

Modeling of the Redox Properties of (Hexamine)cobalt(III/II) Couples

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The thermodynamics (redox potentials) and kinetics (electron transfer rates) of (hexamine)cobalt(III/II) redox couples are interpreted in terms of steric strain induced by the ligand systems. The intersections of potential energy curves (strain energy versus metal–ligand distance plots of pairs of conformers) of the oxidized and reduced forms of a wide range of (hexamine)cobalt(III/II) couples are related to the inner sphere reorganization (ΔH^\ddagger), and correlated with experimentally determined electron self-exchange rates. The minima of these potential energy curves of the reduced and oxidized forms are correlated with the reduction potentials. The perturbation by electronic effects due to differences in nucleophilicity along the series ammonia, primary amine, secondary amine, tertiary amine has been accounted for. The redox potentials of the couples studied ($E^\circ = -0.6\text{V}$ to $+0.8\text{V}$; vs SHE), the electron self-exchange rates (10^{-7}s^{-1} – 10^3s^{-1}), the Co^{3+} –N distances (1.94–2.05 Å), and the ligand field strengths (Co^{3+} : ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$, 16 700–22 200 cm^{-1}) cover a wide range. Accurate computed values for extremely long Co^{3+} –N bonds and for the corresponding low ligand field parameters (MM–AOM), high redox potentials, and specific electron self-exchange rates could only be obtained with a modification of the originally used force field, involving Morse potentials for the metal–ligand bonds. Applications of these methods, involving the design of new oxidants or reductants with specific potentials and electron transfer rates, and the determination of solution structures based on experimentally determined redox properties are presented, limits of this purely steric approach are discussed, and alternatives are evaluated.

Introduction

There are steric contributions to the thermodynamics and the kinetics of electron transfer processes, i.e. to both the reduction potentials and the electron transfer rates, and molecular mechanics calculations have been used in the past to model these.^{1–3} The basic idea of molecular mechanics modeling of redox properties is that the actual coordination geometry is the result of a compromise between the geometric preferences of the metal ion and those of the ligand sphere, and the ligand dictation usually dominates over that of the metal ion.¹ Thus, a ligand enforcing small metal–ligand distances will stabilize the oxidized form of the coordination compound (comparably small or negative redox potentials), while a ligand enforcing long metal–ligand bonds will stabilize the reduced form and lead to comparably large or positive potentials. For electron transfer rates, the situation is slightly more complex, since the steepness of the two potential energy curves as a function of the metal–donor distance, and the position of the two minima in terms of structure and energetics, are related to the energy barrier. Thus, it is not obvious to deduce general trends for electron self-exchange rates. The basic ideas of this simplistic approach toward modeling of redox properties are assembled in Figure

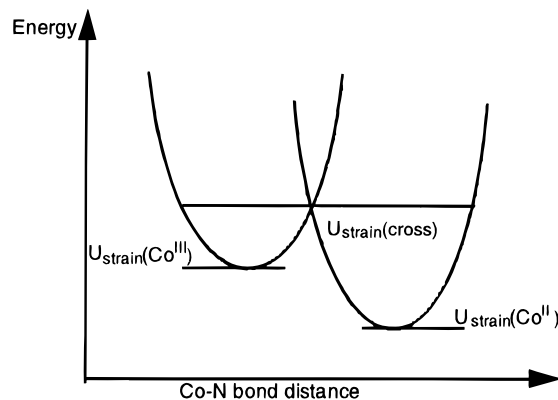


Figure 1. Strain energy versus M–L distance plot and parameters used in the calculations.

1, and the important features are the minima of the potential energy curves ($\Delta G^\circ = -nFE^\circ$; $\Delta G^\circ \sim \Delta U_{\text{strain}}(\text{Co}^{\text{III/II}})$) and the difference in energy between the crossing point of two potential energy curves and that of the corresponding minima ($k_{\text{self-ex}} = f(\Delta G^\ddagger)$; $\Delta G^\ddagger \sim \Delta U_{\text{strain}}^\ddagger$; $\Delta U_{\text{strain}}^\ddagger = 2U_{\text{strain}}(\text{cross}) - U_{\text{strain}}(\text{Co}^{\text{III}}) - U_{\text{strain}}(\text{Co}^{\text{II}})$). A number of approaches that are based on these and similar ideas have been used to compute redox potentials^{1,2} and electron transfer rates.^{1,2b,3} It is apparent that, for both the thermodynamics and the kinetics of electron transfer processes, buildup or relaxation of steric strain due to the coordination sphere reorganization is only one of the contributing factors. Others that have been identified and discussed in the literature include electronic properties, including ligand field effects,^{1b,c,2a,4a,b} specific hydrogen bonding,^{1b,c,4c} ion pairing,^{1b,c,2a,4c,d} solvation,^{1b,c,4d} and hydrophobicity.^{1b,c,4e}

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We have tested the simplistic but rather appealing molecular mechanics approach to both electron transfer kinetics and reduction potentials on a large and structurally very wide range of (hexaamine)cobalt(III/II) couples. The study includes an extensive amount of accurately determined structural, thermodynamic, and kinetic experimental data, using a well-established force field, and screening the whole conformational space of all the species considered. The influences of substituted amines and of unsymmetrical coordination polyhedra are discussed. Applications of the computation of redox properties to the design of new reductants and oxidants with specific potentials and electron transfer rates are discussed, and methods to determine solution structures with the combination of molecular mechanics and the computation of redox and that of ligand field properties, using the well established MM–AOM method,^{1,5} are also presented. The limits of the simplistic approaches used are evaluated and alternatives are discussed.

