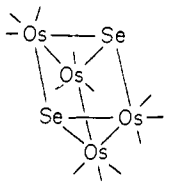

6

are of the two-center, two-electron type). It could, in principle, be formed through the addition of 1 mol of H_2 to **4** accompanied by the complete cleavage of the two weak metal–metal bonds. In **6** these Os···Os distances have increased to approximately 4 Å.

The molecular structure of **5** is shown in Figure 2.[17,26,27] This hexanuclear cluster consists of a square-pyramidal group of five metal atoms with a rare quadruply bridging sulfido ligand, S(1), spanning the square base.[28] An $Os(CO)_3$ group bridges a pair of metal atoms in the square base, and that group of three is bridged by the second sulfido ligand. If both sulfido ligands serve as 4-electron donors, the molecule is electron precise and each metal atom achieves an 18-electron configuration.[29] Thus, all the metal–metal bonds are single, although the Os(4)–Os(5) separation at 2.686 (1) Å is short for an Os–Os single bond.[19] This shortening is probably due to the fact that the Os(4)–Os(5) bond contains four single-atom bridges, S(1), S(2), Os(1), and Os(6). A similar shortening was observed for an analogous metal–metal bond in the structurally related molecule $Os_6(CO)_{16}(\mu_4\text{-CMe})(\mu_3\text{-CMe})$. As one might expect, the Os–S distances to the quadruply bridging sulfide ligand, Os-μ_4-S_{av} = 2.44 (1) Å, are significantly longer than those to the triply bridging ligand, Os-μ_3-S_{av} = 2.34 (2) Å. The Os(1)···S(1) distance at 3.472 (4) Å is probably completely nonbonding. Sixteen linear carbonyl ligands cover the surface of the cluster.

In summary, we have now found that the elimination of benzene from (arenethiolato)osmium carbonyl hydride clusters provides a new and convenient route for the synthesis of higher nuclearity carbonyl clusters containing sulfido bridges.[31] Most importantly, as exemplified by **4**, there appears to be a class of polynuclear metal complexes containing heteronuclear bridges that has anomalous structural and bonding properties. This could have profound implications on reactivity and perhaps ultimately on the use of cluster compounds as catalysts.[32]

Acknowledgment. This research was supported by the National Science Foundation and by the A. P. Sloan Foundation through a fellowship to R.D.A.

Supplementary Material Available: Complete tables of fractional atomic coordinates, bond distances, and bond angles are available for structures **4** and **5** (9 pages). Ordering information is given on any current masthead.

(26) Space group: $P2_1/c$, No. 14; a = 10.083 (4) Å; b = 12.633 (4) Å; c = 21.383 (4) Å; β = 91.73 (2)°; M_r = 1653.50, Z = 4; ρ_{calcd} = 4.03 g/cm³. The structure was solved by a combination of direct methods and difference-Fourier techniques. Least-squares refinement on 2629 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.038 and R_2 = 0.039. IR ν_{CO} (hexane) 2090 s, 2070 s, 2055 s, 2042 s, 2030 m cm⁻¹.

(27) Selected internuclear distances (Å) and angles (deg) for **5** are as follows: Os(1)–Os(2) = 2.849 (1), Os(1)–Os(3) = 2.833 (1), Os(1)–Os(4) = 2.888 (1), Os(1)–Os(5) = 2.843 (1), Os(2)–Os(3) = 2.884 (1), Os(1)–Os(4) = 2.781 (1), Os(3)–Os(5) = 2.863 (1), Os(4)–Os(5) = 2.686 (1), Os(5)–Os(6) = 2.828 (1), Os(1)···S(1) = 3.472 (4), Os(2)–S(1) = 2.432 (4), Os(3)–S(1) = 2.414 (4), Os(4)–S(1) = 2.440 (4), Os(5)–S(1) = 2.476 (4), Os(4)–S(2) = 2.352 (4), Os(5)–S(2) = 2.372 (4), Os(6)–S(2) = 2.285 (4); Os(2)–Os(3)–Os(5) = 87.42 (3), Os(3)–Os(2)–Os(4) = 88.54 (3), Os(2)–Os(4)–Os(5) = 93.15 (3), Os(3)–Os(5)–Os(4) = 90.86 (3), Os(1)–Os(5)–Os(6) = 122.68 (3), Os(1)–Os(4)–Os(6) = 120.49 (3).

