkene}$	4.600	1.460
Valence angle	Force constant [mdyn Å rad^{-2}]	θ_0 [rad]
$Cu^{I}-N_{amine}-C_{alkane}$	0.100	1.920
$Cu^{I}-N_{amine}-H$	0.100	1.920
$Cu^{I}-N_{amine}-C_{alkene}$	0.230	1.920
$Cu^{I}-N_{imine}-C_{imine}$	0.200	2.094
$N_{imine}-Cu^{I}-N_{amine}$	0.000	1.911
$N_{imine}-Cu^{I}-N_{imine}$	0.000	1.911
$N_{amine}-Cu^{I}-N_{amine}$	0.000	1.911
$C_{alkene}-C_{alkene}-H$	0.350	2.094
$C_{alkene}-N_{amine}-C_{alkane}$	0.450	1.911
$N_{amine}-C_{alkene}-C_{alkene}$	0.300	2.094
$N_{amine}-C_{alkene}-H$	0.970	2.094

[a]) Note that the parameterization of $Cu^{I}-N_{amine}$ is different from that in [9c]; the parameters for $N_{amine}-C_{alkane}$ are from [9c].

Table 2. *Computed* (and Observed [10]) *Bond Distances of the Copper(I) Test Structures* **1**–**4**

	1	**2**	**3**	**4**
Cu–N [Å]	2.151 (2.153)	2.150 (2.147)	2.138 (2.148)	2.201 (2.192)

ergy differences within the conformers of one oxidation state, the highly strained species are usually not abundant enough to be detected experimentally [1c]. With one exception [1d], there are no reports of resolved reduction potentials of couples of conformers. Thus, for all structures studied here, the least strained species, based on full conformational analyses, were selected for the computation of the reduction potentials. These data are presented in *Tables 3* and *4*, and the strain-energy difference *vs.* experimentally determined reduction potential correlation curves are shown in *Figs. 1–3*.

It has been observed before that the slopes of strain-energy *vs.* reduction-potential plots are different for primary- and secondary-amine donors [1c]. The following factors may be responsible for this observation: *i*) the different nucleophilicities of differently substituted amines must lead to a decreasing slope for an increasing number of alkyl substituents on the amine donors, *i.e.*, the balance between structural and electronic factors should decrease in favor of the electronic effects from ammonia to primary, secondary, and tertiary amines; *ii*) an increasing substitution at the donor is often leading to more rigid ligands (*e.g.*, macrocyclic *vs.* open-chain) and, therefore, to steeper strain-energy surfaces; this leads to an increasing predominance of the structural term; *iii*) differences in contributions of solvation and entropy terms (see discussion ahead). For $Cu^{II/I}$ couples, there is a significant but small difference between the slopes related

Table 3. *Strain Energies and Observed Reduction Potentials of Tetraaminecopper(II/I) Couples in Water*[a])

Open-chain ligands	$U_{Cu^{II}}$ [kJ/mol]	$U_{Cu^{I}}$ [kJ/mol]	ΔU_{strain} [kJ/mol]	$E_{1/2}$(exp.)[V][b]) *vs.* NHE
$[Cu(en)_2]^{2+/1+}$	5.38	7.85	−2.47	−0.114
$[Cu(dimeen)_2]^{2+/1+}$	20.09	13.42	6.67	−0.065
$[Cu(nten)_2]^{2+/1+}$	22.77	23.61	−0.84	−0.135
$[Cu(tn)_2]^{2+/1+}$	15.71	17.05	3.87	−0.042
$[Cu(dmtn)_2]^{2+/1+}$	66.31	57.98	4.51	−0.044
$[Cu(nnchxn)_2]^{2+/1+}$	27.77	41.60	−9.23	−0.250
$[Cu(2,3,2\text{-tet})]^{2+/1+}$	26.31	37.26	−8.28	−0.300
$[Cu(3,2,3\text{-tet})]^{2+/1+}$	19.51	36.12	−5.56	−0.270
$[Cu(amlin)]^{2+/1+}$	18.85	27.68	−8.83	−0.310
$[Cu(nelin)]^{2+/1+}$	22.51	31.28	−8.77	−0.250
Macrocyclic ligands				
$[Cu\{Me(NO_2)[13]aneN_4\}]^{2+/1+}$	64.06	71.77	−7.71	−0.340 [11a]
$[Cu\{Me(NO_2)[14]aneN_4\}]^{2+/1+}$	39.59	53.19	−13.60	−0.540 [11a]
$[Cu\{Me(NO_2)[15]aneN_4\}]^{2+/1+}$	67.25	65.77	−6.66	−0.420 [11a]
$[Cu\{Me(NO_2)[16]aneN_4\}]^{2+/1+}$	81.24	74.27	6.97	−0.220 [11a]
$[Cu\{\textit{cis}\text{-}Me_2[14]aneN_4(NH_2)_2\}]^{2+/1+}$	33.79	45.29	−11.50	−0.480 [11b]
$[Cu\{\textit{cis}\text{-}Me_2(NO_2)_2[14]aneN_4\}]^{2+/1+}$	36.25	49.12	−12.87	−0.490 [11b]
$[Cu\{\textit{trans}\text{-}Me_2[14]aneN_4(NH_2)_2\}]^{2+/1+}$	40.16	51.38	−11.22	−0.480 [11b]
$[Cu\{\textit{trans}\text{-}Me_2(NO_2)_2[14]aneN_4\}]^{2+/1+}$	39.53	53.82	−14.29	−0.520 [11b]
$[Cu(\textit{anti}\text{-}cyclchxn)]^{2+/1+}$	100.66	106.20	−5.54	−0.380 [11c]
$[Cu(\textit{syn}\text{-}cyclchxn)]^{2+/1+}$	104.47	98.47	−6.00	−0.390 [11c]
$[Cu(chxn\text{-}2,3\text{-}3)]^{2+/1+}$	88.42	90.45	−2.08	−0.320 [11c]

