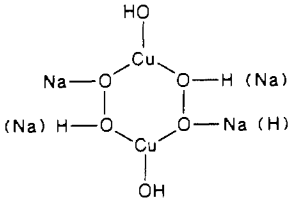
A brown precipitate was observed in several studies[4,9,11] with higher $[Cu^{2+}]_0$ in alkaline H_2O_2. In dilute solution, the negative charge of the HO_2–Cu(I) complex can keep it dissolved. We suggest that the precipitate that occurs at higher concentrations has the "molecular" formula of the ring-structured dimer shown as follows:



Sigel et al.,[6] in a mechanistic study of this reaction in acidic medium, also propose a ring-structured copper peroxide complex as an intermediate in which the copper cation remains in the original oxidation state while two molecules of hydrogen peroxide disproportionate through the ring frame. The d-orbital complex feature of that $(H_2O_2)_2$–Cu(II) complex is consistent with its lack of color. The drastic slowing down of the acidic H_2O_2 decomposition compared with that in basic solution probably results from the extensive steric requirements of all the associated atoms in the complex, with Cu(II) serving as nothing more than a connector for the two reacting H_2O_2 molecules. The transition from the electron-transfer complex to the d orbital is manifested as a sharp color change when the pH of the system is adjusted as described in the Experimental Section.

The most important influence on the alternation of reaction pathway and, consequently, on the dramatic change in reaction rate in going from acidic to alkaline conditions is probably the pH dependence of the redox potential of the couple $HO_2^{\bullet}$ $(O_2^{\bullet -})/H_2O_2$ (HO_2^-).[21] The redox potential drops from 1.4 to 0.18 V over the pH range 0–14. It is obvious that the oxidation of H_2O_2 to $HO_2^{\bullet}$ or $O_2^{\bullet -}$ by metal ions such as Cu^{2+} and Fe^{3+} is highly unfavorable in an acidic medium but possible in an alkaline environment.

Two completely different mechanisms for Fe^{3+}-catalyzed H_2O_2 decomposition have been debated since the 1950s.[7] They are the "free-radical" mechanism proposed by Haber and Weiss[2] and reinvestigated by Barb et al.[3] and the "complex" mechanism developed by Kremer and Stein.[4] Experimental evidence has been obtained both for the existence of $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals and for the formation of a Fe^{3+}–HO_2^- complex. Both mechanisms are successful to some extent, but both have limitations, discussed in detail in a recent review.[7] Unimolecular decomposition of a ferric peroxide complex was one of the key features of the "complex" mechanism. To avoid invoking radicals, the complex is assumed to decompose to another complex, FeO^{3+}, which is less convincingly proved, rather than to a state in which the radical and the reduced metal ion are separated. The latter assumption would lead to a unified mechanism to account for the fact that Fe^{2+} can initiate the catalysis as well as sustain it.[3] We suggest that combination of the two mechanisms, much as has been done in this work, may provide an improved mechanism for Fe^{3+}-catalyzed H_2O_2 decomposition.

However, the much lower redox potential of the Cu^{2+}/Cu^+ couple compared with those of Fe^{3+}/Fe^{2+}, Co^{3+}/Co^{2+}, etc. makes it different from those metal catalysts. The generation of a chemical oscillator with H_2O_2 and KSCN[22] is a consequence of that difference. In fact, this work was initially motivated by the attempt to understand the oscillatory system. With better knowledge of the Cu^{2+} reaction with H_2O_2, progress is being made toward that goal.

Acknowledgment. Prof. Miklôs Orbân is sincerely acknowledged for helpful information and discussions. Y.L. thanks Prof. W. Phil Huskey for help in using some of the computer programs and Eric S. Furfine for assistance in using the O_2-electrode device. This work was supported by the National Science Foundation (Grant No. CHE-8419949).

Registry No. H_2O_2, 7722-84-1; Cu, 7440-50-8; $HO_2Cu(OH)_2^-$, 114720-37-5.

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Contribution from the Department of Inorganic Chemistry,
University of Sydney, Sydney, NSW 2006, Australia

Steric Contributions to the Thermodynamics of Electron Transfer in Cobalt(III) Hexaamine Complexes

Trevor W. Hambley

Received December 1, 1987

Molecular mechanics modeling of the Co(III) and Co(II) oxidation states for a number of complexes with six saturated amine donor atoms shows that differences in the change in strain energy on reduction of Co(III) result from the different abilities of ligands to accommodate the change in bond lengths that occurs concomitant with reduction. This change in strain energy correlates closely with the Co(III)/Co(II) reduction potential. Differences in strain energy changes on reduction contribute up to 96 kJ mol^{-1} (1 V) to the differences in reduction potentials. Thus, steric relaxation contributes significantly to the thermodynamics of electron transfer and needs to be taken into account when reduction potentials of Co(III) complexes are compared. Analysis of the reduction potentials with the steric relaxation contribution removed reveals an empirical correlation with either the degree of substitution at the amine nitrogen or the number of amine hydrogen atoms and suggests that the reduction potential may be dependent on the Lewis basicity of the ligand. A correlation also exists between the strain energy relaxation that occurs on lengthening the Co–N bond and the frequency of the low-energy d–d transition in Co(III) complexes suggesting that this transition is also accompanied by a lengthening of the Co–N bond and that there is a steric contribution to the ligand field strength.