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Substituent Effect of Chelated Cobalt. 5. Acidities of (Carboxymethyl)- and (1-Carboxyethyl)cobaloximes. A Quantitative Analysis of the β Effect[1,2]

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Abstract: pK_a's of the weakly acidic (carboxymethyl)(ligand)cobaloximes and (1-carboxyethyl)(ligand)cobaloximes with 16 different axial ligands have been determined and correlated with those of 11 substituted acetic acids or 9 1-substituted propionic acids, respectively. Comparison of apparent σ_1 values thus calculated with those previously determined by correlation of (carboxyethyl)(ligand)cobaloxime pK_a's with the pK_a's of 2-substituted propionic acid indicates that the (1-carboxyalkyl)cobalt complexes show a substantial β effect as an apparent extreme donation of electron density to the carboxyl carbon. the β effect in these complexes has been quantitated by use of a dual substituent parameter equation, the results of which show that the effect is only some 8–10% enhanced in (1-carboxyethyl)cobaloximes relative to (carboxymethyl)cobaloximes. This result is consistent with the β effect being mediated by σ–π hyperconjugation rather than neighboring group participation. Structural effects on the extent of σ–π conjugation and the effects of σ–π conjugation on reactivity of the cobalt atom in these complexes are discussed.

(Carboxymethyl)cobalt complexes, including both cobalamins[3,4] and cobaloximes,[5–7] as well as several other carboxymethyl transition-metal complexes[6] are well-known to be extremely weak carboxylic acids with acidities ranging from 2 to 3 orders of magnitude lower than that of acetic acid. This phenomenon is

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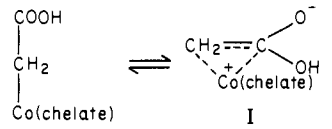
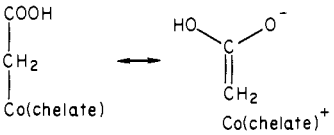
an obvious example of the organometallic β effect[8] which, in the ground state, manifests itself as an apparent extreme electron donation to substitutents β to the metal atom. In an earlier publication[7] we postulated that for (carboxymethyl)cobalt complexes this reduced acidity could be due to equilibrium formation of the valence tautomer, I (eq 1), in solution, essentially an example



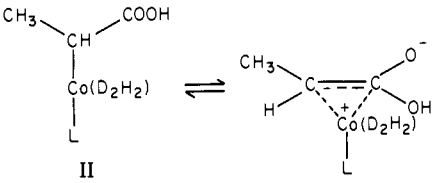
I (1)

of neighboring group participation to which Green et al.[6] had earlier attributed the weak acidity of some (carboxymethyl)metal complexes. This seemed an attractive explanation since π complexes between cobalt(III) chelates and olefinic organic ligands had received considerable, albeit indirect, experimental support.[9-12]

However, an alternative explanation is available in the form of exalted hyperconjugation (σ-π conjugation)



for which there is substantial experimental support[13-22] in both organic and organometallic compounds. As such "vertical stabilization"[14] does not require any geometrical distortion, it seemed possible to distinguish these possibilities by a comparison of the β effect in (carboxymethyl)cobaloximes to that in (1-carboxyethyl)cobaloximes (II) since the position of the valence tautomerization equilibrium (eq 2) might be expected to be

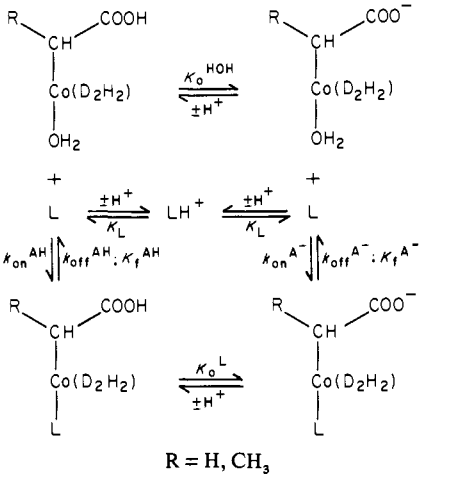


II (2)