[a]) For ligand abbreviations, see *Appendix*. [b]) The compounds measured in this work were prepared by published methods and characterized by elemental analyses.

Table 4. *Strain Energies and Observed Reduction Potentials of Tetraaminecopper(II/I) Couples in MeCN*[a])

Copper(II/I) couple	$U_{Cu^{II}}$ [kJ/mol]	$U_{Cu^{I}}$ [kJ/mol]	ΔU_{strain} [kJ/mol]	$E_{1/2}$(exp.)[V]
$[Cu\{[12]aneN_4\}]^{2+/1+}$	75.27	80.07	−4.80	−0.350 [11d]
$[Cu\{Me_4[12]aneN_4\}]^{2+/1+}$	98.45	95.81	2.64	−0.280 [11d]
$[Cu\{Bz_4[12]aneN_4\}]^{2+/1+}$	158.71	138.33	20.38	−0.080 [11d]
$[Cu\{[14]aneN_4\}]^{2+/1+}$	74.59	67.74	6.85	−0.170 [11e]
$[Cu(mchxn)_4]^{2+/1+}$	56.83	51.95	4.88	−0.220 [11f]

[a]) For ligand abbreviations, see *Appendix*.

to primary- and secondary-amine donor systems, indicating that the various factors are partially canceling (see *Figs. 1* and *2*). The reduction potential of $Cu^{II/I}$ couples with thioether ligands and mixed thia/aza donor sets are shifted to more positive values. Preliminary studies indicate that correlations between the reduction potentials and the strain-energy differences of a similar quality to those reported here may be obtained [7]. It is interesting that the slopes are roughly identical to those for the tetraamine systems

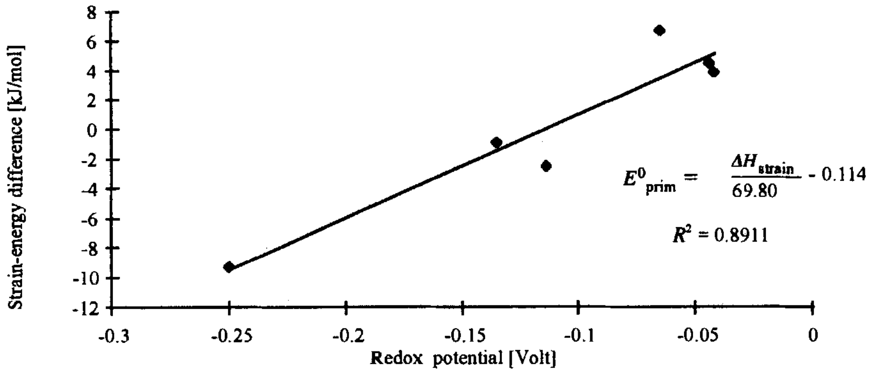


Fig. 1. *Correlation of the strain-energy difference* ΔU_{strain} *of tetraaminecopper(II/I) couples* (primary-amine ligands; first six entries in *Table 3*) *with the experimentally determined reduction potentials* (*vs.* NHE) *in aqueous solution*