Introduction

The recent report of a Co(III)/Co(II) reduction potential of –0.63 V (vs NHE) for the macrocyclic complex $[Co(diammac)]^{3+}$ (diammac = 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, Chart I), when taken with the value of 0.28 V for $[Co(dpt)_2]^{3+}$ [dpt = bis(3-aminopropyl)amine],[2] means that reported reduction potentials for cobalt(III) hexaamine complexes range over more than 0.9 V. Given that these complexes have identical first coordination spheres (i.e. six amine nitrogen donor atoms), the question arises as to what causes such a wide range

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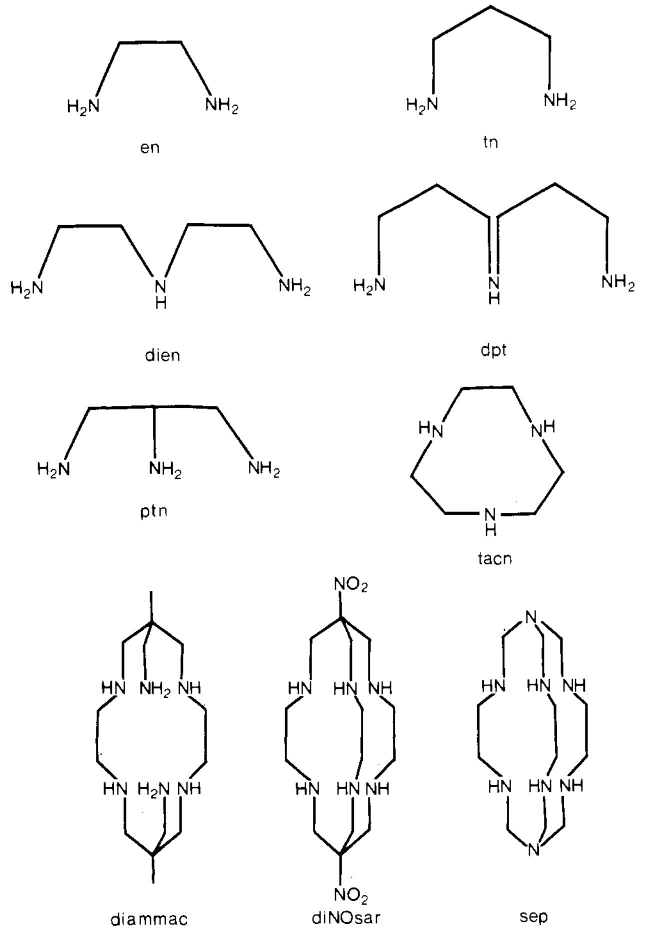
Chart I



en tn

dien dpt

ptn tacn

diammac diNOsar sep

of reduction potentials. There are a number of possible contributing factors that need to be considered:

(i) Electronic Differences. Amine ligands vary in the degree of substitution at the nitrogen atom: from ammonia to primary and secondary amine moieties. Increasing substitution leads to ligands with increasing Lewis base strength that would stabilize the Co(III) oxidation state over the Co(II) state and so decrease the reduction potential. This must only be a minor factor for the two complexes with reduction potentials at the extreme ends of the range since $[Co(diammac)]^{3+}$ and $[Co(dpt)_2]^{3+}$ have similarly substituted donor groups: two $-NH_2R$ and four$-NHR_2$ groups compared with four $-NH_2R$ and two $-NHR_2$ groups, respectively.

(ii) Specific Hydrogen Bonding. (a) The importance of hydrogen-bonding effects in both the thermodynamics and kinetics of electron transfer has been discussed in detail by Lay.[3] In the case of the Co(III)/Co(II) couple, very significant effects result from the different hydrogen-bonding properties of the two oxidation states, which in turn result from the different charge/radius ratios. Specifically, Co(III) forms strong hydrogen bonds with solvent molecules and Co(II) relatively weak hydrogen bonds. Therefore, solvents that hydrogen-bond strongly stabilize the Co(III) oxidation state over the Co(II) state. This has been established most clearly for the complexes $[Co(en)_3]^{3+/2+}$ (en = ethane-1,2-diamine) and $[Co(diNOsar)]^{3+/2+}$, where it has been shown that the Co(III)/Co(II) reduction potential decreases with increasing donor number of the solvent.[4,5] Thus, we would expect that amine complexes with more amine hydrogen atoms would be involved in more hydrogen bonds and so predict that they might be more difficult to reduce. This, too, must only be a minor effect since $[Co(dpt)_2]^{3+}$ has ten such hydrogen atoms and $[Co(diammac)]^{3+}$ eight, yet the former is far more easily reduced. It is interesting to note that the reduction potentials for $[Co(en)_3]^{3+}$ and $[Co(diNOsar)]^{3+}$ show a similar dependence on the solvent donor number[4,5] despite the former having twice the number of amine hydrogen atoms available for hydrogen bonding. This suggests that a decrease in the number of hydrogen bonds may be accompanied by an increase in hydrogen-bonding strength, or an increase in the effect of each hydrogen bond, and that these effects cancel each other.[5]

(b) A second aspect of hydrogen-bonding differences is the solvent reorganization energy contribution to the free energy of reduction. This has been shown to be significant from a study of the solvent dependence of the reduction potentials of the complexes $[Co(sep)]^{3+}$ and $[Co(azacapten)]^{3+}$, which have six and three amine hydrogen atoms respectively.[5]

(iii) Nonspecific Solvation. Lay has also pointed out that nonspecific solvation can be an important factor.[3] However, both couples referred to above involve complexes of similar sizes and reductions from 3+ to 2+ charged species, so this should not be a significant factor in these cases.