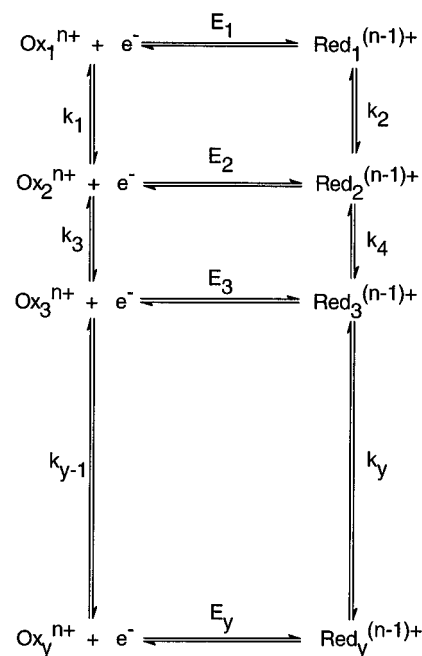
Modeling Procedures

MOMEC⁶ with a published force field⁷ was used to compute the optimized structures and the corresponding minimized strain energies. Effects due to the environment (solvation and ion pairing) and entropy effects were neglected (*vide infra* and ref 1b). Preliminary results indicated that an anharmonic potential is required to model the metal–ligand bonds (see below). Therefore, for substantially elongated Co³⁺–N bonds (>1.98 Å), a Morse function ($V(r) = D[1 - \exp\{\alpha(r - r_0)\}]^2 - D$) was used, and the parameters for Co(III) are as follows: $D = 0.13$ mdyn Å, $\alpha = 2.557$ Å⁻¹, $r_0 = 1.905$ Å (the strain-free metal–ligand distance r_0 is identical to that used in the original force field; α and D are related to the force constant k of the harmonic bonding potential, $V(r) = \frac{1}{2}k(r - r_0)^2$, by $\alpha = (k/2D)^{1/2}$, and were obtained accordingly; tabulated Co^{III}–N bond energies were used for initial values of D). The only other new parameters used in this study involve the parameterization of the dimethylaminodimethylsilane ligand (k_b in mdyn Å⁻¹, r_0 in Å; k_θ in mdyn Å rad⁻², θ° in rad): C–Si, 0.40, 1.868; C–Si–C, 0.55, 1.911; Si–C–H, 0.35, 1.909; Si–C–N, 0.45, 1.911; $r_{vdw}(\text{Si})$ 2.1, $\epsilon_{vdw}(\text{Si})$ 0.165. The conformational space of the complexes was searched deterministically. The strain-energies *vs* metal–ligand distance curves were determined with the module ENERGY available in MOMEC (optimization of the structures with mathematically constrained internal coordinates, i.e. M–L bond distances),¹ and the metal ion dependent energy terms were included in the calculation of the total strain energy. For some of the complexes of asymmetric ligands the six metal–ligand bonds were varied independently, i.e. with different starting values and increments^{1b,8} (a more elegant and more general method, using Lagrange multipliers for constraining the sum of the six bond distances, is currently being developed in our laboratory). MM–AOM calculations were done as described elsewhere,⁵ using the computer program CAMMAG⁹ for the AOM calculations and electronic parameters (transferable e_σ values, adjusted with $1/r^6$ to the computed (MM) metal–ligand distances r) that have been published before.^{5a}

Results and Discussion

Reduction Potentials. Published reduction potentials of (hexaamine)cobalt(III) complexes span a range of over 0.9 V,

Scheme 1. Square Scheme of Conformer Distributions and Redox Equations



with the lowest potential (–0.63 V vs SHE) measured for [Co(*trans*-diammac)]^{3+/2+} (short metal–ligand bonds, high ligand field) and the highest potential (+0.28 V vs SHE) found for [Co(tmen)₃]^{3+/2+} (long bonds, small ligand field; see Appendix for ligand abbreviations and Table 1 for experimentally determined redox potentials and corresponding references). On the basis of the correlations presented below, we have designed and isolated two new (hexaamine)cobalt(III) complexes with extremely low ligand fields and correspondingly high redox potentials ([Co(dmtn)₃]^{3+/2+}, +0.19 V vs SHE; [Co(dmsa)₃]^{3+/2+}, +0.8 V vs SHE (computed value)).¹⁰ These data are also included in Table 1. Recently, a hexaamine cage ligand with an extended cavity has become available, and one of the two isolated stable conformers of the cobalt(III) compound exhibits the extremely high reduction potential of +0.84 V vs SHE,¹¹ a value that we have been able to reproduce with our modeling calculations¹² (data also included in Table 1).

The force field parametrization for (hexaamine)cobalt(III) compounds has been refined to a quality where structural and thermodynamic properties may be computed with rather high accuracies.^{1b} This is specifically true for the parameter set used here, which has been used successfully for the computation of a considerable number of isomer distributions. The parameter set for (hexaamine)cobalt(II) has, due to the smaller data base, not been tested with the same rigor, but due to the identical parametrization of the ligand backbones and on the basis of the good quality of the computed structures, the accuracy of the thermodynamic predictions must be similar to that of the oxidized species.^{1c}

For most (hexaamine)cobalt(III/II) complexes there exists a range of stable isomers and conformers. The structure of each conformer may then be optimized separately, and a pair of strain energy *versus* metal–ligand distance curves (see Figure 1) for each of them may be computed. It follows that each individual pair of conformers will exhibit a separate reduction potential.

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Table 1. Observed and Calculated Redox Potentials (V) of Different Cobalt(III/II) Hexamine Couples