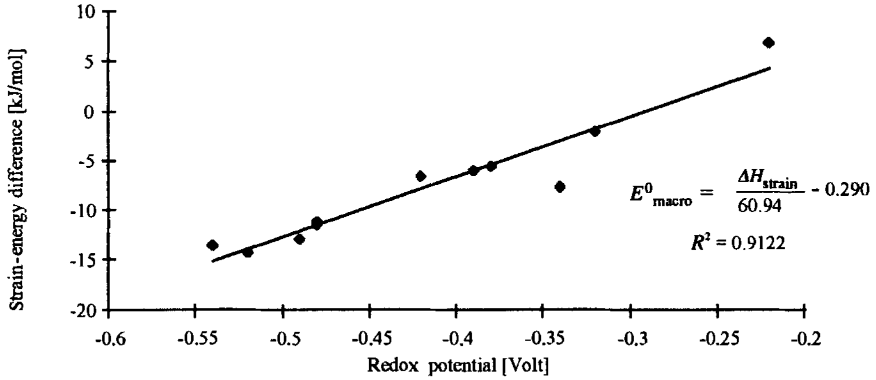


Fig. 2. *Correlation of the strain-energy difference* ΔU_{strain} *of tetraaminecopper(II/I) couples* (macrocyclic tetraamine ligands; lower section of *Table 3*) *with the experimentally determined reduction potentials* (*vs.* NHE) *in aqueous solution*

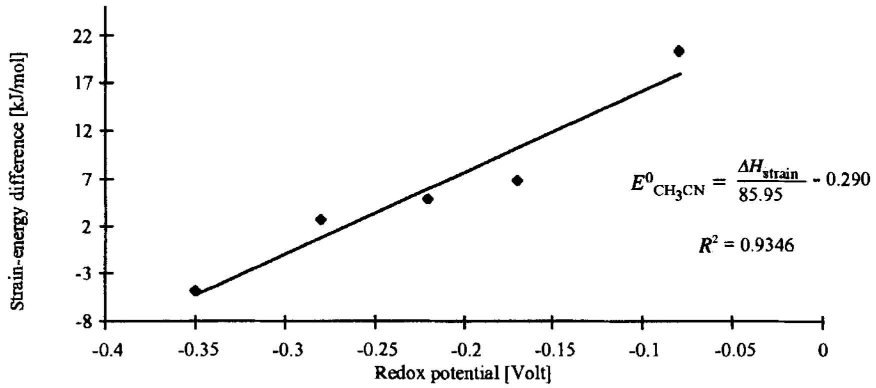


Fig. 3. *Correlation of the strain-energy difference* ΔU_{strain} *of tetraaminecopper(II/I) couples with the experimentally determined reduction potentials* (*vs.* NHE) *in MeCN* (*Table 4*)

reported here, but the intercepts vary by *ca.* 50 kJ mol^{-1}. This indicates that the slope of the correlation function is mainly governed by steric-strain, solvation, and entropy effects, and this also followed from studies involving $Co^{III/II}$ redox couples [1c].

Our analysis assumes that the neglected terms (entropy, specific electronic factors, solvation) vary linearly with the strain-energy differences (see above). For simplicity, the following qualitative discussion is mainly based on the observation that bulky ligands are generally leading to metal–ligand bond elongation. (Note, however, that the stabilization of the reduced or oxidized forms of the couple is dependent on the entire coordination geometry, *i.e.*, not only on the cavity size but also on the angular properties of the chromophore.)

i) The contribution of entropy changes to the thermodynamics of redox processes has been studied in detail, and the vibrational terms have been found to contribute significantly [4e]. As the difference between the Cu–N frequencies of the two oxidation states decreases, the entropy difference decreases also. With increasing Cu–N distances (bulky ligands, increasingly positive reduction potentials), the two frequencies become closer. The entropy contribution is, therefore, expected to decrease as the steric strain increases.

ii) Ligand field spectroscopic properties have been correlated with reduction potentials, and the question whether and where linear relationships may be expected has been discussed controversially [3]. With a constant donor set, as in the systems discussed here, the ligand field of the $[Cu^{II}N_4X_n]$ ($n = 1, 2$) chromophore decreases with increasing Cu–N bond distance, *i.e.*, roughly in parallel with increasing ligand strain.