(iv) Ion Pairing. The reduction potential can be significantly affected by ion pairing, particularly with the electrolyte.[3] In both cases referred to above the electrolyte was a perchlorate salt, and therefore, ion pairing was not likely to have been a significant contributor to the difference in reduction potentials.

(v) Steric Factors. From the Co(III) state to the Co(II) state there is a change in the Co–N bond length of nearly 0.2 Å.[6,7] This change is more easily accommodated by some ligands than others, and in those cases reduction should be more facile and occur at more positive reduction potentials. This factor has already been put forward to explain the unusually high reduction potential of $[Co(dpt)_2]^{3+}$.[2] In that complex the Co(III)–N bond lengths are unusually long (up to 2.04 Å), and this has been shown to be a consequence of the steric strain induced by forming linked six-membered chelate rings.[8] Reduction to Co(II) should allow a relaxation of this strain and so be promoted by the ligand. Conversely, the bond lengths in $[Co(diammac)]^{3+}$ are unusually short (1.936 (1) Å)[1] and it appears that the ligand promotes compressed coordination geometries. Reduction to Co(II), with concomitant extension of the Co–N bond, would not be favored since it would require considerable deformation of the ligand. This accords with the highly negative reduction potential that has been observed.[1] Thus, it appears that steric factors may be significant in determining reduction potentials.

Geselowitz[9] has pointed out that the rigidity of metal–ligand bonds and of the ligands themselves can affect reduction potentials. Busch[10] et al. have shown that the Co(III)/Co(II) reduction potentials of tetraaza macrocylic complexes are influenced by steric factors and correlated $E_{1/2}$ with the strain energy of the complex in the Co(III) state. However, the reduction potential is a property of both the Co(III) and Co(II) states, and therefore a correlation of this type could not be expected to apply generally.

On the assumption that steric factors are at least a contributing cause to the range in reduction potentials for the two compounds mentioned, we set out to quantify this steric contribution by calculating the change in strain energy on going from Co(III) to Co(II) for these two complexes, along with a number of others. The importance of the steric contribution to reduction potential has been established previously for the isomers of $[Co(dien)_2]^{3+/2+}$ by molecular mechanics modeling of each isomer in both oxidation states and has been shown to be a major reason for the differences in reduction potentials.[11] However, in that case, there is no

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variation in ligand structure, only in the ligand arrangement. Here we have determined the steric contribution for complexes of a range of ligands for which we might expect a number of the factors listed above to cause differences in reduction potentials. Additionally, Bond et al.[12] have shown that substitution on the ligand framework of cage complexes of Co(III) can have dramatic effects on the reduction potential. Therefore, in order to minimize electronic effects from outside the first coordination sphere, we have restricted the present study to complexes of saturated ligands made up of only C, H, and N. The aim of the present study was first to delineate the steric contribution to reduction potentials and then, with this term factored out, to analyze the other contributions to differences in reduction potentials.

A possible empirical correlation between the Co(III)/Co(II) reduction potential and the frequency of the low-energy d–d transition in the Co(III) state has been reported previously.[2,13] We have reinvestigated this correlation using extended and improved data. We have also investigated the relationship between the frequency of this transition and the change in strain energy accompanied by extension of the Co–N bond to determine whether the correlation between the frequency and the reduction potential results from related steric contributions to the thermodynamics of both of these processes.

Experimental Section

The Model. Strain energies were calculated according to the formalism

$$U_{\text{tot}} = \sum E_{\text{b}} + \sum E_{\theta} + \sum E_{\varphi} + \sum E_{\text{nb}}$$

where U_{tot} is the total strain energy, E_{b} represents bond deformation energy, E_{θ} valence angle deformation energy, E_{φ} torsion angle deformation energy, and E_{nb} nonbonded interaction energy. Each of these terms was calculated by using standard functions that have been given previously.[14]

The Force Field. We have previously described force fields for both Co(III) and Co(II) hexaamine complexes.[11,14] The force field employed in the present study was derived from these by inclusion of a new set of nonbonded potential functions. Our previous force field[11,14] was developed from earlier force fields for modeling metal complexes by making changes that followed the philosophy of Allinger's MMII force field for organic compounds.[15] Therefore, in the present force field we have adopted the nonbonded potentials of the MMII model. While our previous potentials have given excellent results, the new potentials do appear to give a small improvement in modeling of geometry and energetics (vide infra).

Energy Minimization. Minimization of the total energy (U_{tot}) was achieved by using a program developed in these laboratories.[16] This program employs the Newton–Raphson minimization technique first described by Boyd[17] and allows external definition of all force field parameters. Starting coordinates for the Co(III) state were taken from crystal structure data. Hydrogen atoms were added, where necessary, by using the program HPUT.[18] Starting coordinates for the Co(II) state were taken from the refined coordinates for the Co(III) state. All refinements were continued until the largest shift in a positional coordinate was less than 0.001 Å.

