scription of the disorder was not pursued.

Acknowledgment. A.B. acknowledges the award of a Ted Leggatt scholarship and a North East London Polytechnic Research Studentship. The X-ray diffraction laboratory was established through funds provided by the NSF (Grant CHE-8408407) and The Boeing Co. We thank Johnson Matthey for the loan of the gold compounds.

Supplementary Material Available: Tables of crystal data, hydrogen atom positions, and thermal parameters (4 pages); a table of F_0/F_c data (7 pages). Ordering information is given on any current masthead page.

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Organic Substituent Effects in Macrobicyclic (Hexaamine)cobalt(III/II) Complexes: A New Method of Obtaining Polar Substituent Constants

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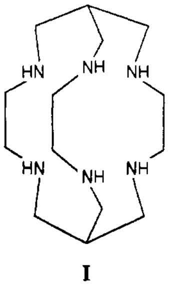
Received April 24, 1990

The redox potentials, $E_{1/2}$, for the reversible cobalt(III/II) redox couples of complexes of substituted macrobicyclic ligands derived from 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane show a substantial variation with the type of substituent. The variation was subjected to a Hammett type treatment yielding a series of inductive or polar substituent constants σ_E that correlate with the organic substituent constants (σ_I) obtained by a variety of other methods. Changes in $E_{1/2}$ with substituent are not reflected in changes in the ligand field spectra of either oxidation states. We deduce, therefore, that the effects are not transmitted via through-space overlap of orbitals or through-bond induction. The effects can be attributed to either a through-space Coulombic mechanism or interactions through the σ framework. In the case of the NHR_2^+ and NR_3^+ substituents, there is a steric substituent effect that forces the Co(III) cage complexes from a *lel*$_3$ to *ob*$_3$ conformation and results in quite different spectroscopic and electrochemical properties. The correlations of σ_E values with the ^1H, ^{13}C, and ^{59}Co NMR chemical shifts are also examined. The σ_E constants are readily obtained, and this may prove to be a more versatile method of obtaining polar substituent constants than those currently used in physical organic chemistry.

Introduction

Macrobicyclic (hexaamine)cobalt(III) complexes of ligands with the parent structures 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (sar, I) and 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane (absar, II) invariably show chemically reversible Co(III)/Co(II) redox couples.[1] An irreversible reduction of the substitutionally inert Co(II) complexes occurs also at appreciably more negative potentials,[1] but there is no sign that the Co(IV) state is accessible. The Co(III)/Co(II) redox couple is affected by ligand cavity size, by ligand conformation, and by the type of substituents on the parent macrobicycles (or "cage" ligands). A physical model for describing these effects has been developed.[2] Generally, the first metal-centered reduction precedes any functional group reduction processes, and hence, substitution-inert cobalt(III) and cobalt(II) complexes with a wide variety of substituents become accessible.



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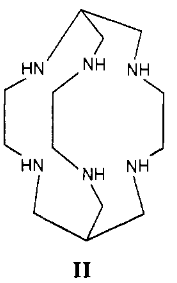

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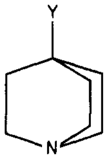
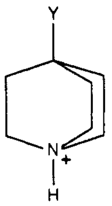


III



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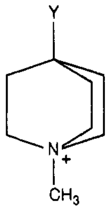

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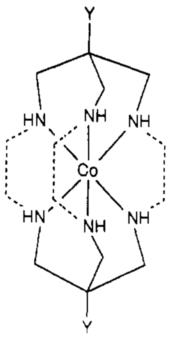

VI

In this paper, the variation of redox potential with substituent is subjected to a Hammett type treatment[3] and correlations with ^1H, ^{13}C, and ^{59}Co NMR spectra are made. Similarities between the apically substituted encapsulated cobalt complexes and quinuclidines (III) and quinuclidium salts (IV, V) are evident, particularly when the disposition of the cobalt ion relative to the substituents on the cage cap (VI) is considered. In general, the large amount of data obtained for the effects of substituents on the physical properties of these related bicyclic organic systems, by Grob and co-workers,[4-6] allows useful comparisons to be made. Previously, correlations between the ligand field parameter (Δ) and $E_{1/2}$ for reduction at the metal center have been reported.[7,8]

[†] Australian National University.
[‡] University of Sydney.

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This aspect is also examined here.

Experimental Section

Details of the electrochemical techniques employed have been described in a preceding paper.[1] All redox potentials are quoted versus the SCE reference electrode in water and the Ag/AgCl/LiCl (saturated, acetone) reference electrode in nonaqueous solvents. Redox potentials were determined at 20 ± 2 °C by DC polarography (±3 mV). Syntheses of the complexes are described elsewhere.[9-17] Absorption spectra were recorded with Cary 14 or Cary 118C spectrometers. ^{1}H NMR spectra were recorded with Jeol 100 MHz Minimar or Varian HA100 spectrometers using TMS or NaTPS standards, while ^{13}C NMR spectra were recorded with a JNM-FX60 Fourier transform spectrometer with 1,4-dioxane as internal standard. ^{59}Co NMR spectra were obtained with a Bruker B-KR spectrometer with $K_3[Co(CN)_6]$ as a standard. Chemical shifts (δ) are expressed in ppm as positive downfield shifts relative to those standards.

Treatment of Data. Variations of $E_{1/2}$ with substituent were subjected to an analysis based on the approach attributed to Hammett.[3] The effect of substituents on a standard chemical equilibrium has been defined in terms of the relationship

$$\log K = \sigma\rho \qquad (1)$$

where σ is the Hammett coefficient. In this analysis, we have defined the standard reaction ($\rho = 1$) as

$$[\mathrm{Co^{III}(XY\text{-}sar)}]^{3+} + [\mathrm{Co^{II}(sar)}]^{2+} \rightleftarrows [\mathrm{Co^{II}(XY\text{-}sar)}]^{2+} + [\mathrm{Co^{III}(sar)}]^{3+} \qquad (2)$$

where X and Y are substituents, usually in the apical sites. Substitution of eq 1 into the thermodynamic relationships

$$\Delta G° = -RT \ln K \qquad (3)$$

$$\Delta G° = -nF\,\Delta E° \qquad (4)$$

and equating these expressions yields

$$\sigma = nF\Delta E°/2.3RT \qquad (5)$$

Specifying the σ parameter in this case as σ_E, and using the relationship that $E° \approx E_{1/2}$ for essentially reversible couples, enables eq 5 to be written as

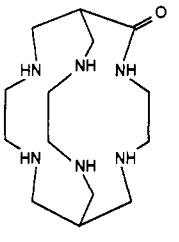
$$\sigma_E = nF\Delta E_{1/2}/2.3RT \qquad (6)$$

where $\Delta E_{1/2}$ is the difference in $E_{1/2}$ values of the substituted and the parent sar cage complexes. Wherever possible, symmetrically substituted cage complexes have been used to obtain σ_E values, whereupon σ_E for one substituent is obtained from half the observed potential shift for the disubstituted complexes. At 20 °C, eq 6 reduces to the form

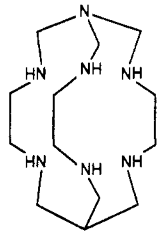
$$\sigma_E = 17.2\Delta E_{1/2} \qquad (7)$$

which has been applied in this work, since $E_{1/2}$ values were determined at 20 ± 2 °C.