iii) The contribution of the difference in solvation free energy between the reduced and the oxidized forms may qualitatively be understood on the basis of *Born*'s equation, *i.e.*, the solvation energy is proportional to $1/V^{1/3}$ (where V is the volume of the molecular cation). Therefore, it decreases with increasing size of the compound. The differences of the Cu–N distances between oxidized and reduced forms are roughly constant in the whole series ($\Delta r \approx 0.2$ Å $\approx$ constant). Also, the size of the ligands increases with increasing reduction potential (increasing total strain energy). Thus, the relevant term in *Born*'s equation, *i.e.*, $(a_{Cu}{}^{II} - a_{Cu}{}^{I})/(a_{Cu}{}^{II} \cdot a_{Cu}{}^{I})$, where a is the radius of the complex cations, decreases with increasing reduction potentials (constant numerator, inceasing denominator). From this qualitative analysis, it follows that the solvation-energy contribution must be different for primary and secondary amines (see above). Also, the fact that correlations of similar quality but different slopes for redox couples measured in H_2O and MeCN are obtained, supports the assumption that the solvation term varies roughly linearly with the strain-energy effects.

The rather appealing method of computing reduction potentials $E°$ with general ligand-based electrochemical parameters, *i.e.*, $E° = S_M \sum E_L + I_M$, where E_L is an electrochemical parameter of the ligand, S_M a metal-dependent parameter (relative M–L bond strength of oxidized and reduced form, and I_M a metal-dependent parameter (ionization potential, spherical part of the ligand field, electrode setup, solvation) [6], seems to be limited to redox couples with small structural changes between the two reactants [1c]. This is not unexpected since the E_L parameters are mainly based on observed electrochemical data of $Ru^{III/II}$ couples, where only small structural differences between the oxidized and the reduced form of the complex are observed. Thus, for four hexaamineruthenium(III/II) complexes, the strain-energy differences between the 2+ and the 3+ cations are constant within the error while the observed reduction potentials differ by 300 mV [12]. It follows that the electrochemical series of ligands [6] is primarily a series based on electronic effects, and different E_L parameters would need to be developed for systems involving considerable geometric differences between the oxidized and reduced form of the redox couple. In contrast, our method is based on constant donor sets, and each type of chromophore needs to be correlated separately. The success of the two approaches, each limited to specific and different applications, is a motivation for developing a more general method for the computation of reduction potentials that combines steric and electronic effects.

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Appendix. – Ligand abbreviations:

amlin	N^1,N^3-bis(2-aminoethyl)-2-methylpropane-1,2,3-triamine
[12]aneN_4	1,4,7,10-tetraazacyclododecane
Me_4[12]aneN_4	1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane
Bz_4[12]aneN_4	1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane
[14]aneN_4	1,4,8,11-tetraazacyclotetradecane (cyclam)
anti-cyclchxn	*anti*-(*R*,*R*,*s*: *S*,*S*,*s*)-4,15-dimethyl-4,15-dinitro-2,6,13,17-tetraazatricyclo-[16.4.0^7.0^{12}]docosane
chxn-2,3,2	(*R*,*R*: *R*,*R*(*S*,*S*: *S*,*S*))-[*N*,*N*′-bis(2-aminocyclohexyl)-2-methyl-2-nitropropane-1,3-diamine]
cis-Me_2[14]ane$N_4(NH_2)_2$	*cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine
cis-$Me_2(NO_2)_2$[14]aneN_4	*cis*-6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane
dmtn	2,2-dimethylpropane-1,3-diamine
en	ethane-1,2-diamine
dimeen	*N*,*N*′-dimethylethane-1,2-diamine
mchxn	cyclohexanamine
nnchxn	*trans*-(*R*,*R*)-cyclohexane-1,2-diamine
nelin	*N*,*N*′-bis(2-aminoethyl)-2-methyl-2-nitropropane-1,3-diamine
$Me(NO_2)$[13]aneN_4	12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane
$Me(NO_2)$[14]aneN_4	6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane
$Me(NO_2)$[15]aneN_4	10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane
$Me(NO_2)$[16]aneN_4	3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane
nten	*N*-ethylethane-1,2-diamine
syn-cyclchxn	*syn*-(*R*,*R*: *S*,*S*)-4,15-dimethyl-4,15-dinitro-2,6,13,17-tetraazatricyclo-[16.4.0^7.0^{12}]docosane
2,3,2-twt	*N*,*N*′-bis(2-aminoethyl)propane-1,3-diamine
3,2,3-tet	*N*,*N*″-(ethane-1,2-diyl)bis[propane-1,3-diamine]
tn	propane-1,3-diamine (trimethylenediamine)
trans-Me_2[14]ane$N_4(NH_2)_2$	*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine
trans-$Me_2(NO_2)_2$[14]aneN_4	*trans*-6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane

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