Results and Discussion

Strain energies and energy-minimized geometries for the Co(III) and Co(II) states of all compounds in Table I were determined. In all cases, excellent agreement between energy-minimized and crystal structure geometries was obtained. Comparisons of the molecular mechanics and crystallographically determined metal–ligand bond lengths are given in Table I. The bond lengths at the extreme ends of the range for Co(III) (i.e. $[Co(diammac)]^{3+}$ and $[Co(dpt)_2]^{3+}$) are well reproduced.

Table I. Comparison of Strain Energy Minimized and Crystallographically Determined Bond Lengths (Å)

	Co(III)		Co(II)	
complex	mol mech	xtal	mol mech	xtal
$[Co(NH_3)_6]^{3+/2+}$	1.972	1.961 (4)^{a}	2.166	2.170 (2)^{k}
$[Co(en)_3]^{3+/2+}$	1.973	1.964 (7)^{b}	2.160	
$[Co(tn)_3]^{3+/2+}$	1.987	1.977 (10)^{c}	2.172	
	1.999	1.989 (5)	2.194	
$[Co(dien)_2]^{3+/2+}$	1.986	1.986 (9)^{d}	2.184	
	1.964	1.940 (6)	2.139	
	1.979	1.976 (13)	2.169	
$[Co(dpt)_2]^{3+/2+}$	2.010	2.021 (8)^{e}	2.211	
	2.044	2.040 (6)	2.228	
	1.981	1.972 (7)	2.176	
$[Co(ptn)_2]^{3+/2+}$	1.968	1.963 (3)^{f}	2.157	
	1.948	1.941 (2)	2.127	
$[Co(tacn)_2]^{3+/2+}$	1.980	1.974 (3)^{g}	2.158	2.155 (16)^{l}
$[Co(diammac)]^{3+/2+}$	1.948	1.937 (2)^{h}	2.075	
	1.956	1.946 (2)	2.126	
$[Co(sep)]^{3+/2+}$	1.988	1.990 (3)^{i}	2.175	2.164 (12)^{m}
$[Co(sar)]^{3+/2+}$	1.978	1.974 (7)^{j}	2.179	

[a] Reference 6. [b] Average of 27 values taken from the Cambridge Crystallographic Data Base. [c] Reference 19. [d] Mer isomer; ref 20. [e] Reference 8. [f] Reference 21. [g] Taken from $[Co((R)\text{-}2\text{-}Metacn)_2]I_3$; ref 22. [h] Reference 1. [i] Reference 23. [j] Reference 24. [k] Reference 7. [l] Reference 25. [m] Reference 26.

Table II. Minimized Strain Energies (kJ mol^{-1}), Strain Relaxation Energies (kJ mol^{-1}), Reduction Potentials (V, vs NHE), and the Frequency of the First d–d Transition (10^{-3} cm^{-1})

complex	U_{tot}-(Co(III))	U_{tot}-(Co(II))	ΔH_{s}	$E_{1/2}$	ν
$[Co(NH_3)_6]^{3+/2+}$	42.3	−16.6	58.9	−0.04^{a}	21.0^{f}
$[Co(en)_3]^{3+/2+}$	83.9	27.2	56.7	−0.18^{a}	21.4^{g}
$[Co(tn)_3]^{3+/2+}$	157.6	74.8	82.8	0.13^{b}	20.6^{f}
$[Co(dien)_2]^{3+/2+}$	112.4	50.5	61.9	−0.20^{c}	21.4^{h}
$[Co(dpt)_2]^{3+/2+}$	224.5	114.0	110.5	0.28^{d}	19.5^{i}
$[Co(ptn)_2]^{3+/2+}$	111.6	69.8	41.8	−0.34^{d}	21.7^{d}
$[Co(tacn)_2]^{3+/2+}$	175.0	112.8	62.2	−0.41^{d}	21.8^{d}
$[Co(diammac)]^{3+/2+}$	152.3	137.5	14.8	−0.63^{e}	22.3^{e}
$[Co(sep)]^{3+/2+}$	199.3	120.2	79.1	−0.27^{a}	21.2^{j}
$[Co(sar)]^{3+/2+}$	202.3	127.6	74.7	−0.42^{a}	21.3^{k}

[a] Reference 12a. [b] Reference 12b. [c] Reference 27. [d] Reference 2. [e] Reference 1. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] Reference 31. [j] Reference 23. [k] Reference 32.

In all cases, the strain energy of the Co(II) state of any given complex is lower than that of the Co(III) state. This is due to the longer Co–N bond lengths in the Co(II) state and the consequent reduction in intraligand, interligand, and inter donor atom interactions. Therefore, we describe the difference between the strain energies of the Co(III) and Co(II) states as the steric "relaxation" contribution to the reduction potential:

$$\Delta H_{\text{s}} = U_{\text{tot}}(\text{Co(III)}) - U_{\text{tot}}(\text{Co(II)})$$