cobalt(III/II) couple ^a	A ^b E _{1/2} (exptl)	B ^{c-e} E _{1/2} (calc)	C ^{d-g} E _{1/2} (calc)
Ammonia			
[Co(NH ₃) ₆] ^{3+/2+}	-0.02 [1]	-0.10 (0.08)	-0.29 (0.27)
Primary Amines			
[Co(tame) ₂] ^{3+/2+}	-0.43 [1]	-0.18 (0.25)	-0.26 (0.17)
[Co(trap) ₂] ^{3+/2+}	-0.34 [1]	-0.32 (0.02)	-0.43 (0.09)
[Co(trab) ₂] ^{3+/2+}	-0.31 [1]	-0.21 (0.10)	-0.29 (0.02)
<i>R-lel</i> ₃ -[Co(chxn) ₃] ^{3+/2+}	-0.20 [1]	-0.15 (0.05)	-0.22 (0.02)
[Co(en) ₃] ^{3+/2+}	-0.17 [1]	-0.15 (0.02)	-0.22 (0.05)
<i>R-lel</i> ₃ -[Co(pn) ₃] ^{3+/2+}	-0.11 [1]	-0.06 (0.07)	-0.13 (0.00)
<i>R-lel</i> _{2ob} -[Co(pn) ₃] ^{3+/2+}	-0.12 [1]	-0.06 (0.05)	-0.12 (0.01)
<i>R-ob</i> ₂ <i>l</i> <i>l</i> -[Co(pn) ₃] ^{3+/2+}	-0.13 [1]	-0.08 (0.04)	-0.15 (0.03)
<i>R-ob</i> ₃ -[Co(pn) ₃] ^{3+/2+}	-0.13 [1]	-0.13 (0.00)	-0.21 (0.08)
[Co(tn) ₃] ^{3+/2+}	+0.13 [1]	+0.16 (0.03)	+0.14 (0.01)
[Co(tmen) ₃] ^{3+/2+}	+0.28 [1]	+0.32 (0.04)	+0.33 (0.05)
[Co(dmtn) ₃] ^{3+/2+}	+0.19 [2]	+0.23 (0.04)	+0.22 (0.03)
Primary/Secondary Amines			
[Co(<i>trans</i> -diammac)] ^{3+/2+}	-0.63 [1]	-0.79 (0.16)	-0.78 (0.15)
[Co(tacn)(tame)] ^{3+/2+}	-0.46 [3]	-0.20 (0.26)	-0.18 (0.28)
[Co(<i>cis</i> -diammac)] ^{3+/2+}	-0.41 [4]	-0.42 (0.01)	-0.40 (0.01)
[Co(tacn)(trap)] ^{3+/2+}	-0.40 [3]	-0.30 (0.10)	-0.29 (0.11)
[Co(diamecyclam)] ^{3+/2+}	-0.38 [1]	-0.39 (0.01)	-0.37 (0.01)
[Co(sen)] ^{3+/2+}	-0.30 [5]	-0.22 (0.08)	-0.20 (0.10)
[Co(tacn)(dien)] ^{3+/2+}	-0.29 [3]	-0.21 (0.08)	-0.20 (0.09)
[Co(trap)(dien)] ^{3+/2+}	-0.28 [3]	-0.25 (0.03)	-0.27 (0.01)
<i>sym</i> -[Co(dien) ₂] ^{3+/2+}	-0.27 [1]	-0.20 (0.07)	-0.19 (0.08)
<i>asym</i> -[Co(dien) ₂] ^{3+/2+}	-0.25 [1]	-0.15 (0.10)	-0.13 (0.12)
<i>fac</i> -[Co(dien) ₂] ^{3+/2+}	-0.21 [1]	-0.07 (0.14)	-0.03 (0.18)
[Co(azasen)] ^{3+/2+}	-0.20 [5]	-0.11 (0.09)	-0.08 (0.12)
<i>mer</i> -[Co(dpt) ₂] ^{3+/2+}	+0.28 [1]	+0.13 (0.15)	+0.31 (0.03)
Secondary Amines			
[Co(dimesar)] ^{3+/2+}	-0.48 [5]	-0.50 (0.02)	-0.41 (0.07) [-0.45 (0.03)]
[Co(tacn) ₂] ^{3+/2+}	-0.41 [1]	-0.19 (0.22)	-0.14 (0.27)
[Co(sar)] ^{3+/2+}	-0.40 [1]	-0.41 (0.01)	-0.33 (0.07) [-0.36 (0.04)]
<i>S,S</i> -[Co(dimechar)] ^{3+/2+}	-0.36 [6]	-0.32 (0.04)	-0.26 (0.10) [-0.29 (0.07)]
[Co(azamesar)] ^{3+/2+}	-0.34 [5]	-0.39 (0.05)	-0.31 (0.03) [-0.27 (0.07)]
[Co(ammesar)] ^{3+/2+}	-0.34 [5]	-0.49 (0.15)	-0.40 (0.06) [-0.38 (0.04)]
[Co(mammesar)] ^{3+/2+}	-0.34 [5]	-0.52 (0.18)	-0.43 (0.09) [-0.41 (0.07)]
[Co(homesar)] ^{3+/2+}	-0.30 [5]	-0.48 (0.18)	-0.39 (0.09) [-0.33 (0.03)]
[Co(diamsar)] ^{3+/2+}	-0.30 [5]	-0.48 (0.18)	-0.39 (0.09) [-0.32 (0.02)]
[Co(dimamsar)] ^{3+/2+}	-0.29 [5]	-0.55 (0.26)	-0.46 (0.17) [-0.38 (0.09)]
[Co(dihosar)] ^{3+/2+}	-0.20 [5]	-0.46 (0.26)	-0.38 (0.18) [-0.21 (0.01)]
[Co(sep)] ^{3+/2+}	-0.26 [1]	-0.28 (0.02)	-0.22 (0.04) [-0.12 (0.15)]
[Co(18N6)] ^{3+/2+}	-0.14 [1]	+0.13 (0.27)	+0.15 (0.29)
<i>R-fac-l</i> <i>el</i> ₃ -[Co(diampnsar)] ^{3+/2+}	+0.02 [7]	-0.10 (0.12)	-0.06 (0.08) [+0.02 (0.01)]
<i>R-fac-ob</i> ₃ -[Co(diampnsar)] ^{3+/2+}	-0.29 [7]	-0.40 (0.11)	-0.32 (0.03) [-0.25 (0.04)]
<i>R-mer-l</i> <i>el</i> ₃ -[Co(diampnsar)] ^{3+/2+}	+0.02 [7]	-0.12 (0.14)	-0.07 (0.085) [0.00 (0.02)]
<i>R-mer-l</i> <i>el</i> ₃ -[Co(diampnsar)] ^{3+/2+}	-0.32 [7]	-0.40 (0.08)	-0.32 (0.00) [-0.25 (0.07)]
<i>twist-l</i> <i>el</i> ₃ -[Co(dimetrcs)] ^{3+/2+}	+0.84 [8]	+0.95 (0.15)	+0.89 (0.09) [+0.86 (0.02)]
<i>twist-ob</i> ₃ -[Co(dimetrcs)] ^{3+/2+}	0.00 [8]	-0.15 (0.15)	-0.10 (0.10) [-0.13 (0.13)]
Primary/Tertiary Amines			
[Co(trap)(medien)] ^{3+/2+}	-0.21 [3]	-0.09 (0.12)	-0.07 (0.14)
<i>sym</i> -[Co(medien) ₂] ^{3+/2+}	-0.01 [1]	-0.12 (0.11)	-0.09 (0.08)
[Co(teatacn)] ^{3+/2+}	-0.12 [9]	-0.04 (0.08)	-0.01 (0.11)
Secondary/Tertiary Amines			
[Co(amsartacn)] ^{3+/2+}	-0.08 [10]	-0.21 (0.13)	-0.12 (0.04)
[Co(septacn)] ^{3+/2+}	-0.06 [10]	-0.05 (0.01)	+0.00 (0.06)
[Co(dtne)] ^{3+/2+}	-0.02 [1]	-0.03 (0.01)	+0.01 (0.03)

^a For abbreviations see the Appendix ^b References: (1) Hendry, P.; Ludi, A.; *Adv. Inorg. Chem.* **1990**, 35, 117. (2) Unpublished data. (3) Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. Z. *Anorg. Allg. Chemie* **1987**, 551, 33. (4) Bond, A. M.; Hambley, T. W.; Mann, D. R.; Snow, M. R. *Inorg. Chem.* **1987**, 26, 2557. (5) Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1990**, 29, 4808. (6) Geue, R. J.; McCarthy, M. B.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, 106, 8282. (7) Geue, R. J.; Hendry, A. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Comm.* **1989**, 1646. (8) Geue, R. J.; Hanna, J.; Höhn, A.; Qin, C. J.; Ralph, S. F.; Sargeson, A. M.; Willis, A. C. In *Electron Transfer Reactions; Isied, S., Ed.*; ACS Symposium Series; American Chemical Society: Washington, DC, 1997; Chapter 8. (9) Warren, R. M. L.; Lappin, A. G.; Mehta, B. D. Neumann, H. M. *Inorg. Chem.* **1990**, 29, 4185. (10) Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, 99, 5158. ^c See Figure 2. ^d Difference to observed potentials in parentheses. ^e Potentials that are not used for the correlation in italics (see text). ^f See eq 2 and Figure 5. ^g Values obtained with eq 3 in brackets.

A square scheme has been proposed to describe this situation (see Scheme 1).¹³ Molecular mechanics calculations have been used to compute the abundances of each conformer (cobalt(III)

and cobalt(II)) and the corresponding reduction potentials.^{4d,14} Large strain energy differences within the conformers of one oxidation state lead to situations where the highly strained

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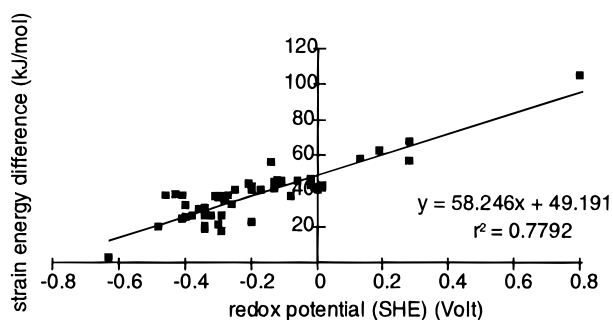


Figure 2. Strain energy difference versus observed redox potential plot for all cobalt(III/II) hexaamine couples considered in this study.