displaced further to the right in the latter complexes due to geometrical constraints. Recent confirmation of this expectation comes from the X-ray crystal structure of the secondary alkylcobaloxime, isopropyl(pyridine)cobaloxime,[23] in which both a substantial increase in C–Co bond length (2.085 Å compared with 2.040 Å in ((carbomethoxy)methyl)(pyridine)cobaloxime[24] and 1.998 Å in methyl(pyridine)cobaloxime[25]) and a substantial flattening of the tetrahedron about the α-carbon atom (C_β–C_α–C_β = 112.3°) are evident. Similar, although less severe, distortions are seen in the X-ray structure of ((*R*)-1-(carbomethoxy)-ethyl)((*R*)-(+)-α-methylbenzylamine)cobaloxime[26] (Co–C distance = 2.067 Å). Hence, secondary alkylcobaloximes appear to adopt a solid-state conformation, due to steric constraints, in which the carbon–cobalt σ bond is substantially stretched and the β carbon is placed in a position which should allow enhanced direct interaction with the metal atom.

Although exalted hyperconjugation is known not to require geometrical distortion, the extent to which it is sensitive to such distortion is not completely clear. While the influence of bending strain, which enhances hyperconjugation by increasing the polarizability of the strained σ bond, is well documented,[14h,i,k] the influence of stretching strain is much less well supported.[14k] We consequently undertook the following comparative study of the

Scheme I



(2) Abbreviations: $RCo(D_2H_2)L$ = organo(ligand)bis(dimethylglyoximato)cobalt(III) = organo(ligand)cobaloxime.

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acidities of (carboxymethyl)- and (1-carboxyethyl)cobaloximes with various trans-axial ligands to see if these competing explanations of the β effect in such systems could, indeed, be distinguished in this manner.

Experimental Section

Materials. Dimethylglyoxime, cobaltous acetate, cobaltous chloride, sodium borohydride, organic solvents, buffer components, and inorganic salts and acids were obtained in the highest purity commercialy available and used without further purification.

All axial ligands except methyl (methylthio)acetate and all substituted propionic and acetic acids except (1-methylthio)propionic and (1-methylthio)acetic acid were purchased commercially and recyrstallized or redistilled under argon before use.

Mercaptoacetic acid was methylated with dimethyl sulfate[27] and esterified with methanol[28] as previously described.[29] 1-Thiopropionic acid was methylated by the procedure of Schmolka and Spoerri:[27] yield 23.4%; bp 117–120 °C (20 torr) (lit.[28] bp 105–108 °C (8 torr)); NMR (neat) δ_{Me_4Si} (external) 1.39 (d, 3.00 H, J = 7.2 Hz), 2.16 (s, 3.00 H), 3.35 (q, 1.05 H, J = 7.2 Hz).

(Carboxymethyl)aquocobaloxime was obtained by sulfuric acid catalyzed hydrolysis of its methyl ester as previously described.[5,7] (1-Carboxyethyl)aquocobaloxime was obtained by reaction of diaquocobaloxime(II) with acrylic acid under hydrogen as described by Schrauzer and Windgassen.[5] Both cobaloximes gave satisfactory elemental analysis[30] and had the expected ^{1}H NMR spectra.

Methods. All work with organocobaloximes was performed in dim light. Glass-distilled, deionized water was used throughout, and ionic strength was maintained at 1.0 M with KCl. EDTA (10^{-4} M) was employed to retard air oxidation of thiolate anions.

NMR measurements were made on a Varian T-60 NMR spectrometer. UV-visible spectra were recorded on a Cary 14 or Cary 219 recording spectrophotometer. Single wavelength absorbance measurements were made on a Cary 219 or a Gilford Model 250 spectrophotometer with the sample compartments thermostated to 25.0 ± 0.1 °C. pH measurements were made on a Radiometer PHM 64 pH meter with samples, standards, and electrodes incubated at 25.0 ± 0.1 °C.

All substituted propionic and acetic acids were titrated potentiometrically at 25.0 ± 0.1 °C and ionic strength 1.0 M. pK_a values were determined by least-squares fits of the data to eq 3[31] as previously described.[29]

$$pH = pK_a + \log \{([A^-] + [H^+])/([AH] - [H^+])\} \quad (3)$$

Equilibrium constants, K_f^{app}, for ligand binding to the (carboxyalkyl)aquocobaloximes or their conjugate bases (eq 4 and 5) were de-

$$RCo(D_2H_2)OH_2 + L \underset{}{\overset{K_f^{app}}{\rightleftharpoons}} RCo(D_2H_2)L \quad (4)$$