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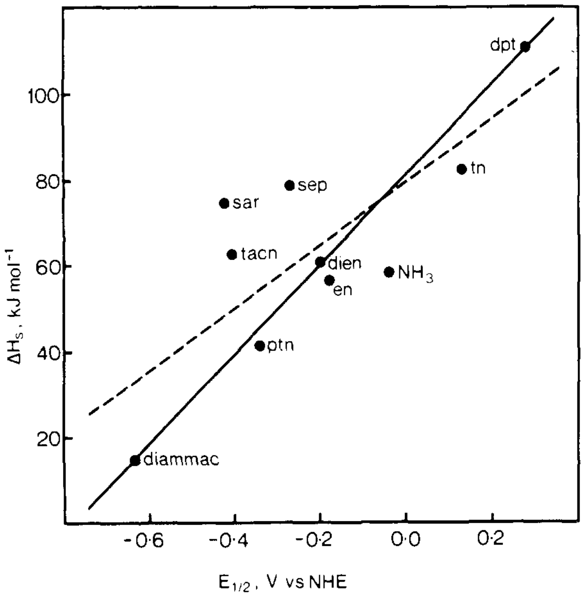

Figure 1. Plot of the steric relaxation energy against the Co(III)/Co(II) reduction potential for the complexes listed in Table I. The dashed line is the line of best fit. The solid line joins the extreme points (see text).

It should be noted that this definition is in the direction of oxidation rather than reduction and, therefore, ΔH_s will correlate positively with reduction potential.

Steric relaxation energies for all compounds considered are given in Table II along with their reduction potentials. Looking first at the relaxation energies for the two extreme cases referred to above, $[Co(dpt)_2]^{3+/2+}$ and $[Co(diammac)]^{3+/2+}$, we see very different results. Both the crystal structure and previous molecular mechanics calculations on $[Co(dpt)_2]^{3+}$ showed that this molecule is highly strained in the Co(III) state,[8] and the extended Co–N bond lengths led to the suggestion that reduction to Co(II) should relieve some of this strain.[2] The present calculations confirm this and produce a very large relaxation energy of 110.5 kJ mol^{-1}. Conversely, very short Co–N bond lengths are observed for $[Co(diammac)]^{3+}$,[1] indicating that the ligand prefers a "compressed" geometry and that reduction to Co(II) would be difficult. Again, the present calculations confirm this, giving a relaxation energy of only 14.8 kJ mol^{-1}. Thus, nearly 100 kJ mol^{-1} more strain energy is released on reduction of $[Co(dpt)_2]^{3+}$ than on reduction of $[Co(diammac)]^{3+}$. Clearly this correlates qualitatively with the far more positive reduction potential of $[Co(dpt)_2]^{3+}$, but does it correlate quantitatively? Energy can be related to $E_{1/2}$ by

$$\Delta G° = -nFE_{1/2}$$

which gives an energy difference of 88 kJ mol^{-1} from the 0.91 V difference in the reduction potentials of $[Co(dpt)_2]^{3+}$ and $[Co(diammac)]^{3+}$. This is close to the 95.7 kJ mol^{-1} difference in relaxation energies for the two complexes, indicating that differential strain relaxation is indeed the major cause of the dramatic difference in their reduction potentials.

It is also interesting to compare the reduction potentials and steric relaxation energies for pairs of complexes where the only change is in the number of atoms in the chelate rings. For the complexes $[Co(en)_3]^{3+/2+}$ and $[Co(tn)_3]^{3+/2+}$ (tn = propane-1,3-diamine), steric relaxation energies of 56.7 and 82.8 kJ mol^{-1} are calculated. Thus, 26.1 kJ mol^{-1} more steric energy is released on relaxation of three six-membered chelate rings than for three five-membered rings. This accords well with the difference in reduction potentials, which corresponds to 30 kJ mol^{-1} (0.31 V). A similar situation is observed for $[Co(dien)_2]^{3+/2+}$ [dien = bis(2-aminoethyl)amine] and $[Co(dpt)_2]^{3+/2+}$, though the difference is magnified because there are four chelate rings and they are linked in two pairs, which increases the strain. The difference in steric relaxation energies is 48.6 kJ mol^{-1} and in reduction potentials is 46 kJ mol^{-1} (0.48 V). Thus, in these two pairs of complexes, for which electronic and hydrogen-bonding differences are expected to be minimal, an excellent agreement between differences in steric relaxation energy and reduction potentials is obtained.

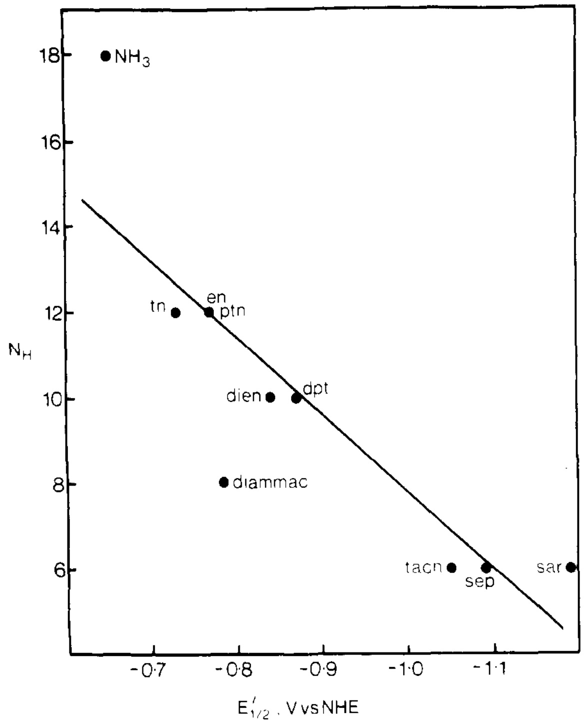

Figure 2. Plot of the number of amine hydrogen atoms in the complex (N_H) against the Co(III)/Co(II) reduction potential corrected for the effects of steric relaxation. The line of best fit is shown.