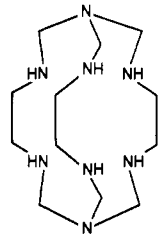
The empiricism applied for calculating substituent effects for apical substituents was extended to account for changes in ligand structure on the rest of the complex, based on $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ as standards. Thus, a substituent component, σ_E(en), was assigned to the ethylene bridge of the 1,2-ethanediamine chelate rings relative to $[Co(NH_3)_6]^{3+/2+}$ as a redox standard, by applying eq 7 in the usual manner. This analysis is complicated by the irreversibility of the $[Co(NH_3)_6]^{3+/2+}$ couple under these conditions. Therefore, the subsequent assignment of σ_E(en) is somewhat arbitrary. However, this does not effect the empiricism provided that $E_{1/2}$ values are measured under the same conditions. By contrast, the reversibility of the $[Co(en)_3]^{3+/2+}$ couple under these conditions enables an accurate thermodynamic analysis of the effect of capping these complexes. Subsequently, a substituent component was assigned to the total capping unit, σ_E(cap), relative to $[Co(en)_3]^{3+}$ as a standard. The advantage of this approach was that it allowed the different caps present in sar (I), and related oxosar (VII), azasar (VIII), sep (IX), and absar (II) cage ligands to be accommodated as complete units.



VII



VIII



IX

Ultimately, any macrobicyclic cage complex can be assigned a composite substituent effect

$$\sum\sigma_E = \sigma_E(X) + \sigma_E(Y) + \sigma_E(\mathrm{cap_1}) + \sigma_E(\mathrm{cap_2}) + 3\sigma_E(\mathrm{en}) \qquad (8)$$

where X and Y are the apical substituents, en is the ethylene bridge unit, and cap$_1$ and cap$_2$ are the two caps of the cage ligand. This composite parameter was used to calculate $E_{1/2}$ for each cage complex, relative to $[Co(NH_3)_6]^{3+}$ ($E_{1/2} = -0.26$ V, $\sum\sigma_E = 0$, in water), $[Co(en)_3]^{3+}$ ($E_{1/2} = -0.37$ V, $\sum\sigma_E = -1.86$, in water), and $[Co(sar)]^{3+}$ ($E_{1/2} = -0.64$ V, $\sum\sigma_E = -6.52$, in water). Thereby, $E_{1/2}$ values of new or uncharacterized cage complexes can be conveniently calculated and applied as a guide in the characterization of these complexes. Related macromonocyclic and multidentate ligand complexes were treated in the same manner, by using group σ_E parameters. Similar calculations were performed for selected compounds in the aprotic solvents, acetonitrile and acetone, since trifluoromethanesulfonate ($CF_3SO_3^-$, triflate) salts of the complexes are usually soluble in a wide range of solvents, including ketones, nitriles, alcohols, and amides.

Nomenclature. The nomenclature is based on defining a trivial name for each macrobicyclic or multidentate parent and then adding the 1,8-substituents as prefixes, while protonation or deprotonation is described by using a suffix (H or -H, respectively).

Results

Substituent Effects on the Co(III)/Co(II) Redox Couple. The sensitivity of the redox potentials of Co(III)/Co(II) couples of macrobicyclic hexaamine complexes to substituents on the cage ligand has been demonstrated previously.[1] $E_{1/2}$ values for these couples vary over ~0.6 V. The effects of substituents reflected in this physical property have been accommodated in a Hammett treatment outlined in the Treatment of Data section, where for each substituent an electrochemical inductive substituent effect, σ_E, relative to $\sigma_E(H) = 0$ was calculated. Shifts in $E_{1/2}$ for substituents ($\Delta E_{1/2}$) and the corresponding parameters σ_E are included in Table I. Data determined in different solvents, such as acetonitrile (Table I), indicated that the substituent effects were dependent on the nature of the solvent. Protonic functional groups, $-N^+HR'R''$, $-NHR$, and $-OH$, displayed the largest solvent-dependent shifts, with the values of σ_E for these groups being smaller in acetonitrile than water. Comparable solvent dependencies have been observed for the organic systems.[18]

In addition to the apical functional group parameters σ_E(Y), it proved possible to assign analogous parameters to residues of the macrobicycle, such as the ethylene bridge of the 1,2-ethane-

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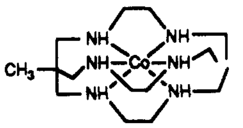
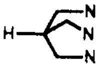
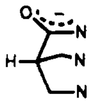
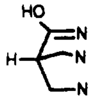
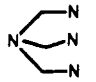
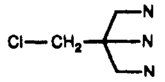
Table I. Constants for the Inductive Substituent Effect

substituent[a]	$\Delta E_{1/2}$(aq)[b]	σ_E(aq)	$\Delta E_{1/2}$(AN)[b,c]	σ_E(AN)	σ_I(Grob)[d]	σ_I(Taft)[e]	σ_I(Charton)[f]
$-N(CH_3)_3^+$	$+0.22_5$	$+3.8_7$			+4.15	+0.92[i]	+0.73
$-NH(CH_3)_2^+$	$+0.22_7$[g]	$+3.8_9$					+0.70
$-NH_2Bz^+$	$+0.22_5$[g]	$+3.8_7$					
$-NH_2OH^+$	$+0.23_0$[g]	$+3.9_1$					
$-NH_3^+$	$+0.22_9$[g]	$+3.9_4$	$+0.17_4$	$+2.9_9$		+0.60[j]	+0.60
$-NO_2$	$+0.22_0$	$+3.7_8$	$+0.23_2$	$+3.9_9$	+3.54	+0.65	+0.76
-CN	$+0.14_5$	$+2.4_9$			+3.04	+0.56	+0.58
-Cl	$+0.13_4$	$+2.3_0$	$+0.13_4$	$+2.3_0$	+2.51	+0.46	+0.47
-COOH	$+0.10_8$[h]	$+1.8_5$					+0.39
$-COOC_2H_5$	$+0.09_3$	$+1.5_9$			+1.70	+0.30	+0.34
-COCl			$+0.12_5$	$+2.1_5$			
-COOAc			$+0.11_1$	$+1.9_1$			
-OH	$+0.09_9$	$+1.6_9$	$+0.07_5$	$+1.2_9$	+1.76	+0.25[j]	+0.25
-NHAc	$+0.08_3$	$+1.4_3$			+1.66	+0.26	+0.28
-NPhth	$+0.07_0$	$+1.2_0$					
-NHOH	$+0.06_6$[i]	$+1.1_4$					
$-N(CH_3)_2$	$+0.05_3$[i]	$+0.9_1$			+1.12	+0.12	
-NHBz	$+0.06_1$[i]	$+1.0_5$					+0.27
$-NH_2$	$+0.05_0$[i]	$+0.8_6$			+1.08	+0.10[j]	
-N=CHPh	$+0.05_5$	$+0.9_5$					
-NHTs	$+0.02_0$	$+0.3_4$					+0.32
$-COO^-$	$+0.03_0$	$+0.5_1$			+0.72	−0.35[j]	−0.17
-H	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$-CH_3$	-0.01_1	-0.1_8	-0.02_8	-0.4_8	+0.11	−0.04	−0.05
							+0.77[k]

[a] Abbreviations in the substituent column are as follows: Bz = $-CH_2C_6H_5$; Et = $-CH_2CH_3$; Ac = $-COCH_3$; NPhth = phthalimide; Ph = $-C_6H_5$; Ts = $-SO_2$-4-$C_6H_4(CH_3)$. [b] Shift in reduction potential of substituent cage complex relative to $[Co(sar)]^{3+}$ unless otherwise stated; shift normally deduced from half the shift of a symmetrically substituted complex; μ = 0.1 M ($NaClO_4$ or $NaCF_3SO_3$). Value in V. [c] AN = acetonitrile, μ = 0.1 M ($Me_4NCF_3SO_3$). [d] Reference 4; obtained from pK_a values of apically substituted quinuclidium salts in water, 25 C, μ = 0.1 M (KCl). [e] Reference 18; obtained from acid- and base-catalyzed hydrolyses of substituted acetates. [f] Reference 20; obtained from pK_a values of substituted acetic acids. [g] 0.1 M $HClO_4$ or CF_3SO_3H. [h] 1 M CF_3SO_3H. [i] pH 7. [j] Reference 19. [k] Obtained from the pK_a of the carboxylic acid derivative $[Co(COOH,CH_3\text{-sar})]^{3+}$.