species may not be detected experimentally; very similar strain energy differences of pairs of conformers lead to small differences of the corresponding reduction potentials, and these may then not be resolved. Thus, it is not unexpected that, so far, the proposed square scheme could not be confirmed, with the exception of the cobalt(III/II) hexaamine cage compound mentioned above, where two stable conformers were isolated.^{11,12}

The experimentally determined (*vs* SHE) and the computed reduction potentials (linear regression of the strain energy differences between the cobalt(III) and cobalt(II) compounds with the experimental redox potentials of all entries in Table 1) of a wide range of (hexaamine)cobalt(III/II) couples are given in Table 1 (columns A and B, respectively), and the data are presented graphically in Figure 2. All possible conformers have been considered in the computations, and the calculated potentials given correspond to the cobalt(III) species with the highest abundance (lowest strain energy). The linear regression has a slope of 61 kJ mol⁻¹ V⁻¹ and a correlation coefficient of $r^2 = 0.78$. The deviation of the slope from the theoretical value of 96 kJ mol⁻¹ V⁻¹ is not unexpected and due to the neglect of the influence of the environment, the neglect of entropy contributions, the neglect of electronic effects, and remaining deficiencies of the force field parametrization. The fact that the calculated value of the slope is ca. 65% of that theoretically expected indicates that strain relaxation is a major component, and from the fact that the variation is linear, it follows that the neglected factors vary roughly linearly with strain energy effects. The mean error of calculated reduction potentials is ± 0.1 V (± 0.08 V, when the least accurate values are neglected; see footnote in Table 1 and Figures 2–5 for the couples that have been omitted and the discussion below for reasons to do that).

Our analysis does not include a quantitative treatment of solvation effects. However, on a qualitative basis, it is conceivable that the solvation energy term varies linearly with the strain energy differences: According to Born's equation the solvation free energy is proportional to $1/V^{1/3}$; i.e. it decreases with increasing size of the complex cation. Therefore, the effect of solvation related to the reduction process is proportional to $(1/a_{\text{Co(III)}} - 1/a_{\text{Co(II)}})$, where a is the radius of the complex cation. The difference in size between the oxidized and reduced forms is mainly governed by the difference in Co–N distances ($\Delta r \sim 0.2$ Å, roughly independent of the ligand system within the whole series in Table 1). The stabilization of the reduced Co(II) form (highly positive reduction potentials, large strain energy differences) is generally due to sterically demanding ligands, leading to large molecular cations, both for the reduced and the oxidized form (large values for $a_{\text{Co(III)}}$ and $a_{\text{Co(II)}}$). Therefore, for similar types of ligands the relevant term $(a_{\text{Co(III)}} - a_{\text{Co(II)}})/a_{\text{Co(III)}}a_{\text{Co(II)}}$ decreases with increasing redox potentials (constant numerator, increasing denominator). It also follows then, that couples with ammonia and primary, secondary, and tertiary amines each have slightly different correlation functions (see also below). That the solvation term is linear with respect to

the strain energy differences is also supported by the observation that in copper(II/I) systems¹⁵ correlations of similar quality but with different slopes are observed for redox couples in water and acetonitrile.

Entropy changes related to the reduction of cobalt(III) hexaamines have been measured, and there are published methods to compute them.¹⁶ The vibrational entropy term has been found to be a significant contribution to the overall reaction entropy. Our analysis (see above) requires that the entropy contribution varies as a function of the strain energy difference. In the present study we have not treated these terms quantitatively. On a qualitative basis, the variation of the entropy contribution along the series of cobalt(III/II) couples may be related to the fact that increasingly positive cobalt(III/II) potentials are observed for ligand systems enforcing long Co–N bonds, and these lead to large strain energy differences. With increasing Co–N distances the frequencies of the two forms of the redox couples become closer and, therefore, the vibrational entropy contribution decreases.

A third factor that has not been considered explicitly here is the influence of varying ligand field contributions. Redox potentials have been correlated with ligand field spectroscopic parameters, and reasons for satisfactory correlations and deficiencies have been discussed in detail.^{1,4a,17} A main feature is that for (hexaamine)cobalt(III/II) couples there is a linear correlation between the redox potential and the ligand field stabilization energy Δ of the oxidized cobalt(III) form (or of its first ligand field transition energy). Thus, if part of the difference between the observed and the theoretically expected slope may be attributed to changes in the ligand field, it varies in the way predicted from our correlations. Note, that a ligand field based term is related to the relative stability of the cobalt(III) form, i.e. to the Co(III)–N bonding potential, and this has been accounted for in our correlation by the corresponding molecular mechanics bonding potential. Thus, if ligand field terms would be added in our analysis, the corresponding force field terms would possibly have to be subtracted (see Conclusions for a further discussion of electronic factors related to the ligand field).

From Table 1 and Figure 2 it emerges that the correlation of the redox potentials with the strain energies might be different for couples with primary and secondary amines. Possible reasons are as follows: (i) Electronic effects, neglected in our approach, may be responsible for part of the remaining ca. 35% of the slope. The predominance of steric strain must then decrease with increasing nucleophilicity of the donor groups; i.e., the slope for the secondary amines should be smaller than that for the primary amines. (ii) The secondary amines are generally more rigid (sterically reinforced, macrocyclic and/or cage ligands), leading to a steeper strain energy surface and therefore to an increasing importance of the strain energy effects, i.e. the slope for the secondary amines should be larger than that for the primary amines. (iii) For contributions of solvation and entropy differences, and for ligand field based effects, see discussion above. Obviously, there may be partial cancellation of various contributing factors, and this is one of the reasons

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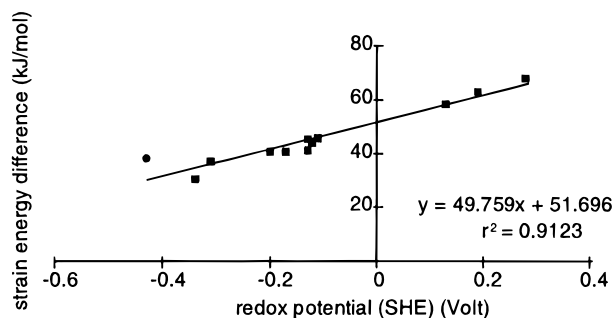


Figure 3. Strain energy difference versus observed redox potential plot for cobalt(III/II) hexamine couples with primary amine ligands. (Inaccurate data pairs (filled circles; see text) are not included in the correlation).

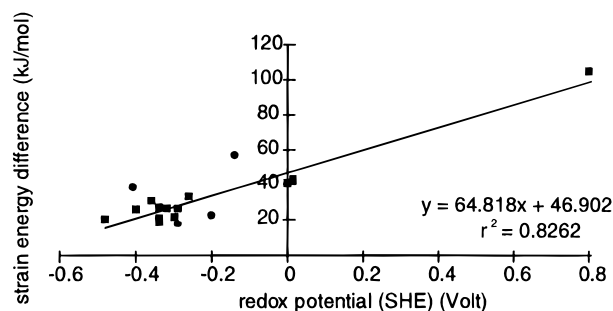


Figure 4. Strain energy difference versus observed redox potential plot for cobalt(III/II) hexamine couples with secondary amine ligands. (Inaccurate data pairs (filled circles; see text) are not included in the correlation).

why mixed amine ligand systems are leading to the reasonably well behaved linear correlation shown in Figure 2. Separate correlations for primary and secondary amines are presented in Figures 3 and 4, and the accuracy is increasing ($r^2 = 0.91$ (primary amines), 0.83 (secondary amines) vs 0.78).