The steric relaxation energy for all complexes considered is plotted against $E_{1/2}$ (vs NHE) in Figure 1. There is clearly a correlation between $E_{1/2}$ and ΔH_s, particularly for those compounds with unusually high or low reduction potentials, confirming that steric relaxation is indeed an important component of the reduction potential energy. If steric relaxation was the only varying contributor to the reduction potential across the range of compounds considered, then a linear relationship with a slope of F (F = Faraday constant = 96.5 kJ mol^{-1} V^{-1}) would be expected. The least-squares line through the points in Figure 1 gives a slope of 73.2 kJ mol^{-1} V^{-1} (correlation coefficient 0.781), similar to the value expected and reconfirming that steric relaxation is the primary cause of the difference in reduction potentials for these compounds.

It is more informative (vide infra) to consider the line that connects the two extreme points on the plot (Figure 1). When this is done, we see that six of the redox couples lie close to the line, one ($[Co(NH_3)_6]^{3+/2+}$) significantly below and three ($[Co(sep)]^{3+/2+}$, $[Co(sar)]^{3+/2+}$, and $[Co(tacn)_2]^{3+/2+}$) significantly above the line. The question now is, can we understand the deviations from the line in terms of the other factors referred to above contributing to the differences in reduction potentials? The complexes lying closest to the line have 8, 10, or 12 amine hydrogen atoms; the one below has 18 and the three above all have 6. Thus, there appears to be some correlation between the number of amine hydrogen atoms, or alternatively the degree of amine substitution, and the deviations from linearity.

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In order to further investigate the possible correlation between the reduction potential and the number of amine hydrogen atoms, we have calculated the reduction potential corrected for the effects of steric relaxation as

$$E'_{1/2} = E_{1/2} - \Delta H_s/F$$

The number of amine hydrogen atoms is plotted against the corrected reduction potential, $E'_{1/2}$, in Figure 2. The proposed correlation is more clearly seen in this plot. The least-squares line through the points ($R = 0.859$) gives a slope of 18.3, corresponding to an increase of 0.055 V (or a decrease of 5.3 kJ mol^{-1}) with each additional amine hydrogen atom. Thus, stabilization of the Co(III) state increases as the number of amine hydrogen atoms decreases.

Two factors were considered that might explain a dependence on the number of amine hydrogen atoms:

(i) Hydrogen Bonding. There are two aspects to be considered here:

(a) Increasing numbers of amine hydrogen atoms should result in an increase in the number of hydrogen bonds. If this led to electron density being shifted toward the cobalt atom, an increase in stabilization of Co(III) and a negative shift in the reduction potential would result. This is exactly the opposite to what is observed. The complex with the greatest number of amine hydrogen atoms, $[Co(NH_3)_6]^{3+/2+}$, lies on the positive side of the line, and those with the fewest, on the negative side.

(b) The solvent reorganization energy contribution has been shown to be greater for complexes with more amine hydrogen atoms.[5] This would also lead to the shift in $E_{1/2}$ opposite to what is observed since solvent reorganization is greatest for the complex with the most amine hydrogen atoms.

Thus, we must conclude that an increasing number of hydrogen bonds is not the most significant contribution to the relative stabilization of the Co(III) state found for the complexes studied. At first sight this may seem surprising, particularly given the large variation of the reduction potential with solvent donor number that has been reported for $[Co(en)_3]^{3+}$ and $[Co(diNOsar)]^{3+}$.[4,5] However, as noted above, the reduction potentials of these complexes show a similar dependence on solvent donor number despite the former having twice the number of amine hydrogen atoms, suggesting that an increase in the number of hydrogen bonds to the former is counteracted by an increase in the strength of the hydrogen bonds to the latter.[5]

(ii) Electronic Differences. Increasing substitution at the amine nitrogen atoms results in an increase in the Lewis basicity of the ligand. Therefore, the more substituted ligands sep, sar, and tacn should stabilize Co(III) and so lead to a negative shift in the reduction potential. This accords with the observations, since the reduction potentials of these three ligands lie on the negative side of the line and that of the least substituted complex, $[Co(NH_3)_6]^{3+/2+}$, lies on the positive side.

Thus, it appears that the Lewis basicity of the ligand may be a significant contributor to differences in reduction potentials for the complexes considered here. The effects of increased hydrogen bonding and increased Lewis basicity are expected to be opposite, but both are proportional to the number of amine hydrogen atoms. Therefore, since we can only observe the total effect of these and other factors, we cannot assess the absolute importance of these factors.