Table II. Apparent Group Substituent Effects

group	$\Delta E_{1/2}$, V	σ_E(aq)
	-0.03_6[a]	-0.6_2
	-0.13_6[b]	-2.3_3
	-0.31_2[b]	-5.3_8
	-0.05_9[b,c]	-1.0_1
	-0.06_4[b]	-1.1_0
	-0.23_3[b]	-4.0_1

[a] Shift in reduction potential relative to that of $[Co(NH_3)_6]^{3+}$. [b] Shift in reduction potential relative to that of $[Co(en)_3]^{3+}$. [c] 6 M CF_3SO_3H.

diamine chelate rings and the total capping units at each end of the parent $[Co(en)_3]^{3+/2+}$ couple. The apparent σ_E group parameters are collected in Table II. The basis of this concept is to accommodate structures other than apically substituted sar molecules and to allow, via eq 8, calculation of $E_{1/2}$ values based on the σ_E parameters. The transportability of these parameters, determined from a limited number of compounds, is illustrated by the excellent linear relationship between the composite parameter σ_E for any cage and the experimental $E_{1/2}$ value for that compound (Figure 1). Included in this correlation are data for the oxosar, azasar, and absar cage complexes, in addition to the more common sar cage complexes. While this correlation also includes the complexes used to calculate σ_E values, these constitute a minority of points on Figure 1. Experimental $E_{1/2}$ values for the Co(III)/Co(II) couple of the complexes have been tabulated previously,[1] and calculated $E_{1/2}$ values are normally within ±5 mV and seldom differ by more than ±0.02 V (supplementary material, Table S1).

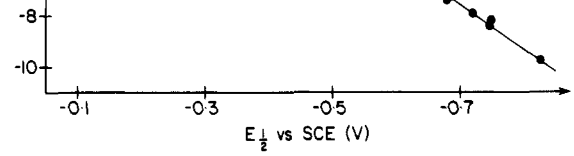


Figure 1. Relationship of the calculated $\sum\sigma_E$ and experimental $E_{1/2}$ values for the macrobicyclic complexes.

Inductive or polar substituent constants have been determined previously by Taft,[19] Charton,[20] and Grob[4] using carefully selected organic molecules. Their constants,[4,19,20] σ_I, are included in Table I for comparative purposes. The relationship of σ_E with the three

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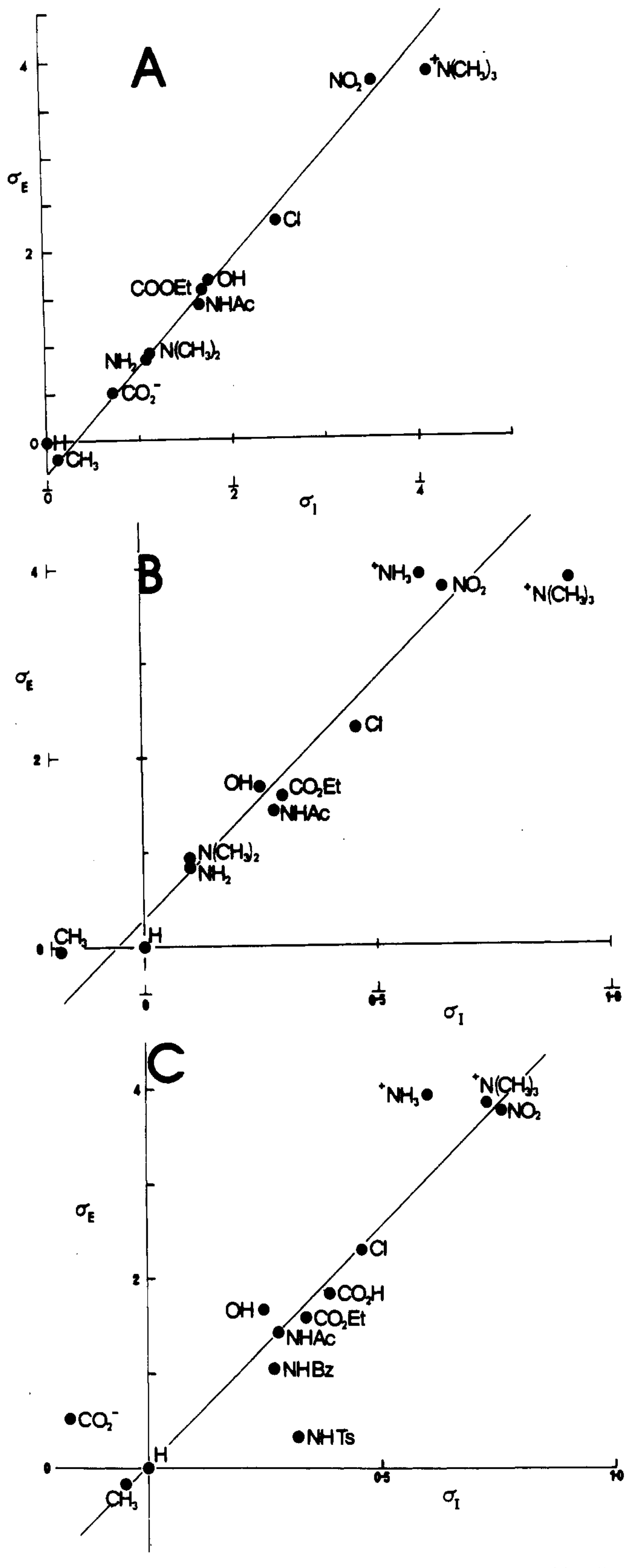

Figure 2. Correlation of σ_E for apical substituents on the macrobicyclic cobalt(III) complexes with σ_I values of (a) Grob, (b) Charton, and (c) Taft.

sets of parameters is illustrated in Figure 2, and a close correlation is apparent. This is particularly true for the comparison with the parameters of Grob, where the quinuclidium salts (IV) employed as probes are the closest analogies to the cage complexes (VI) and the σ_I values were determined in water (μ = 0.1 M) in each case.