$$K_f^{app} = [RCo(D_2H_2)L]/[RCo(D_2H_2)OH_2][L] \quad (5)$$

termined spectrophotometrically as previously described.[29,32] Measurements of ligand dissociation rate constants, k_{off}^{app} (eq 6 and 7), were

$$RCo(D_2H_2)L \xrightarrow{k_{off}^{app}} RCo(D_2H_2)OH_2 + L \quad (6)$$

$$\text{rate} = k_{off}^{app}[RCo(D_2H_2)L] \quad (7)$$

made spectrophotometrically as previously described.[7,29] Ligand association rate constants, k_{on}^{app}, were calculated from eq 8 and the measured equilibrium constants. (1-Carboxyethyl)aquocobaloxime was titrated spectrophotometrically as previously described.[7]

$$k_{on}^{app} = k_{off}^{app} K_f^{app} \quad (8)$$

Determinations of the pK_a's of the (carboxyalkyl)(ligand)cobaloximes, pK_a^L (eq 9, R = CH_3 or H), were made in conjunction with Scheme I.

$$K_a^L = [^-OOCCH(R)Co(D_2H_2)L][H^+]/[HOOCCH(R)Co(D_2H_2)L] \quad (9)$$

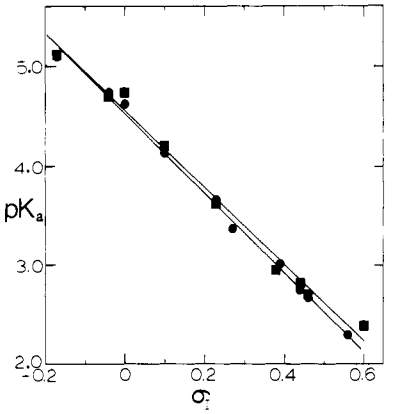

Figure 1. Plot of the pK_a's of substituted acetic acids (●) and 1-substituted propionic acids (■) vs. σ_1 for the substituent (Table III). The solid lines are least-squares fits: XCH_2COOH, slope = −3.898 ± 0.089, intercept = 4.524 ± 0.029, f = 0.016; $CH_3CH(X)COOH$, slope = −3.848 ± 0.155, intercept = 4.549 ± 0.052, f = 0.027.

Several methods were used depending on the axial ligand, L, its affinity for the cobalt center, and its dissociation rate. In method I, $K_f^{A^-}$ (eq 10)

$$K_f^{A^-} = [^-OOCCH(R)Co(D_2H_2)L]/[^-OOCCH(R)Co(D_2H_2)OH_2][L] \quad (10)$$

$$K_f^{AH} = [HOOCCH(R)Co(D_2H_2)L]/[HOOCCH(R)Co(D_2H_2)OH_2][L] \quad (11)$$

and K_f^{AH} (eq 11) were directly measured at pH > pK_a^{HOH} + 2 and pH < pK_a^{HOH} − 2, respectively. When necessary, observed ligand association constants, K_f^{app}, were corrected for ligand protonation by eq 12, where

$$K_f^{A^-} \text{ or } K_f^{AH} = K_f^{app}/\alpha_L \quad (12)$$

α_L is the fraction of ligand as the unprotonated species (Scheme I) as calculated from the pK_a of the conjugate acid of the ligand and eq 13.

$$\alpha_L = K_L/(K_L + [H^+]) \quad (13)$$

K_a^L was then calculated from eq 14 based on the cyclic nature of the

$$K_a^L = K_a^{HOH}K_f^{A^-}/K_f^{AH} \quad (14)$$

equilibria in Scheme I. Method II involved determination of the pH dependence of the ligand dissociation rate constants, k_{off}^{app}, which is given by eq 15, derived from Scheme I and the law of mass action. Data were

$$k_{off}^{app} = \left(k_{off}^{AH}[H^+] + k_{off}^{A^-}K_a^L\right)/(K_a^L + [H^+]) \quad (15)$$

fit to eq 15 to provide values of K_a^L, k_{off}^{AH}, and $k_{off}^{A^-}$. K_a^L values were then used in conjunction with spectrophotometrically determined values of $K_f^{A^-}$ and eq 14 to calculate K_f^{AH}. Method III involved determination of the pH dependence of K_f^{app}, given by eq 16, which is derived from

$$K_f^{app} = K_f^{AH}(1 - \alpha_{cob})\alpha_L + K_f^{A^-}\alpha_{cob}\alpha_L \quad (16)$$