The fact that the slope for secondary amines is larger than that for primary amines ($65 \text{ kJ mol}^{-1} \text{ V}^{-1}$ vs $45 \text{ kJ mol}^{-1} \text{ V}^{-1}$, 70% vs 50% of $96 \text{ kJ mol}^{-1} \text{ V}^{-1}$) indicates that, for amine ligands coordinated to cobalt(III/II) redox couples, the rigidity of the ligand is more important than the nucleophilicity of the donor. This also emerges from the intercept of the correlation curves: Ligands with an electronic preference for the reduced form shift the potential toward more positive values. This emerges also from studies involving copper(II/I) couples with tetrathia- and tetraazamacrocyclic ligands, where the slopes of strain energy vs redox potential curves are close to identical, while the intercepts vary by ca. 50 kJ mol^{-1} .¹⁵ For cobalt(III/II) hexamines with primary and secondary amines (Figures 3 and 4), the intercepts are identical within the error. These observations support the validity of our purely steric approach for the computation of redox potentials of cobalt(III/II) hexamine couples. That is, for constant metal centers and types of donor atoms, electronic effects may be neglected if there are large structural changes between the reduced and the oxidized form. The separation into groups of compounds with primary and secondary amines then is somewhat artificial, and this also emerges from some systems with rather poor agreement (see footnotes in Table 1 and Figures 2–5). Some particularly unsatisfactory examples are compounds with rather flexible ligands (e.g. 18aneN6) and macrocyclic ligands which are not efficiently encapsulating the metal center (e.g. tacn; see also Conclusions). Also excluded from the correlation were some couples involving hexamine cage ligands for which strong electronic effects from the substituents on the apical caps were observed (see below).

For couples with mixed primary/secondary amine donor sets the two correlation functions may be combined; i.e., the dif-

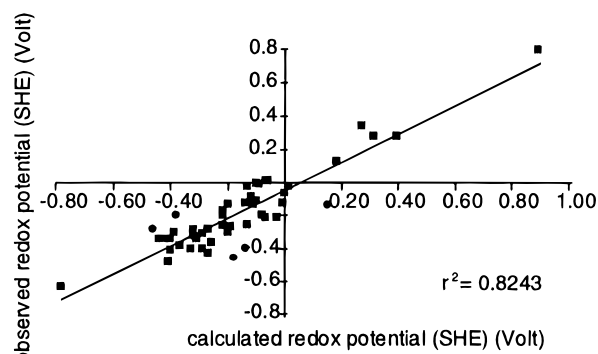


Figure 5. Correlation between observed and calculated redox potentials for all cobalt(III/II) hexamine couples considered in this study. (Inaccurate data pairs (filled circles; see text) are not included in the correlation).

ference in slope and intercept between the functions for primary and secondary amines may be used as a correction factor to mix n secondary amine ligands with $6 - n$ primary amines (eq 1). An extrapolation of the correction factor for secondary

$$E^\circ = \frac{\Delta U_{\text{strain}}}{49.759} - 1.039 - \frac{n}{6} \left(\frac{\Delta U_{\text{strain}}}{214.18} - 0.315 \right) \quad (1)$$

amines to ammonia (0th order amine) and tertiary amines leads to eq 2 which allows the computation of redox potentials of any mixed donor set (hexamine)cobalt(III/II) couple.

$$E^\circ = \frac{\Delta U_{\text{strain}}}{40.378} - 1.354 - a \left(\frac{\Delta U_{\text{strain}}}{1285.1} - 0.0525 \right) \quad (2)$$

a = number of alkyl groups at the nitrogen donors

Equation 2 has been used to compute the redox potentials of all couples listed in Table 1 (see column C). The mean accuracy of these computed redox potentials is $\pm 0.10 \text{ V}$ ($\pm 0.08 \text{ V}$ if the least accurate samples are neglected; see above and footnotes to Table 1 and Figures 2–5). The overall accuracy is acceptable, and this also emerges from Figure 5, which shows the correlation between experimentally determined and computed redox potentials with a correlation coefficient of $r^2 = 0.83$.

The redox potentials of the sepulchrate and sarcophagine type hexamine cage couples in Table 1 cover a range of ca. 500 mV. It has been found that the redox potentials of these compounds are dependent on the substituents on the two "caps" of the cage ligands, and a dependence on the Hammet parameters of these substituents has been found.¹⁸ The computation of the redox potentials of hexamine cage cobalt(III/II) couples, involving the strain energy differences (eq 2) and a correction based on Hammet parameters leads to a very good correlation with $r^2 = 0.95$ (eq 3; the corrected redox potentials appear in

$$E^\circ = \frac{\Delta U_{\text{strain}}}{64.565} - 0.773 + (0.0606 \sum \sigma_E + 0.0234) \quad (3)$$

brackets in Table 1). Preliminary studies with $\text{Co}^{\text{III/II}}\text{S}_n\text{N}_{6-n}$,¹⁹ and with $\text{Ni}^{\text{III/II}}$,¹⁹ $\text{Ni}^{\text{II/I}}$,¹⁹ and $\text{Cu}^{\text{II/I}}$ couples¹⁵ indicate that correlations of quality similar to those observed with the cobalt(III/II) hexamines may be obtained for these systems.

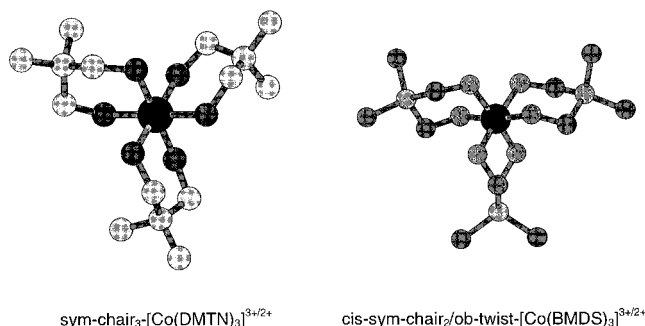
Design of Couples with High Redox Potentials. The recent report of an extremely high redox potential of an extended cobalt(III/II) cage compound, based on 1,3-diamino-2,2-dimethylpropane,¹¹ suggested that the analogous tris-bidentate complex

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Table 2. Strain Energies and Calculated Reduction Potentials of all 16 Possible Conformers of $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ and $[\text{Co}(\text{bmds})_3]^{3+/2+}$