Correlation of the Values of Co(III)/Co(II) Redox Potentials with Physical Properties. Visible absorption spectra, ^{13}C and ^{1}H NMR spectra, and limited ^{59}Co NMR spectra for the complexes have been obtained, and these data have been deposited as supplementary material (Table S2). With the exception of the $-N(CH_3)_3^+$ and $-NH(CH_3)_2^+$, dicapped sar cage complexes, the maxima of the d–d absorption bands were remarkably invariant, 472 ± 3 nm (origin $^1A_{1g} \rightarrow {}^1T_{1g}$) and 342 ± 3 nm (origin $^1A_{1g} \rightarrow {}^1T_{2g}$). Furthermore, the small variations observed do not follow any clear relationship with the Co(III)/Co(II) redox potentials. Maxima for $[Co(N(CH_3)_3)_2\text{-sar})]^{5+}$ (445, 329 nm) and the protonated complex, $[Co((NH(CH_3)_2)_2\text{-sar})]^{5+}$ (459, 331 (sh) nm), were markedly different[13] and approximated those observed for cage complexes with an ob_3 conformation.[21] The ^{1}H NMR chemical shifts of the coordinated N–H protons of substituted sar cage complexes, determined in 36% DCl/D$_2$O, show a good linear correlation with $E_{1/2}$ values for these complexes (Figure 3), again with the exception of the $(N(CH_3)_3^+)_2$- and $(NH(CH_3)_2^+)_2$-sar cage complexes. However, correlations of the ^{13}C NMR chemical shifts for the apical (quaternary) carbon and for the adjacent and equivalent methylenes of the capping group with either $E_{1/2}$ or the appropriate substituent parameter σ_E were poor, particularly for the methylene carbons. This effect is best illustrated graphically (Figure 4). However, since ^{13}C chemical shifts are sensitive to steric effects, and other proximity effects,[22] a direct and accurate correlation is not expected. Plots of $\delta(^{13}C)$ for the apical carbons against the electronegativity of the substituents (ι or χ_w)[23–25] showed somewhat better correlations (Figure 5).

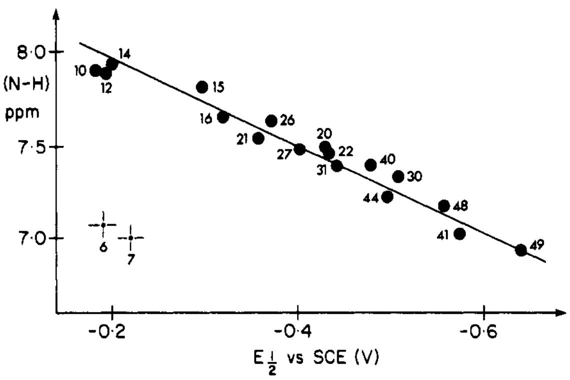

Figure 3. Relationship of δ(N–H) of the macrobicyclic cobalt(III) complexes, determined in 36% DCl, and $E_{1/2}$ for the Co(III)/Co(II) couple of the complexes. Numbers on the figure correspond with reference numbers of the complexes in deposited Table S1 of the supplementary material. Points 6 and 7 refer to the $(CH_3)_3N^+$– and the $(CH_3)_2NH^+$– substituents, respectively.

A more apposite comparison was that obtained between the quinuclidines and quinuclidium salts (III–V) and the cobalt complexes (VI). The ^{13}C NMR chemical shifts of the apical carbon and the adjacent methylene carbons of substituted sar cage complexes, and of the bicyclic organic equivalents, are collected in Table III. When the chemical shifts of the cage complexes were plotted against the chemical shifts for the organic equivalents, linear correlations were observed. Some of these correlations are presented in Figure 6.

The ^{59}Co NMR spectra of selected cage complexes were also determined, and a general linear relationship between $\delta(^{59}Co)$ and $E_{1/2}$(Co(III)/Co(II)) was observed (supplementary material). Although $[Co(NH_2)_2\text{-sar})]^{3+}$ and $[Co(sar)]^{3+}$ were exceptions, both these complexes were measured under conditions different from those for the remaining complexes. The effects of concentration, counterions, and pH are known to be significant in ^{59}Co NMR spectroscopy.[26] A more detailed study is therefore required,

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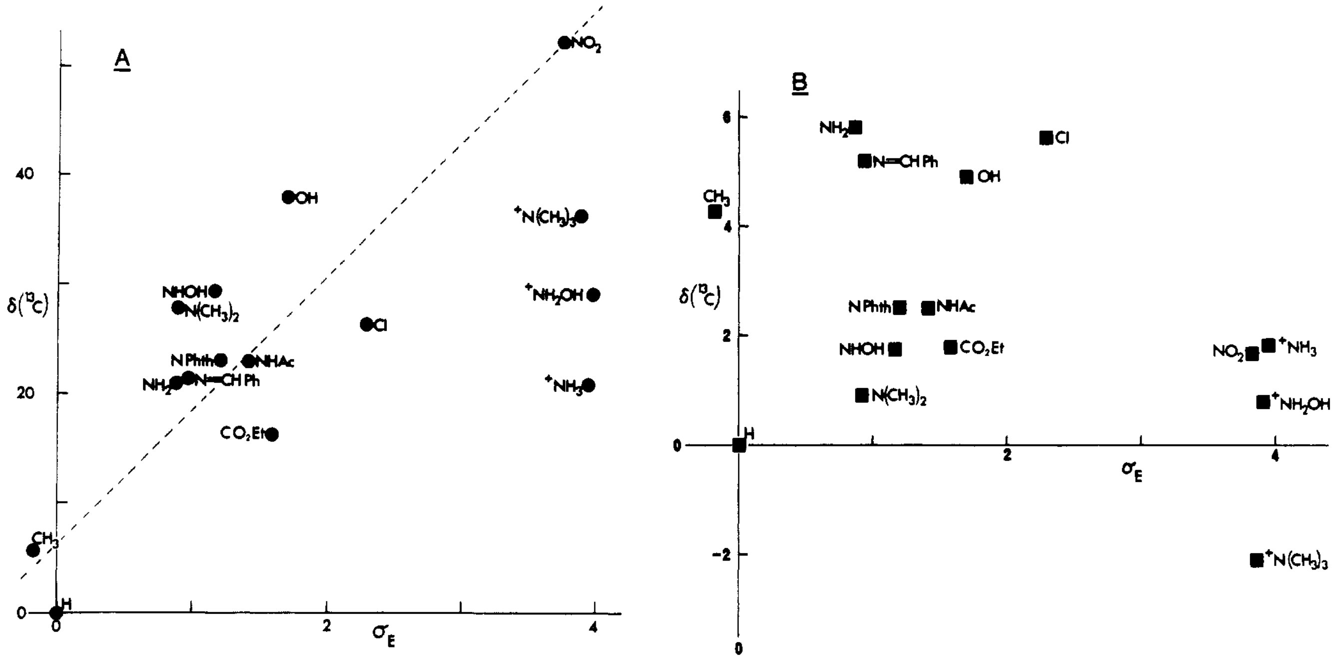

Figure 4. Relationships of $\Delta[\delta(^{13}C)]$ of the symmetrically substituted $Co(X_2\text{-sar})^{n+}$ (except with X_2 = CH_3,H and CO_2Et,CH_3) complexes with σ_E: (A) apical carbon; (B) cap methylene carbons.