Scheme I and eq 10–13, where α_{cob} is the fraction of (carboxyalkyl)aquocobaloxime as the anionic conjugate base, given by eq 17. Data

$$\alpha_{cob} = K_a^{HOH}/(K_a^{HOH} + [H^+]) \quad (17)$$

were collected at at least five pHs and fit to a rearranged form of eq 16 (eq 18). K_a^L was then calculated from the resulting values of K_f^{AH} and

$$K_f^{app}/\alpha_L = K_f^{AH} + \left(K_f^{A^-} - K_f^{AH}\right)\alpha_{cob} \quad (18)$$

$K_f^{A^-}$ and eq 14. Finally, the extremely slow rate of dissociation of some ligands allowed the direct spectrophotometric titration of preformed solutions of (carboxyalkyl)(ligand)cobaloximes (method IV). In such cases it was always possible to show that absorbance measurements at various pHs could be made prior to any significant ligand dissociation.

Results and Discussion

Quantitation and Nature of the β Effect. Ligand binding constants and proton dissociation constants for (carboxymethyl)cobaloximes are given in Table I and those for (1-carboxyethyl)cobaloximes are given in Table II. Inspection of

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Table I. Equilibrium Constants for Axial Ligation and Deprotonation of (Carboxymethyl)cobaloxime with Various Ligands

ligand	pK_L[b]	K_f^{AH}, M^{-1}	$K_f^{A^-}$, M^{-1}	pK_a^L	method[c]	σ_I^{app}[d]	σ_I[e]	σ_β[f]
water				6.30 ± 0.01[g]	h	−0.445	−0.162	−1.130
(2-methylthio)ethanol		(4.55 ± 0.11) × 10	(5.52 ± 0.10) × 10	6.22 ± 0.02	I	−0.425	−0.045	−1.516
methyl (methylthio)acetate		5.54 ± 0.44	7.31 ± 0.31	6.18 ± 0.04	I	−0.415	−0.065	−1.423
4-cyanopyridine	2.24 ± 0.02[i]	(3.86 ± 0.10) × 10^2	(3.35 ± 0.07) × 10^2	6.36 ± 0.02	I	−0.460	−0.132	−1.293
4-(carboxamido)pyridine	3.77 ± 0.01[i]	(1.34 ± 0.04) × 10^3	(1.03 ± 0.02) × 10^3	6.41 ± 0.02	I	−0.473	−0.155	−1.268
pyridine	5.56 ± 0.01[g]	(6.33 ± 0.21) × 10^3	(3.65 ± 0.19) × 10^3	6.54 ± 0.03	I	−0.505	−0.226	−1.114
4-methylpyridine	6.36 ± 0.02[i]	(1.34 ± 0.10) × 10^4	(7.37 ± 0.35) × 10^3	6.56 ± 0.03	I	−0.510	−0.252	−1.031
4-aminopyridine	9.40 ± 0.02[i]	(6.09 ± 0.20) × 10^4	(2.41 ± 0.18) × 10^4	6.70 ± 0.04	III	−0.546	−0.297	−0.991
2,2,2-trifluoroethylamine	5.68 ± 0.01[i]	(1.17 ± 0.08) × 10^2	(7.31 ± 0.20) × 10	6.50 ± 0.02	II	−0.495	−0.090	−1.617
glycine ethyl ester	7.86 ± 0.01[j]	(2.59 ± 0.12) × 10^3	(1.15 ± 0.05) × 10^3	6.65 ± 0.01	IV	−0.533	−0.097	−1.739
2,2-dimethoxyethylamine	8.86 ± 0.01[i]	(6.92 ± 0.50) × 10^3	(2.90 ± 0.19) × 10^3	6.68 ± 0.01	II	−0.540	−0.123	−1.665
2-methoxyethylamine	9.68 ± 0.02[i]	(1.45 ± 0.09) × 10^4	(5.40 ± 0.26) × 10^3	6.73 ± 0.01	IV	−0.553	−0.136	−1.663
n-propylamine	10.80 ± 0.02[i]	(4.60 ± 0.29) × 10^4	(1.48 ± 0.08) × 10^4	6.79 ± 0.01	IV	−0.568	−0.149	−1.672
methyl thioacetate	7.83 ± 0.01[k]	(7.87 ± 0.24) × 10^6	(8.68 ± 0.38) × 10^5	7.26 ± 0.01	IV	−0.686	−0.271	−1.655
methyl thiopropionate	9.27 ± 0.01[j]	(2.57 ± 0.09) × 10^7	(1.79 ± 0.09) × 10^6	7.46 ± 0.01	IV	−0.736	−0.291	−1.775
2-thioethanol	9.51 ± 0.01[k]	(2.42 ± 0.06) × 10^7	(1.68 ± 0.08) × 10^6	7.46 ± 0.01	IV	−0.736	−0.304	−1.723