	$[\text{Co}(\text{dmtn})_3]^{3+/2+}$ / $[\text{Co}(\text{bmds})_3]^{3+/2+}$			
	$U_{\text{Co(II)}} \text{ (kJ/mol)}$	$U_{\text{Co(III)}} \text{ (kJ/mol)}$	$\Delta U \text{ (kJ/mol)}$	$E_{1/2} \text{ (V)}$
<i>asym-chair</i> ₂ / <i>ob-twist</i>	59.74 {−13.43}	125.90 {72.96}	66.16 {86.39}	0.35 {0.80}
<i>trans-sym-chair</i> ₂ / <i>lel-twist</i>	62.84 {−8.62}	131.04 {83.83}	68.20 {92.45}	0.40 {0.94}
<i>trans-sym-chair</i> ₂ / <i>ob-twist</i>	60.71 {−15.08}	125.86 {78.92}	65.15 {94.00}	0.33 {0.97}
<i>asym-chair</i> ₂ / <i>lel-twist</i>	61.59 {−12.19}	128.10 {77.42}	64.51 {89.60}	0.31 {0.87}
<i>cis-sym-chair</i> ₂ / <i>lel-twist</i>	61.46 {−12.47}	129.91 {81.29}	68.45 {93.76}	0.40 {0.97}
<i>cis-sym-chair</i> ₂ / <i>ob-twist</i>	58.67 {−16.15}	125.72 {70.74}	67.05 {86.89}	0.37 {0.81}
<i>sym-chair</i> ₃	59.01 {−16.43}	121.76 {73.24}	62.75 {89.67}	0.28 {0.88}
<i>asym-chair</i> ₃	59.76 {−15.08}	125.42 {78.93}	65.66 {97.30}	0.34 {1.05}
<i>chair/twist</i> ₂ - <i>ob</i> ₂	60.79 {−10.73}	125.42 {74.12}	64.63 {84.85}	0.32 {0.77}
<i>chair/twist</i> ₂ - <i>lel</i> ₂	63.79 {−8.83}	134.00 {78.72}	70.21 {87.55}	0.44 {0.83}
<i>chair/twist</i> ₂ - <i>lel</i> ₂	63.41 {−8.83}	133.07 {79.53}	69.66 {88.36}	0.43 {0.85}
<i>chair/twist</i> ₂ - <i>lelob</i>	64.40 {−6.61}	132.16 {78.53}	67.76 {85.14}	0.39 {0.77}
<i>twist</i> ₃ - <i>lel</i> ₃	62.47 {−8.09}	125.18 {73.11}	62.71 {81.20}	0.27 {0.69}
<i>twist</i> ₃ - <i>lel</i> ₂ <i>ob</i>	68.35 {−0.75}	141.95 {82.78}	73.60 {86.53}	0.52 {0.74}
<i>twist</i> ₃ - <i>ob</i> ₃	64.96 {−8.22}	137.12 {80.55}	72.16 {88.77}	0.49 {0.86}
<i>twist</i> ₃ - <i>lelob</i> ₂	66.85 {−3.64}	136.18 {74.63}	69.33 {78.27}	0.42 {0.62}

**Figure 6.** Computed structures of the most stable conformers of (a, left) $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ (*sym-chair*₃) and (b, right) $[\text{Co}(\text{bmds})_3]^{3+/2+}$ (*cis-sym-chair*₂/*ob-twist*)

might also lead to strongly oxidizing cobalt(III) hexaamines. Also, the substitution of the central carbon atom of that diamine by silicon should further increase the redox potential due to an increasing steric demand (extended bite distance). Computed structural parameters, strain energies, and reduction potentials of all possible conformers of the two new (hexaamine)cobalt couples $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ (dmtn = 1,3-diamino-2,2-dimethylpropane) and $[\text{Co}(\text{dmsa})_3]^{3+/2+}$ (dmsa = dimethyl(dimethylamino)silane) are given in Table 2, and the computed structures of the most stable cobalt(III) isomer each are shown in Figure 6. The experimental data for $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ are included in Tables 1 and 3; those for $[\text{Co}(\text{dmsa})_3]^{3+/2+}$ are not yet available.¹⁰ All the computed redox potentials presented here are based on the strain energy minimization using a Morse function for the metal–nitrogen bonds (see section on Modeling Procedures). Note that calculated reduction potentials of only slightly inferior accuracy are obtained, when the harmonic bond stretching potential and the corresponding, previously published,⁷ force field parameters are used, even for the two new compounds with rather long cobalt–nitrogen bonds. This is not unexpected since the reduction potentials are related to the strain energy difference between the oxidized and reduced forms of the cobalt hexaamine and, therefore, to the strain energy of the cobalt(III) complex and not to its structure. In other words, the rigidity of the ligand, described by the ligand part of the force field, is responsible for the amount of energy loss enforced by its coordination to the metal ion. Thus, the shape of the energy surface of the metal–ligand bonds and corresponding valence angles does only slightly influence this strain energy, as long as the curvatures of these potentials are not too dissimilar. However, changes in terms of the optimized structures might be considerable. This emerges also from the comparison of calculated and observed ligand field spectra, which indicates that the description of the metal–ligand bonds

by Morse potentials is required for an accurate computation of the d–d transitions of highly strained species (see separate section ahead). This is due to the fact that the ligand field properties are strongly dependent on the metal–ligand distances ($1/r^5$, $r = \text{M–L}$). Also, the structures and energetics of the activated state of the electron transfer reaction might depend considerably on the shape of the metal–donor potentials (see ahead). An important point to note here is that the quality of the structural predictions are not necessarily coupled to those of thermodynamic properties. These are typical properties of models that are basically based on interpolations.^{1c}

There are a large number of possible conformers for $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ and $[\text{Co}(\text{dmsa})_3]^{3+/2+}$, but only those with the six-membered chelate rings in *chair* or *twist* (*skew-boat*) conformation have been considered; the *boat* conformation is strongly destabilized by the orientation of the methyl substituents on the central carbon or silicon atom. There are two possible orientations of the chelate rings in *twist* conformation, i.e. oblique (*ob*) or parallel (*lel*) to the C_3 axis. With more than one ring in *chair* conformation, these may be symmetric (*sym*) or antisymmetric (*asym*) to the C_3 axis, i.e. *syn* or *anti* to each other. The corresponding 16 conformers are listed in Table 2. The most stable conformer of $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ has *sym-chair*₃ conformation; for $[\text{Co}(\text{dmsa})_3]^{3+/2+}$ *cis-sym-chair*₂/*ob-twist* is the most stable form, with *asym-chair*₂/*ob-twist* and *twist*₃-*lel*₃ slightly less abundant. The computed redox potential of $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ is in reasonable agreement with the experimentally determined value (+0.28 V vs +0.19 V), and this is nearly 100 mV more positive than the redox potential of the related $[\text{Co}(\text{tn})_3]^{3+/2+}$ couple. The potential of the couple with the silicon-substituted ligand is expected to be around +0.8 V.

Ligand Field Spectra. MM–AOM calculations, i.e. the prediction of energy levels by AOM (angular overlap model) calculations based on computed structures (MM, molecular mechanics), of chromium(III), cobalt(III), nickel(II), and copper(II) complexes have generally lead to rather accurate predictions of ligand field spectra, with deviations to experimental data of the order of 200–500 cm^{-1} , i.e. ca. 2–5 nm depending on the wavelength of the transition.⁵ Using our original approach with a harmonic metal–ligand stretching function, the computed spectra of the two new (hexaamine)cobalt(III) compounds $[\text{Co}(\text{dmtn})_3]^{3+/2+}$ and $[\text{Co}(\text{dmsa})_3]^{3+/2+}$ were unacceptably poor (see Table 3). This indicated that the cobalt(III)–nitrogen distances were underestimated due to a ligand-strain-induced elongation over the harmonic limit of the bonding potential. The structural data based on the Morse function and the corresponding AOM calculations show the improved accuracy of the computed structural and spectroscopic parameters.