Table III. ^{13}C NMR Shifts of Apically Substituted $[Co^{III}(sar)]^{n+}$ Complexes and Comparative Shifts of Quinuclidines and Quinuclidium Salts

	$[Co(X_2\text{-sar})]^{3+}$ [a,b]		III[a,c,d]		IV[a,c,e]		V[a,c,e]	
substituent (X)	1	2	1	2	1	2	1	2
$N(CH_3)_3^+$	+36.4	-2.1	+50.9	-2.3	+48.4	-0.5	+48.0	-0.3
$NH(CH_3)_2^+$	+29.5	-1.2			+40.0	+0.4		
NH_2Bz^+	+25.5	+0.5						
NH_2OH^+	+29.1	+0.8						
NH_3^+	+20.9	+1.8			+28.6	+3.8		
NO_2	+52.5[f]	+1.7[f]			+60.4	+4.4		
Cl	+26.3[f]	+5.6[f]	+43.0	+9.8	+39.0	+9.7	+38.7	+9.5
CO_2H					+16.0	+7.4		
OH	+37.7	+4.9	+45.8	+7.8	+45.5	+7.3	+45.3	+7.1
CO_2Et	+16.2[g]	+1.8[g]	+15.3	+1.7	+16.2	+2.3	+16.3	+2.4
NHTs	?	+5.3						
NPhth	+23.0	+2.5						
$NHCOCH_3$	+22.9[e]	+2.5[e]			+27.8	+4.1		
NHOH	+29.4[e]	+1.8[e]						
N=CHPh	+21.3[e]	+5.2[e]						
NH_2	+20.9[e]	+5.8[e]						
$N(CH_3)_2$	+27.9[e]	+0.9[e]	+31.4	0			+32.7	+0.9
H	0	0	0	0	0	0	0	0
CH_3	+5.9[g]	+4.3[g]			+5.4	+6.6		
aza		+17.8[h]						+25.0[i]

[a] Carbon 1 refers to apical carbon adjacent to substituent, and carbon 2 refers to methylene carbons adjacent to carbon 1; shifts in ppm downfield from compounds with a hydrogen substituent. [b] 0.1 M DCl, unless otherwise stated. [c] Compounds III–V; data from ref 6. [d] $CDCl_3$. [e] D_2O. [f] Reference 14. [g] Extrapolated from complexes with mixed substituents. [h] $[Co(sep)]^{3+}$. [i] Compound X.

especially in the light of the small range of chemical shifts 7900 ± 40 ppm observed for those presently studied. Such a small range of chemical shifts was not unexpected, since recent results indicate that $\delta(^{59}Co)$ is governed by the internal ligand strength (Δ/B) considerations[27,28] and these are practically invariant, as mentioned earlier.

Discussion

Nature of Polar or Inductive Substituent Effects. There are a number of possible mechanisms for the transmission of substituent effects through saturated frameworks to a probe. The through-bond interaction described by Hoffmann for bicyclo[2.2.2]octane systems[29] is a repulsive interaction between the apical combination of orbitals with σ and σ^* orbitals of the same symmetry. This is distinct from through-bond induction used by many physical organic chemists, which is an induced change in the polarity of a σ bond through an effect transmitted through a σ-bonding network.[25,30–34] Here, these distinct mechanisms will be called σ-frame orbital repulsion and σ induction, respectively. Similar confusion is evident with through-space interactions. While Hoffmann[29] takes this to mean direct orbital overlap through space, many physical organic chemists[25,30–34] use the same term for Coulombic interactions between a probe (for which a physical property is measured) and the dipole induced in a C–X bond by a substituent X. Again, to avoid confusion, the orbital

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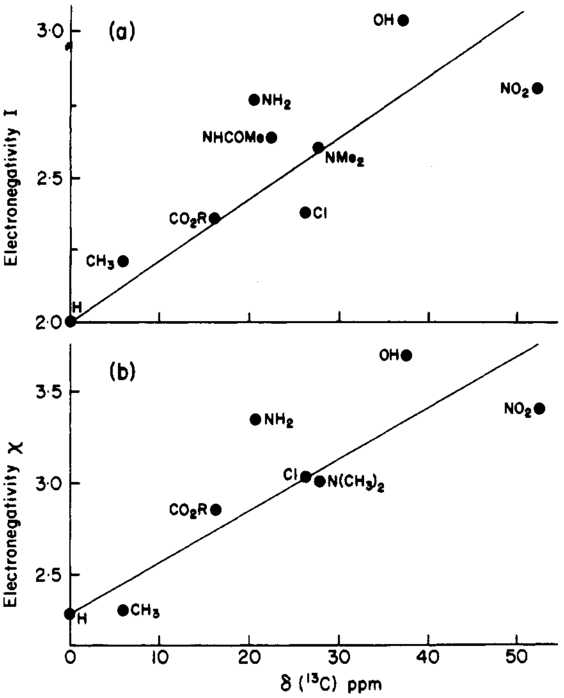

Figure 5. Relationships of $\Delta[\delta(^{13}C)]$ of the apical carbons of the symmetrically substituted $[Co(X_2\text{-sar})]^{n+}$ complexes (except for $X_2 = CH_3,H$ and CO_2Et,CH_3) with measures of substituent electronegativities: (a) $\Delta[\delta(^{13}C)]$ vs ι; (b) $\Delta[\delta(^{13}C)]$ vs χ_w.

interaction will be called a through-space orbital overlap and the Coulombic interaction, a through-space electric field interaction.

Previously, the polar effects of substituents have been determined by measuring the influence of various substituents on a physical property of a probe incorporated in the organic molecule. Taft has applied the effect on the ^{19}F chemical shift in fluorobenzenes and the acid- and base-catalyzed hydrolysis rates of substituted acetates as probes.[18,19] Charton has determined the variation in pK_a of a carboxylic acid group in substituted acetic acids with substituent,[20] while Grob has applied the variation in the pK_a of the ammonium group in quinuclidium perchlorates with substitution at the opposite apex.[4] These separate approaches have led to the assertion that polar substituent effects are chiefly Coulombic in nature. Correlations between the various sets of substituent parameters obtained from different probes are good, which implies a similar mechanism of transmission of these effects applies in each instance. A summary of the previous work in this area may be found in recent reviews.[25,30-34]

In addition to polar effects, resonance and steric effects can contribute to physical properties.[31-35] As discussed previously,[2] the relative positions of the substituent (Y) and probe (Co^{3+}) in the complexes used in the present study are such that steric effects are minimal with the exception of the $-NHR_2^+$ and $-NR_3^+$ substituents[36] (structure VI), since the substituent is located at an apex remote from the encapsulated metal ion and usually with only methylene groups adjacent. Further, the ion and substituents are connected only by saturated alkylamine groups, which do not transmit resonance effects. The only reasonable through-space orbital interaction that could occur would be that between an antibonding orbital on the carbon and nonbonding orbitals of the cobalt, and there is no evidence in the visible spectroscopy for such an interaction. The good correlations between σ_I values obtained in organic chemistry (Figure 2) with the σ_E values offers strong support for a similar mechanism of transmission of these polar substituent effects in both organic and inorganic systems.