[a] 25.0 ± 0.1 °C, ionic strength 1.0 M. [b] pK_a of the conjugate acid of the ligand. [c] See Experimental Section. [d] Calculated from pK_a^L and eq 19 using ρ_I and pK_a^0 for substituted acetic acids (Table III and Figure 1). [e] From correlation of (carboxyethyl)(ligand)cobaloxime pK_a^L's with those of 2-substituted propionic acids, see ref 29. [f] Calculated from eq 20 using $\rho_I = -3.989$, $\rho_\beta = -1.00$, and $pK_a^0 = 4.524$. [g] Reference 7. [h] Spectrophotometric titration. [i] Reference 33. [j] Reference 29. [k] Reference 34.

Table II. Equilibrium Constants for Axial Ligation and Deprotonation of (1-Carboxyethyl)cobaloximes with Various Ligands[a]

ligand	pK_L[b]	K_f^{AH}, M^{-1}	$K_f^{A^-}$, M^{-1}	pK_a^L	method[c]	σ_I^{app}[d]	σ_I[e]
water				6.43 ± 0.01	f	−0.489	−0.162
(2-methylthio)ethanol		(3.67 ± 0.05) × 10	(4.45 ± 0.14) × 10	6.34 ± 0.02	I	−0.465	−0.045
methyl (methylthio)acetate		3.23 ± 0.09	6.93 ± 0.24	6.10 ± 0.02	I	−0.403	−0.065
4-cyanopyridine	2.24 ± 0.02[g]	(2.16 ± 0.03) × 10^2	(2.13 ± 0.09) × 10^2	6.43 ± 0.02	I	−0.489	−0.132
4-(carboxamido)pyridine	3.77 ± 0.01[g]	(6.49 ± 0.16) × 10^2	(5.46 ± 0.07) × 10^2	6.50 ± 0.02	I	−0.507	−0.155
pyridine	5.56 ± 0.01[h]	(2.57 ± 0.09) × 10^3	(1.57 ± 0.02) × 10^3	6.64 ± 0.02	I	−0.543	−0.226
4-methylpyridine	6.36 ± 0.02[g]	(5.46 ± 0.33) × 10^3	(3.05 ± 0.07) × 10^3	6.68 ± 0.03	I	−0.554	−0.252
4-aminopyridine	9.40 ± 0.02[g]	(2.63 ± 0.07) × 10^4	(9.37 ± 0.58) × 10^3	6.88 ± 0.03	III	−0.606	−0.297
2,2,2-trifluoroethylamine	5.68 ± 0.01[g]	(5.30 ± 0.05) × 10	(4.21 ± 0.04) × 10	6.53 ± 0.01	III	−0.515	−0.090
glycine ethyl ester	7.86 ± 0.01[i]	(1.53 ± 0.03) × 10^3	(6.61 ± 0.24) × 10^2	6.79 ± 0.02	III	−0.582	−0.097
2,2-dimethoxyethylamine	8.86 ± 0.01[g]	(2.38 ± 0.11) × 10^3	(1.01 ± 0.04) × 10^3	6.80 ± 0.01	II	−0.585	−0.123
2-methoxyethylamine	9.68 ± 0.02[g]	(7.07 ± 0.40) × 10^3	(2.52 ± 0.12) × 10^3	6.88 ± 0.01	II	−0.606	−0.136
n-propylamine	10.80 ± 0.02[g]	(1.51 ± 0.08) × 10^4	(4.94 ± 0.24) × 10^3	6.91 ± 0.01	II	−0.614	−0.149
methyl thioacetate	7.83 ± 0.01[j]	(3.07 ± 0.08) × 10^6	(1.98 ± 0.08) × 10^5	7.62 ± 0.01	IV	−0.798	−0.271
methyl thiopropionate	9.27 ± 0.01[i]	(9.99 ± 0.33) × 10^6	(4.93 ± 0.23) × 10^5	7.73 ± 0.01	IV	−0.827	−0.291
2-thioethanol	9.51 ± 0.01[j]	(9.58 ± 0.27) × 10^6	(4.45 ± 0.18) × 10^5	7.76 ± 0.01	IV	−0.834	−0.304