Steric Contributions to the Frequency of d–d Transitions

A correlation between the frequency of the low-energy d–d transition ($^1A_1 \rightarrow {}^1T_1$) and the Co(III)/Co(II) reduction potential has been investigated previously[2] for many of the complexes considered in the present study. We have replotted these variables with the values for $[Co(diammac)]^{3+}$ and $[Co(tn)_3]^{3+}$ and a more recently determined value for the reduction potential of $[Co(NH_3)_6]^{3+}$ included (Figure 3). An excellent correlation is observed with a correlation coefficient of 0.930. However, the slope of this line, -2.60×10^3 cm^{-1} V^{-1}, is not what would be predicted (-8.04×10^3 cm^{-1} V^{-1}) if there was a 1:1 correspondence of the energy of these two processes. A similar correlation (slope -3.43×10^3 cm^{-1} V^{-1}, correlation coefficient 0.936) has been reported recently for 32 cobalt(III) hexaamine complexes with various triamine ligands.[13]

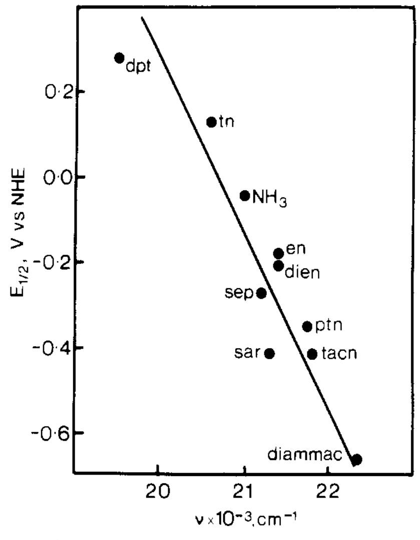

Figure 3. Plot of the Co(III)/Co(II) reduction potential against the frequency of the low-energy d–d electronic transition for the complexes listed in Table I. The line of best fit is shown.

There is no obvious theoretical justification for a correlation between reduction potential and the energy of the electronic transition; the former is a difference property dependent on both the Co(III) and Co(II) states and the latter is a property of the Co(III) state alone. In ligand field terms, the reduction potential corresponds to the energy difference between the electrode and the acceptor (e_g) orbital and is dependent on the spherical component of the ligand field. The energy of the electronic transition depends on the energy difference between the donor (t_{2g}) and the acceptor (e_g) orbitals (i.e. $10Dq$), which is dependent on the directional component of the ligand field. Thus, unless a correlation exists between the spherical and directional components of the ligand field, no general correlation between the reduction potential and the energy of the electronic transition would be expected. Indeed, Lintvedt and Fenton have shown that such correlations are not observed for complexes of Cr(III) or Ru(III).[33] However, a similar correlation (though again not a 1:1 relationship) has been observed previously for Co(III) complexes.[34] The correlation might be understandable if both processes are accompanied by a similar change in the geometry of the complex, such as a lengthening of the Co–N bond. A longer Co–N bond in the excited state resulting from the d–d transition would be expected, since the likely acceptor orbital, e_g, is believed to be largely antibonding. If this were the case, then steric relaxation would also contribute to differences in the energy of the d–d transition. In order to investigate this possibility, the strain relaxation energy is plotted against the frequency of the low-energy d–d transition in Figure 4. A good correlation is observed. The difference between the energies of the d–d transition of the complexes at the extreme ends of the plot is 34.3 kJ mol^{-1} compared to the strain energy relaxation difference of 95.8 kJ mol^{-1}. Since the steric relaxation was calculated by assuming a Co(II)–N bond length, a one-to-one correspondence would only be expected if the d–d transition was accompanied by a lengthening of the Co–N bond length to the value found for Co(II). Rather, the correlation suggests that the strain energy relaxation contribution may be important but has been overestimated by a factor of nearly 3. What this means in terms of the bond length in the excited state cannot be calculated, since the force constant for the Co–N bond in the excited state is unknown. However, if it is intermediate between the values for Co(III) and Co(II), we would expect a

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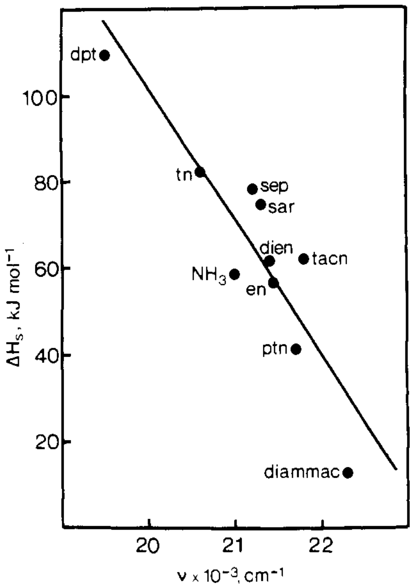

Figure 4. Plot of the steric relaxation energy against the frequency of the low-energy d–d electronic transition for the complexes listed in Table I. The line of best fit is shown.

Co–N bond length of 2.05–2.10 Å in the excited state. It appears from the present calculations that the frequency of spectral transitions is correlated with strain relaxation. This is observable qualitatively; highly strained complexes such as $[Co(dpt)_2]^{3+}$ are red, while less strained complexes or those with compressed Co–N bonds are yellow. The observed correlation between reduction potential and frequency of the d–d transition (Figure 3) is probably due to both processes being influenced by the steric relaxation that occurs on extension of the Co–N bond.

A variation in ligand field strength with hole size for (tetraaza macrocycle)cobalt(III) complexes has been reported by Busch et al.[10] who suggested that the higher ligand field observed for smaller macrocycles resulted from compression of the metal–ligand bonds. This accords with the present analysis, since extension of a compressed Co–N bond would require more energy. Thom et al.[35] put forward the alternative explanation that the ligand field was at its maximum when the ligands best fit the metal, since this gave maximum orbital overlap. We do not rule this out as a plausible explanation for the variation in ligand field strength, since there is an obvious correlation between Co(III)–N bond length and the frequency of the low-energy d–d transition for the complexes considered here (Tables I and II). If this explanation is correct, then the correlation between reduction potential and the frequency of the low-energy d–d transition is a consequence of the coincidental correlation between the Co(III)–N bond length and the steric relaxation energy.