Traditionally, polar substituent effects have been considered to be a combination of induction via σ bonds (I_σ), through-space field effects (F), π induction (π_σ), and π-field effects (π_F).[25,30-35] The latter two effects do not contribute in the present study, since no π systems connect the probe and substituents. Field effects are transmitted through space electrostatically, with the magnitude proportional to $\mu(\cos\theta)/r^2D_E$, where μ is the dipole moment in the C–X bond, D_E is the effective dielectric of the medium, and θ and r define the spatial disposition of the probe and substituent.[25,30-34] If induction through a single bond is represented by χ, then the total induction for the systems under study (VI) is $3\chi^3$ (assuming equal induction along the various single bonds).[25,30-34] Although direct calculations of the expected effects by either mechanism are difficult,[25] there is mounting evidence that the dominant contributions to polar or inductive effects are through-space field (i.e. Coulombic) contributions.[25,30-35,37] For transition-metal complexes, σ induction should be reflected in both the ligand field parameters (of both oxidation states) and the electrochemical potential of the Co(III)/Co(II) couple, since it implies a change in electron density on the coordinated amine groups.[2] Conversely, field effects should be mainly reflected in electrochemical potentials, with minor contributions to ligand field

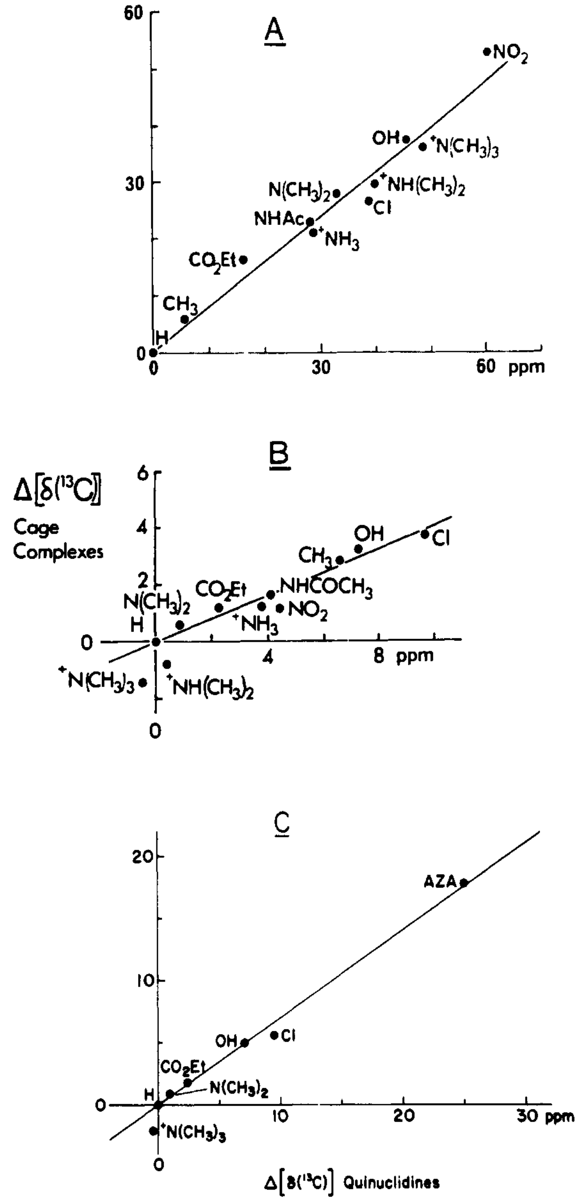

Figure 6. Plots of $\Delta[\delta(^{13}C)]$, the difference in chemical shifts of substituted species relative to the proton-capped analogue, for macrobicyclic complexes and quinuclidium salts: (A) apical carbons; (B) cap methylene carbons; (C) cap methylenes of quinuclidines vs cage complexes.

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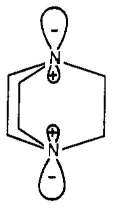
parameters. Since the latter situation pertains for a wide range of substituents, with the exceptions $-NH(CH_3)_2^+$ and $-N(CH_3)_3^+$, an electrostatic mechanism of the polar effects is consistent with these observations. However, the expectations from a mechanism involving repulsive interactions between the ligand field states and charge-transfer states of the same symmetry are the same as those predicted by the electrostatic field mechanism.[2] Calculations on organic molecules using the σ-frame orbital repulsion mechanism[29] imply that this is the major form of interaction. Since the new mechanism proposed[2] is conceptually similar (but theoretically more correct especially with systems involving transition-metal ions), this is favored as the predominant mechanism, although Coulombic effects are also likely to contribute to these substituent effects. Furthermore, the excellent correlations between constants obtained here and those obtained from using purely organic probes[25,30-34] would imply this to be a general result.

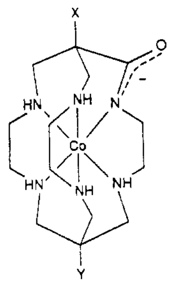
It was thought that the p_z orbital of the nitrogen of the aza cap could directly overlap with the nonbonding orbitals of the Co(III) center, since the cap is considerably flattened and approaches an sp^2 nitrogen configuration, but there is no evidence of such an interaction in the ligand field spectra of the aza-capped cage complexes.[9,10] Calculations of similar interactions have been performed for the 1,4-diazabicyclo[2.2.2]octane molecule (X).[29,38,39] If such an effect dominated the interaction between the aza group and the cobalt probe in these cage complexes, then the magnetic anisotropy of its cobalt center would be different from those of the other cage complexes. Clearly, this is not the case since the aza-capped species behave "normally" in various correlations (Figures 3 and 4, Table III, and Table S2 (supplementary material)) involving NMR spectroscopy.



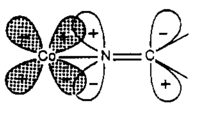
X

The observation that the aza group has a polar substituent effect similar to that of the amino group, despite the latter's increased distance from the cobalt center, probably arises from a cancellation of competing factors. All factors being equal, the aza group would be expected to have a much stronger polar substituent effect than that of the amino group because of its closer proximity to the cobalt center. However, the former is clearly intermediate between an sp^3 and an sp^2 nitrogen center,[9,10] unlike the sp^3 nitrogen center of the amino group, and different substituent effects are expected.

While most of the cage complexes investigated were of the fully saturated sar type (I), several compounds with the $[Co(oxosar-H)]^{2+}$ skeleton (XI) were studied. In these complexes, the possibility of resonance substituent effects, as well as polar effects, arise. Such resonance effects could arise in several ways: e.g. electron density could be transferred from a filled t_{2g} orbital to a π^* orbital of the imine resonance hybrid (XII) or an energetically less favorable transfer from the filled π_p system of the ligand to an unoccupied 4d orbital of appropriate symmetry on the metal ion (XIII). Therefore, the various resonance and inductive substituent effects cannot be separated in these particular complexes. That further contributions exist is implied by the electrochemistry, since protonation of the amide group causes a marked positive shift in the Co(III)/Co(II) redox couple potential, whereas a much smaller change is involved for protonation/deprotonation of a noncoordinated amine substituent.[1] Protonation affects both the resonance and inductive properties of the substituent, and therefore, it is not possible to delineate the various contributions. Nevertheless, the apparent group substituent effects assigned in Table II, while not distinguishing these effects, are sufficient to allow calculation of $E_{1/2}$ values by combination of the appropriate component values.



XI



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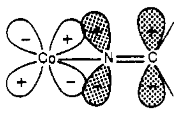

XIII

The excellent agreement between experimental and calculated $E_{1/2}$ values introduces a predictive capacity into the electrochemistry of sar cage complexes, which has been applied on several occasions for identification of newly synthesized complexes. For instance, the structure of one of the nitrosation products of $[Co(NH_2)_2\text{-sar})]^{3+}$, which was previously uncertain, was correctly deduced as being the 1-chloromethyl-8-amino-substituted absar complex $[Co(ClCH_2,NH_3\text{-absar})]^{4+}$ by such a method.[13,14]

Correlations of Co(III)/Co(II) Redox Potentials with Physical Properties. The redox potential measures the differences in energy between two states (Co(III) and Co(II)) as a function of the substituent. Since the substituents effect the ground-state energies of both oxidation states by the same mechanism, the difference in ground-state energies (i.e. the redox potential) as a function of substituent will also depend on the same mechanism. Therefore, the electrochemical substituent constants should also correlate with other physical properties of the individual oxidation states, provided these physical properties are affected by the substituents via the same mechanism.