Table 3. Calculated and Observed Metal–Ligand Bond Distances and Ligand Field Spectra of (Hexaamine)cobalt(III) Complexes

Co(III) complex	Co(III)–N bond length (Å)		abs maxima (cm ⁻¹)	
	exptl	calc: Morse (harmonic)	exptl	calc: Morse (harmonic)
<i>sym</i> ₃ - <i>chair</i> ₃ -[Co(dmtn) ₃] ³⁺		2.011 (1.986)	18 050/26 300	17 730/25 770 (19 120/27 320)
<i>cis-sym-chair</i> ₂ / <i>ob-twist</i> -[Co(bmds) ₃] ³⁺		1.992 (1.974)	19 190/27 850	19 530/27 780 (20 700/29 070)
<i>lel</i> ₃ -[Co(en) ₃] ³⁺	1.964	1.964 (1.955)	21 410/29 500	21 190/29 500 (21 740/30 200)
<i>λδ</i> -[Co(<i>trans</i> -diammac)] ³⁺	1.941	1.940 (1.937)	22 170/30 580	23 090/31 650 (23 920/32 470)
<i>R-fac-lel</i> ₃ -[Co(diampnsar)] ³⁺		1.980 (1.968)	20 830/28 900	20 620/28 980 (21 600/29 940)
<i>R-fac-ob</i> ₃ -[Co(diampnsar)] ³⁺		1.967 (1.959)	22 220/30 210	21 790/30 210 (22 730/31 250)

Electron Transfer Rates. There is a continuing interest in electron transfer reactivities and their correlation to molecular structures, based on the Marcus theory.^{3,20} A number of approaches to compute homogeneous and heterogeneous electron transfer rates, based on the simple model presented in Figure 1, have been discussed. These include a simple²¹ and a more elaborate^{2b} harmonic oscillator model, and various methods based on molecular mechanics calculations.³ All these models have in common that, apart from minor exceptions,^{3c} entropic and electronic effects are excluded and that the computations are generally based on effects due to inner sphere reorganization energies. The assumption is^{3,20,21} that electron self-exchange reactions involving (hexaamine)cobalt(III/II) couples are basically adiabatic and that the activation is dominated by the loss of energy due to the reorganization of the first coordination sphere.

The central problem of using force field calculations to compute the minimum coordination sphere reorganization energy for the electron self-exchange process is that of finding the structure where both reactants have the same nuclear configuration and where the sum of the distortion energies for both reactants is at a minimum. Note that this does not necessarily mean that the strain energies of the activated reduced and oxidized forms of the complex are identical. The problem to be solved is to minimize the sum of the strain energy differences between the ground states of the two reactants and a transition state with a common nuclear configuration. This is a task that molecular mechanics programs generally are not able to fulfill. The problem has been circumvented in a study based on a simple and rather crude mechanical approach leading to qualitatively satisfactory results,^{1b} and molecular mechanics based models that use Figure 1 as a basis³ give a slightly distorted view; i.e. the transition state is not necessarily on the intersection of two potential energy curves. The admittedly simplistic approach that we have used is to compute strain energy vs metal ligand distance curves for all possible conformers of each (hexaamine)cobalt(III/II) system and to select as the transition state structure that which is related to the lowest strain energy crossing point involving all conformers of the two reactants. The computed kinetic data presented in Table 4 are based on these assumptions. The data have been fitted to eq 4 with $k_B T/h$

$$k = \frac{k_B T}{h} \exp - \left[A \frac{\Delta U_{\text{strain}}^\ddagger}{RT} + B \right] \quad (4)$$

$= 6.211 \times 10^{12}$, $RT = 2.478$, $A = 1.178$, and $B = 13.339$. The correction factors A and B and the correlation coefficient $r^2 = 0.70$ indicate that the neglect of solvent sheath reorganization, entropy, and electronic effects and deficiencies in the molecular mechanics model and parametrization scheme used are only leading to rough guesses of the electron transfer rates. Future studies will have to show whether more accurate force field

Table 4. Calculated and Observed Self-Exchange Rates of 23 (Hexaamine)cobalt(III/II) Complexes

Co(III/II) complex	k_{11} (calc) (mol ⁻¹ s ⁻¹)	k_{11} (exptl) ^a (mol ⁻¹ s ⁻¹)
[Co(tmen) ₃] ^{3+/2+}	8.5×10^{-8}	8.5×10^{-8}
[Co(NH ₃) ₆] ^{3+/2+}	3.53×10^{-5}	$\approx 1 \times 10^{-6}$
[Co(chxn) ₃] ^{3+/2+}	1.69×10^{-4}	$\approx 1 \times 10^{-5}$
[Co(en) ₃] ^{3+/2+}	2.25×10^{-4}	2.9×10^{-5}
[Co(dien) ₂] ^{3+/2+}	7.04×10^{-5}	1.9×10^{-4}
[Co(medien) ₂] ^{3+/2+}	2.23×10^{-6}	8.0×10^{-4}
[Co(tacn)(dien)] ^{3+/2+}	1.3×10^{-3}	9.2×10^{-4}
[Co(dtne)] ^{3+/2+}	7×10^{-4}	1.3×10^{-3}
[Co(tacn)(medien)] ^{3+/2+}	1.7×10^{-5}	3.4×10^{-3}
[Co(tame) ₂] ^{3+/2+}	3.63×10^{-4}	8.7×10^{-3}
[Co(tacn) ₂] ^{3+/2+}	6.33×10^{-3}	6.6×10^{-2}
[Co(amsartaen)] ^{3+/2+}	1×10^{-3}	8.6×10^{-2}
<i>R,R-fac-lel</i> ₃ -[Co(diampnsar)] ^{3+/2+}	3.4×10^{-4}	0.031
<i>R,R-mer-lel</i> ₃ -[Co(diampnsar)] ^{3+/2+}	5.98×10^{-4}	0.033
[Co(diampnsar)] ^{3+/2+}	0.77	0.5
<i>R,R-fac-ob</i> ₃ -[Co(diampnsar)] ^{3+/2+}	0.04	0.97
<i>R,R-mer-ob</i> ₃ -[Co(diampnsar)] ^{3+/2+}	0.04	1.00
[Co(diamchar)] ^{3+/2+}	0.16	1.0
[Co(sar)] ^{3+/2+}	0.77	2.1
[Co(sep)] ^{3+/2+}	0.038	5.1
[Co(chep)] ^{3+/2+}	3.36×10^{-3}	23
[Co(<i>trans</i> -diammac)] ^{3+/2+}	17	680 ^b

^a Hendry, P.; Ludi, A. *Adv. Inorg. Chem.* **1990**, *35*, 117. ^b Reference 3d.

parametrization schemes, including Morse potentials for all metal–donor bonds, and less severe approximations will lead to substantially more accurate predictions.