Conclusions

It is clear from the present study that relaxation of strain which occurs on extension of the Co–N bond length concomitant with Co(III)/Co(II) reduction contributes significantly to the thermodynamics of the reduction process. Indeed, for the complexes considered, it is the major cause for the observed differences in reduction potential. Therefore, when differences in redox potentials are analyzed for those cases in which a significant change in the metal–ligand bond length occurs, the effects of steric strain must be taken into account. We have also shown that the molecular mechanics method can be used to calculate and so delineate the steric relaxation contribution to reduction potentials in order that other contributions can be more easily investigated. In so doing, we have demonstrated a possible dependence of the reduction potential on the Lewis basicity of the ligand. This study also shows how steric aspects of ligand design might be used to produce desired redox properties.

A correlation between steric relaxation resulting from extension of the Co–N bonds and the frequency of the low-energy d–d transition has also been established, indicating a possible steric contribution to ligand field strength. This suggests that this electronic transition is also accompanied by a change in the metal–ligand bond length and may explain the correlation that has been observed between reduction potential and the frequency of the d–d transition.

Acknowledgment. We wish to thank Dr P. A. Lay for critical comment and helpful discussion.

Registry No. $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_3]^{2+}$, 15365-75-0; $[Co(en)_3]^{3+}$, 14878-41-2; $[Co(en)_3]^{2+}$, 23523-25-3; $[Co(tn)_3]^{3+}$, 16786-53-1; $[Co(tn)_3]^{2+}$, 46469-74-3; $[Co(dien)_2]^{3+}$, 18703-28-1; $[Co(dien)_2]^{2+}$, 23624-01-3; $[Co(dpt)_2]^{3+}$, 86709-83-3; $[Co(dpt)_2]^{2+}$, 113376-50-4; $[Co(ptn)_2]^{3+}$, 113430-55-0; $[Co(ptn)_2]^{2+}$, 113376-54-8; $[Co(tacn)_2]^{3+}$, 89637-25-2; $[Co(tacn)_2]^{2+}$, 91760-59-7; $[Co(diammac)]^{3+}$, 114595-74-3; $[Co(diammac)]^{2+}$, 114595-75-4; $[Co(sep)]^{3+}$, 72496-77-6; $[Co(sep)]^{2+}$, 63218-22-4; $[Co(sar)]^{3+}$, 85663-77-0; $[Co(sar)]^{2+}$, 71935-80-3.

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Contribution No. 7690 from the Arthur Amos Noyes Laboratory,
California Institute of Technology, Pasadena, California 91125

Electronic Spectra of $Ru_2(carboxylate)_4^+$ Complexes. Higher Energy Electronic Excited States

Vincent M. Miskowski* and Harry B. Gray*

Received December 4, 1987

Solution (CH_3CN, CH_2Cl_2, CH_3OH, poly(methyl methacrylate)) electronic absorption data are reported for $[Ru_2(butyrate)_4X_n]^{(1-n)+}$ ($n = 0, 1, 2$; $X = Cl, Br, I$). Single-crystal visible absorption data are reported for $Ru_2(propionate)_4Cl$, $Ru_2(acetate)_4Cl$, $Ru_2(butyrate)_4Br$, and two crystal forms of $Ru_2(butyrate)_4Cl$. The only visible absorption band that develops vibronic structure at low temperature is an ~570-nm ⊥ *c*-polarized feature of the $I\bar{4}2d$ polymorph of $Ru_2(butyrate)_4Cl$; the long progression in $\Delta\nu \approx 330\ cm^{-1}$ is attributed to the excited-state $\nu(Ru-O)$. The transition is assigned to $\delta^*(Ru_2) \rightarrow \sigma^*(Ru-O)$, intensified in a crystal site of low symmetry. A molecular *x*,*y*-polarized transition at ~570 nm ($\epsilon = 150-200$) in all of the compounds is assigned to $\pi^*(Ru_2) \rightarrow \sigma^*(Ru-O)$. Assignments of $\pi(Ru-O,Ru_2) \rightarrow \sigma^*(Ru-O)$ and $\delta(Ru_2) \rightarrow \pi^*(Ru_2)$ are suggested for an *x*,*y*-polarized system at ~450 nm ($\epsilon = 70-135$) and an extremely weak ($\epsilon \approx 20$) band at ~630 nm, while an intense band at ~460 nm ($\epsilon \approx 1000$) is assigned to $\pi(Ru-O,Ru_2) \rightarrow \pi^*(Ru_2)$. An intense ($\epsilon = 4000-10\,000$) axial halide sensitive band in the near-UV region is assigned to an axial ligand-to-metal charge-transfer transition, most likely $\pi(X) \rightarrow \pi^*(Ru_2)$.

The diruthenium(II,III) carboxylates, $Ru_2(O_2CR)_4^+$, possess a remarkable spin-quartet ground state.[1,2] This ground state was eventually explained by Norman and co-workers[3] according to the pattern of metal–metal bonding and antibonding orbitals that