As mentioned previously, the lack of a correlation between the ligand field parameter, Δ, and σ_E is consistent with either the electrostatic field and/or interacting states mechanisms of the substituent effects.[2] Although it was long thought that such correlations should exist,[7,8,40] it was recently pointed out that this need not be the case,[41] and this has been reaffirmed here.[2] However, the complexes containing the $-N(CH_3)_3^+$ and $-NH(CH_3)_2^+$ substituents are clearly anomalous. It has now been shown that the reason for the markedly different properties of the complexes with $-N(CH_3)_3^+$ and $-NH(CH_3)_2^+$ substituents is that these substituents induce a conformational change from a *lel*$_3$ isomer to an *ob*$_3$ isomer, which has markedly different spectroscopic properties.[36]

The change in electronic distribution brought about by conformational changes for the $-N(CH_3)_3^+$- and $-NH(CH_3)_2^+$-substituted complexes will result in ^{59}Co magnetic anisotropy effects different from those observed in the other cobalt complexes. This is manifest in the chemical shifts of the coordinated N–H protons, which show a good linear correlation with $E_{1/2}$ except for complexes with alkylammonium substituents in the apical positions (Figure 3). It was expected that the variation in electron density between the apical carbons and the cobalt center would also alter the magnetic anisotropy of ^{13}C nuclei in this region. Although a reasonable correlation between $\delta(^{13}C)$ for apical carbons and σ_E was observed, with the exception of alkylammonium-substituted complexes, no such correlations was found for $\delta(^{13}C)$ of the cap methylene groups (Figure 4). Since ^{13}C chemical shifts are sensitive to steric, magnetic anisotropy, and other proximity substituent effects,[22] the absence of any firm correlations is expected. There is substantial evidence to show that for atoms directly bound to a substituent, NMR chemical shifts are more closely related to σ induction than to polar field effects.[25] However, the correlations are only slightly better when ^{13}C NMR chemical shifts for the apical carbons are plotted against

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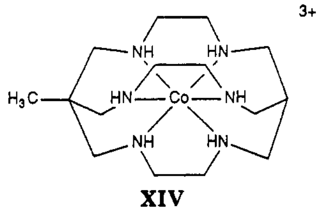
parameters used to represent σ induction.[23-25] It is likely that both factors contribute in this instance. However, a more pertinent analysis, in view of the geometrical relationship, is the comparison between the ^{13}C NMR spectra of 4-substituted quinuclidines and quinuclidium salts[6] with the cage complexes, where inductive substituent effects for each system are observed to correlate closely (Figure 2). When the chemical shifts of the apical carbons and cap methylene carbons are plotted against their counterparts in the quinuclidium salts (II), good linear correlations are also observed (Figure 6). Deviations involved principally the alkylammonium salts, and this is consistent with the earlier anomalies noted for these substituents in the complexes. It is clear that effects which determine substituent–probe relationships operate in a like manner on the ^{13}C NMR spectra of both the quinuclidines and the cage complexes.

The ^{13}C chemical shifts of the methylenes of the 1,2-diaminoethane residues in the complexes are not particularly sensitive to substituent effects, which is consistent with their remoteness from the apical site. In the cases of the $-N(CH_3)_3^+$ and $-NH(CH_3)_2^+$ substituents, significantly different ^{13}C NMR shifts for these methylene groups are attributed to changes in ligand conformations.[36]

These substituents, as a result of steric interactions, transform the *lel*$_3$ conformer to the *ob*$_3$ conformer,[36] which has a smaller cavity size. As a result it is more difficult to reduce Co(III) to Co(II).[21] Thus, the redox potential is not only related to a polar substituent effect, in these instances. This in turn explains the difficulty in assigning an appropriate polar substituent constant, since the steric effects will depend on the geometries of the probe molecules or ions used in the different methods of determination.

In a previous paper,[1] it was shown that the pK_a values of functional groups of the charged metal ion cage complexes were reduced in comparison to their aliphatic analogues. For example, the pK_a values of 1.6 for the carboxylic acid derivative $[Co(COOH,CH_3\text{-sar})]^{3+}$ and 2.4 and 3.3 for the ammonium derivatives of $[Co(NH_3)_2\text{-sar})]^{5+}$ [14] are considerably less than those of 4.8 (CH_3CO_2H)[42] and 10.7 ($(CH_3NH_3)^+$)[42] observed for regular organic molecules. Since the apical substituent groups affect the redox properties of the cobalt center by polar substituent effects, it follows that the cobalt center must influence the pK_a values of the substituents in a like manner. Therefore, a polar substituent effect for the cobalt cage complex substituent may be obtained by using a procedure analogous to that of Charton, i.e. the pK_a of the carboxylic acid complex $[Co(COOH,CH_3\text{-sar})]^{3+}$. The σ_I value for this moiety (XIV) of +0.77 corresponds to that observed for the very strong polar substituents, $-NMe_3^+$, $-NH_3^+$, or NO_2. The larger decrease in pK_a values induced by the cage complex for ammonium salts in comparison to carboxylic acids may arise from both a charge repulsion and a proximal effect arising from the site of deprotonation of the former species. When the amine group is placed one bond closer to the cobalt center, as in the aza-capped species, then the polar constant of the amine group would be anticipated to be ≥3-fold of that observed normally.[31] The pK_a values of the ammonium salts of $[Co(NH_3)_2\text{-sar})]^{5+}$ are reduced by ~7 in comparison to $CH_3NH_3^+$, therefore, the pK_a values of ammonium ions of $[Co(sepH_2)]^{5+}$ are estimated to be ≤–10, which is consistent with the observation that the $[Co(sep)]^{3+}$ complex is not protonated, even under strongly acidic conditions.[9,10] Furthermore, the increased acidity of the ammonium groups of $[Co(sepH_2)]^{5+}$ is not a result of direct interaction between the t_{2g} orbitals of the cobalt center and the p_z orbital of the flattened uncoordinated aza groups, as it has been shown in the previous discussion that such effects are minimal.