[a] 25.0 ± 0.1 °C, ionic strength 1.0 M. [b] pK_a of the conjugate acid of the ligand. [c] See Experimental Section. [d] Calculated from pK_a^L and eq 19 using ρ_I and pK_a^0 for 1-substituted propionic acids (Table III and Figure 1). [e] From correlation of (carboxyethyl)(ligand)cobaloxime pK_a^L's with those of 2-substituted propionic acids, see ref 29. [f] Spectrophotometric titration. [g] Reference 33. [h] Reference 7. [i] Reference 29. [j] Reference 34.

the pK_a^L values in these tables shows that the (1-carboxyethyl)cobaloximes are, in fact, slightly less acidic than the (carboxymethyl)cobaloximes, the pK_a^L values for most of the former being on the average 0.10 unit higher than the latter, with the exception of thee thiolato complexes where the difference averages 0.31 unit. In order to accurately compare the reduced acidity of these cobalt-substituted carboxylic acids in the absence of complicating electronic effects due to the α-methyl group, we have correlated the pK_a^L values for the (carboxymethyl)cobaloximes with those of 11 substituted acetic acids (Table III, Figure 1) via eq 19 while

$$pK_a = \rho_I\sigma_I + pK_a^0 \quad (19)$$

those of the (1-carboxyethyl)cobaloximes have been correlated with the pK_a's of nine 1-substituted propionic acids (Table III, Figure 1). The *apparent* σ_I values thus obtained for the cobaloxime-chelated cobalt centers, which are greatly enhanced from the true σ_I values due to the β effect, are listed in Tables I and II along with the previously determined[29] true σ_I values obtained by correlation of (carboxyethyl)cobaloxime pK_a's (in which β-effect complications are prevented by the insulation provided by the extra methylene group) with those of 2-substituted propionic acids. Comparision of the apparent σ_I values with the true σ_I values for these cobalt centers clearly shows that the β effect is quite substantial in these systems, the former values being as much as ten times as negative as the latter. Furthermore, comparison of the apparent σ_I values in the two systems shows that the β effect is only slightly enhanced in (1-carboxyethyl)cobaloximes compared to (carboxymethyl)cobaloximes, the average difference in σ_I^{app} being only 0.049, which is quite small compared to the average

Table III. pK_a's of Substituted Acetic Acids and 1-Substituted Propionic Acids[a]

		pK_a[c]	
X	σ_I[b]	XCH_2COOH	CH_3-CHXCOOH
^-OOC	−0.17[d]	5.09	5.11
CH_3	−0.04	4.74[e]	4.70
H	0	4.62	4.74[e]
C_6H_5	0.10	4.13	4.20
CH_3S	0.23	3.66	3.63
CH_3O	0.27	3.37	
C_6H_5O	0.38	2.96	2.96
I	0.39	3.02	
Br	0.44	2.75	2.82
Cl	0.46	2.67	2.70
NC	0.56	2.30	
H_3N^+	0.60[d]		2.39

[a] 25.0 ± 0.1 °C, ionic strength 1.0 M. [b] Reference 35, except as noted. [c] All standard deviations ≤0.01. [d] Reference 36. [e] Reference 29.

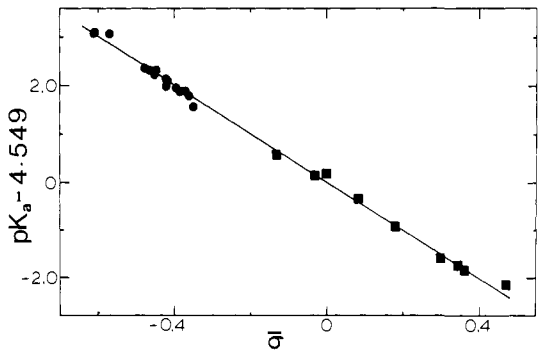

Figure 2. Derived two-dimensional plot of the dual substituent parameter analysis (eq 20) of the pK_a's of cobalt-substituted (●) and non-cobalt-substituted (■) 1-propionic acids according to eq 21–24: $\bar{\rho} = -5.034$, $\lambda = 0.274$, $N = 25$, $f = 0.051$.

difference between σ_I^{app} and σ_I for (carboxymethyl)cobaloximes (0.364).