Conclusions

The computation of redox potentials of cobalt(III/II) hexaamines based on steric effects alone leads in general to satisfactory results. That of electron self-exchange rates will need some further modifications of the model. One reason for this observation is that, for the kinetic parameters, the shape of the potential energy surface *and* the position of the energy minima are critical parameters; i.e. the force field has to be fitted to both structural and thermodynamic data. Also, the shape of the metal–donor distance vs strain energy curves might be rather critical, and the approach neglecting solvation, entropy, and electronic effects is an oversimplification. The main problem, however, is that of localizing the common transition state structure with a minimum reorganization energy.

The prediction of redox potentials of cobalt(III/II) hexaamine couples based on the correlation of strain energies with observed potentials of a large series of (hexaamine)cobalt(III/II) couples is a simple and efficient tool for the design of oxidants and reductants and, in combination with other methods such as MM–AOM, for the determination of structures of cobalt(III/II) couples in solution.^{1b,c,12} From eqs 5 and 7 (see below) it also follows that computed redox potentials may be used to estimate stability constants of the oxidized and/or reduced forms of metal complexes. In order to analyze the limits and deficiencies of the MM–redox method, and to evaluate possible future developments, it is worthwhile to review other approaches that have been used to compute redox potentials of coordination

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compounds and to identify the common basis of these methods. The modified Nernst equation (eq 5) for a system in equilibrium

$$E_{\text{complex}}^{\circ} = E_{\text{aqua ion}}^{\circ} - \frac{RT}{nF} \ln \frac{\beta^{\text{ox}}}{\beta^{\text{red}}} \quad (5)$$

relates the redox potentials to the stabilities (β) of the oxidized and reduced complex ions. This also emerges from eq 6

$$\Delta G^{\circ} = I + \Delta(\Delta G_{\text{c}}^{\circ}) + \Delta(\Delta G_{\text{aq}}^{\circ}) \quad (6)$$

($\Delta G^{\circ} = -nFE^{\circ}$), which describes the free energy of the redox process as a sum of terms according to a Born–Haber cycle (I is the ionization potential of the gaseous metal ion, $\Delta(\Delta G_{\text{c}}^{\circ})$ is the difference of the complexation free energies of the reduced and oxidized forms in the gas phase, $\Delta(\Delta G_{\text{aq}}^{\circ})$ is the difference of the aquation free energies of the two gaseous complexes, and the constant c depends on the reference electrode and the solvent). Assuming constant ionization potentials and solvation effects within a given system (metal ion, solvent, type of ligand), this reduces to eq 7, where c' is a function of the metal ion

$$E^{\circ} = -\frac{1}{nF}(\Delta(\Delta G_{\text{c}}^{\circ})) + c' \quad (7)$$

(ionization potential), electrode, and solvent. Various effects contributing to $\Delta(\Delta G_{\text{c}}^{\circ})$ have been identified: electronic effects, e.g. the d-orbital splitting (Dq), and steric strain. The recently developed method based on general electrochemical parameters (eq 8)^{4b,22} and correlations of redox potentials with ligand field

$$E^{\circ} = S_{\text{M}} \sum E_{\text{L}} + I_{\text{M}} \quad (8)$$

transitions^{2c,4a,17} do not specifically account for steric contributions, and the MM–redox approach neglects electronic effects. For redox couples with large geometric differences between the oxidized and the reduced form the steric contribution dominates. This is the case for cobalt(III/II) couples, where the difference of Co–N distances between the reduced and oxidized forms is of the order of 0.2 Å. This is probably the main reason for the success of the MM–redox method for cobalt(III/II) couples and for the failure of the approach based on electrochemical parameters. The correlation between ligand field parameters and redox potentials for cobalt(III/II) hexaamines leads to reasonable results since the ligand field strength is strongly dependent on the coordination geometry, in particular on the M–L distance. For systems with only marginal structural changes during electron transfer, such as for Ru(III/II) couples, the electronic effects dominate and the MM–redox method is expected to fail.

Thus, a more generally applicable approach will have to include both steric and electronic contributions to $\Delta(\Delta G_{\text{c}}^{\circ})$ and also a more realistic approach to account for solvation and entropy effects. Such a model, which now is being developed, should lead to a generally applicable and more accurate prediction of redox potentials of coordination compounds, and it will combine the advantages of the method based on electrochemical parameters (easily extendable to various metal ions) with those of the strain energy based approach (general parameters for donor types).

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Appendix: Ligand Abbreviations

18N6	1,4,7,10,13,16-hexaazacyclooctadecane
ammesar	1-amino-8-methyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
amsartacn	9-amino-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2 ^{4,14}]-docosane
azasen	1,1,1-tris((2-aminoethyl)aminomethyl)amine
bmbs	bis(aminomethyl)dimethylsilane
captame	9,17-dimethyl-13-nitro-1,3,5,7,11,15-hexaazatetracyclo[11.5.1.1.3 ^{9,15,1}]henicosane
<i>R,R</i> -chep	Δ -(<i>R,R</i>) ₃ -1,3,10,12,14,21,24,31-hexaazapentacyclo[10.10.10.0.4 ^{9,15,20} ,0 ^{25,30}]dotriacontane
<i>R,R</i> -chxn	trans-1(<i>R</i>),2(<i>R</i>)-diaminocyclohexane
<i>R,R</i> -diamchar	Δ -(<i>R,R</i>) ₃ -1,12-diamino-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.0.4 ^{9,15,20} ,0 ^{25,30}]dotriacontane
diammac	6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine
<i>R,R</i> -diampnsar	1,8-diamino-(4 <i>R</i> ,11 <i>R</i> ,17 <i>R</i>)-trimethyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
diamsar	1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dien	<i>N,N'</i> -bis(2-aminoethyl)amine (diethylenetriamine)
dihosar	1,8-dihydroxo-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dimamsar	1,8-bis(dimethylamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dimetrcs	1,5,5,9,13,13,20,20-octamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]triacontane
dimesar	1,8-dimethyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dinosar	1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dmsa	dimethyl(dimethylamino)silane
dmtn	1,3-diamino-2,2-dimethylpropane (dimethyltrimethylenediamine)
dpt	<i>N,N'</i> -bis(3-aminopropyl)amine (dipropylenetriamine)
dtne	1,2-bis(1,4,7-triaza-1-cyclononyl)ethane
en	1,2-diaminoethane (ethylenediamine)
homesar	1-hydroxy-8-methyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
mammesar	1-(dimethylamino)-8-methyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
medien	<i>N,N'</i> -bis(2-aminoethyl)methylamine (4-methyldiethylenetriamine)
pn	1,2-diaminopropane (propylenediamine)
sar	3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane (sarcophagine)
sen	1,1,1-Tris((2-aminoethyl)aminomethyl)ethane
sep	1,3,6,8,10,13,16,19-tetraazabicyclo[6.6.6]eicosane (sepulchrates)
septacn	1,4,7,9,11,14,19-heptaazatricyclo[7.7.4.2 ^{4,14}]-docosane
tacn	1,4,7-triazacyclononane
tame	1,1,1-tris(aminomethyl)ethane
tentacn	<i>N,N',N''</i> -tris(1-aminoethyl)-1,4,7-tetraazacyclononane
tmen	2,3,-diamino-2,3-dimethylbutane (tetramethylethylenediamine)
tn	1,3-diaminopropane (trimethylenediamine)
trab	1,2,4-triaminobutane
trap	1,2,3-triaminopropane

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