XIV

The pK_a values of the coordinated amine groups are also influenced by the polar effects of the apical groups. The measured pK_a values of coordinated amine groups of the $[Co(NO_2,CH_3\text{-sar})]^{3+}$ and $[Co(COO,CH_3\text{-sar})]^{2+}$ complexes are 9.2 (this pK_a was incorrectly reported as 7.2 in our previous paper)[1] and 12.3, respectively. Overall, the pattern is consistent with the σ_E values of $+3.7_8$ for the NO_2 group and $+0.5_1$ for the CO_2^- group. The site of deprotonation is most likely to be adjacent to the NO_2 and CO_2^- groups, respectively, since the CH_3 group has a negative polar substituent effect (σ_E -0.1_8). It is apparent from Figure 3 that the average proton chemical shifts of the coordinated N–H groups correlate with the σ_E values, and therefore, the average pK_a values should also correlate with σ_E. Where the two apical groups have similar σ_E values, only one N–H resonance is observed in the ^1H NMR spectra. However, as the difference in σ_E between the two apical groups increases, two distinct resonances of equal intensity are observed and their chemical shift differences correspond to the magnitude of $\Delta\sigma_E$. These observations are also indicative of a σ_E control of the pK_a values of the coordinated amines. However, the increased acidity of the coordinated amines is not only influenced by the polar substituent effects of the cobalt center and the apical substituents. Clearly, there is the possibility of resonance stabilization of the deprotonated amine groups by direct interaction between the filled p_z orbital of the amido ion and d orbitals of the cobalt center, as discussed previously. This π overlap will be influenced by the geometrical restrictions of the ligand to π overlap and may also be influenced indirectly by the polar effects of the apical groups on the cobalt center. Similar arguments apply to the deprotonation of the coordinated amide groups of the oxosar cage complexes.

As expected, the polar substituent effects of the metal centers increase with the formal charge of the metal ions. For example, the pK_a values for the hydroxylamine groups of $[M(NH_2OH)_2\text{-sar})]^{n+}$ are ~1 for M = Co, $n = 5$,[1,13] and >0 for M = Pt, $n = 6$.[43,44] Similarly, the basicities of the aza groups in $[Co(sep)]^{3+/2+}$ increase in the order $Co^{III} < Co^{II}$.[9,10] Therefore, the polar substituent effects of the metal centers decrease in the order Co(II) < Co(III) < Pt(IV), as expected. The enhanced acidity of the coordinated amide group of $[Co(COOC_2H_5,CH_3\text{-oxosar})]^{3+}$ (pK_a ≤–1) in comparison to the corresponding Co(II) complex (pK_a 3.6)[15] is not due solely to polar substituent effects, since the ability of the different ions to undergo π interactions will also be altered. Hence, both resonance and inductive effects influence the pK_a values to differing degrees in the two oxidation states.

The heterogeneous rate constants (k_s) for the cobalt cage complexes, determined at their $E_{1/2}$ values, show little variation for the large range of complexes of the sar type investigated.[1] This observation is consistent with the predictions of the theories of Marcus[45-47] and Hush[48,49] for adiabatic outer-sphere electron transfer, for which these cage complexes are excellent models as a consequence of encapsulation of the metal ion in a coordinatively saturated system.[50] At $E_{1/2}$, $\Delta G°$ is zero and reorganizational and work terms are essentially constant for complexes with the same charge (3+), as a consequence of structural similarities in the cage complexes, leading to the observed constancy in k_s. Larger rate constants for the protonated amine cage complexes

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can be ascribed to different Coulombic work terms associated with the higher charges, since the work-correlated rate constant (k_{cor}) and k_{obsd} are related by

$$\log k_{cor} = \log k_{obsd} + \frac{F}{2.303RT}(Z_r - \alpha_I)\phi_r \qquad (9)$$

where ϕ_r is the potential at the reaction site with respect to the bulk solution, Z_r is the charge carried by the reactant, and α_I is the intrinsic transfer coefficient.[51] Differences observed in k_s for Hg, Au, and Pt are apparently due to a dependence on the ϕ_r term for the different electrodes, i.e. different double-layer effects result in different values of k_{obsd}. Similar electrode dependencies have been noted with complexes of Fe, Co, Mn, and Cr containing thia and oxa donor groups,[52] and therefore, a specific interaction of the electrode with the cobalt amine cage complexes can be ruled out. However, the rate constants are complicated by adsorption of the complexes on the electrodes and a more detailed analysis of the applicability of the Marcus–Hush theories in terms of heterogeneous and homogeneous rate characteristics of the cage complexes is continuing and will be described at a later date.

Conclusions

The use of the Co(III/II) reduction potentials of substituted cage complexes is a new and effective method for obtaining substituent effects. It is not limited to studying the substituents listed in this paper, and work is proceeding toward expanding the series. In addition, work is in progress for obtaining detailed solvent dependencies and temperature dependencies of polar substituent constants. These are important areas to investigate, since a single source for such constants is still not available.[31] The comparatively large NMR coupling constants between the apical carbons and the metal ions can also be analyzed in terms of a mechanism similar to that given here.[53]

Acknowledgment. We wish to thank the ANU NMR Service for the many ^{13}C NMR and ^{59}Co NMR spectra, Dr. J. Bromilow for many helpful and stimulating discussions, and Drs. J. MacB. Harrowfield, R. J. Geue, and W. Petri for supplying some spectral results prior to publication.

Supplementary Material Available: Listings of observed and calculated redox potentials, ^{13}C and ^{1}H NMR chemical shifts, and electronic absorption maxima of the Co(III) complexes (Tables SI and SII) and a plot of δ_{Co} vs $E_{1/2}$ (Figure S1) (9 pages). Ordering information is given on any current masthead page.

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Mechanism of Intramolecular Rearrangements of (Acetylacetonato)bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)ruthenium(III)

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Received December 7, 1989

Time variations of mole fractions of the three isomers of [Ru(acac)(tfpb)$_2$] (acac$^-$ = acetylacetonate ion, tfpb$^-$ = 4,4,4-trifluoro-1-phenyl-1,3-butanedionate ion) were measured in *N,N*-dimethylformamide at 90, 110, and 130 °C. They were analyzed by a numerical method for the reversible, first-order, triangular network reactions previously developed. The results show that the direct conversion between the *fc,de*-(tfpb)$_2$ isomer and the *cf,ed*-(tfpb)$_2$ isomer was forbidden, which indicates that the bond-rupture mechanism through trigonal-bipyramidal intermediates with a single rearrangement is more plausible than the twist mechanism. Analysis of the rate constants according to the former mechanism suggests that the rate of rupture of a particular Ru–O bond is mainly, but not completely, determined by the kind of the nearest β-substituents.

Introduction

A tris(β-diketonato)metal complex with three unsymmetrical β-diketonate ligands can have two geometrical isomers: the facial and the meridional forms. A number of studies have been directed to the stereochemical rearrangement of the geometrical and optical isomers of "slow" type[3] tris complexes of various metals, for example, cobalt(III),[4-7] rhodium(III),[5] chromium(III),[8] and ruthenium(III).[9,10] Two basic pathways are generally considered in explaining the kinetics of these reactions: twist mechanisms and bond-rupture mechanisms.[11] The former involves no bond breakage, and the latter involves five-coordinated intermediates, whose structures may be essentially square-pyramidal (SP) or trigonal-bipyramidal (TBP), each with a dangling ligand at the axial or equatorial position. The kinetics of these complexes have been interpreted by a combination of several bond-rupture mechanisms rather than a single mechanism. For instance, Girgis and Fay[6] studied the interconversion of the four isomers of tris(1-phenyl-1,3-butanedionato)cobalt(III) in detail and explained the kinetics in terms of a combination of paths through the TBP-axial and SP intermediates. It is difficult to obtain sufficient kinetic information for clarifying the mechanisms of intramolecular rearrangements when homoleptic tris complexes are employed.

When two of the three β-diketonate ligands are unsymmetrical ligands, A–B, and the third ligand, C–C, is symmetrical (general formula [M(A–B)$_2$(C–C)]), there can be three geometrical isomers, each having a pair of enantiomers. This type of complex is more suitable than tris complexes for inferring the isomerization mechanism, since a certain interconversion among the three

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