We can now quantitate the β effect in these systems by use of a dual substituent parameter type equation[35] such as eq 20 which

$$pK_a - pK_a^0 = \rho_I\sigma_I + \rho_\beta\sigma_\beta \quad (20)$$

will allow separation of the inductive and β-effect tendencies of a given substitutent. Equation 20 has been applied to the data in Table I, using as ρ_I the slope of the correlation of substituted acetic acid pK_a's with σ_I (−3.989, Figure 1) and as pK_a^0 the intercept of this correlation (4.524). The latter assignment seems a reasonable alternative to using the pK_a of acetic acid for pK_a^0 in order to minimize the effect of a single data point on the overall correlation. Since no σ_β values are available to allow an independent determination of ρ_β, ρ_β has been arbitrarily assigned the value of −1.000, the sign having been chosen to agree with the sign convention for σ_I. The σ_β values for the cobaloxime-chelated cobalt centers listed in Table I have thus been determined by using eq 20 and the σ_I values for these substituents from our previous work.[29] The utility of these values, as well as that of eq 20 for quantitating the β effect, can now be checked by application to the data for the (1-carboxyethyl)cobaloximes in Table II. This can be done in either of two ways. ρ_I and pK_a^0 may be taken to be the slope (−3.848, Figure 1) and intercept (4.549), respectively, of the correlation of 1-substituted propionic acids with σ_I (Figure 1) allowing a calculation of ρ_β for each value of pK_a^L in Table II. The average ρ_β thus obtained is -1.096 ± 0.073. The values of pK_a^L in Table II are, in fact, excellently correlated by eq 20 using these values for ρ_I, ρ_β, and pK_a^0 ($N = 16$, $f = 0.045$[37]). Alternatively, the pK_a^L values in Table II along with those for the non-cobalt-substituted propionic acids (Table III) may be fit directly to eq 20 by the method of least squares (again the value 4.549 has been used for pK_a^0 rather than the pK_a of propionic acid in order to minimize the effect of the single data point on the correlation). This analysis gives $\rho_I = -3.950$ and $\rho_\beta = -1.084$ ($N = 25$, $f = 0.051$[37]), values not appreciably different from those obtained above. A two-dimensional plot[39] of this excellent correlation, based on eq 21–24, is shown in Figure 2.

$$pK_a - 4.549 = \bar{\rho}\bar{\sigma} \quad (21)$$

$$\bar{\rho} = \rho_I + \rho_\beta \quad (22)$$

$$\bar{\sigma} = (\sigma_I + \lambda\sigma_\beta)/(1 + |\lambda|) \quad (23)$$

$$\lambda = \rho_\beta/\rho_I \quad (24)$$

Having thus quantitated the β effect, we can now see that the enhancement of susceptibility to it in the secondary (carboxyalkyl)cobaloxime system relative to the primary (carboxymethyl)cobaloxime system amounts to only 8–10% (i.e., $\rho_\beta = -1.000$ (defined) for the primary system, but $\rho_\beta = -1.084$ (or −1.096) for the secondary system). As pointed out in the introduction, based on geometrical considerations of X-ray cyrstal structures of secondary alkylcobaloximes (including the methyl ester of (1-carboxyethyl)cobaloxime[26]), neighboring group participation (or internal displacement) would be expected to cause a substantially larger enhancement of the β effect in secondary alkylcobaloximes. It seems reasonable to conclude, then, that the β effect, at least in these systems, is due to exalted σ–π conjugation (or vertical stabilization in Traylor's terms[14]) which does not require geometrical distortion. It would seem that this conclusion must be drawn regardless of the extent to which hyperconjugation is affected by geometrical distortion, particularly bond stretching strain, an anticipated effect for which there is some evidence but which has not been quantitated (a point to which we shall return shortly). Had this quantitation shown a substantial increase in sensitivity to the β effect in the secondary alkylcobaloxime relative to the primary system, it would then have been impossible to distinguish between the two mechanisms given the unknown extent to which hyperconjugation can be enhanced by bond stretching, which certainly occurs in the secondary alkylcobaloximes. Since the difference in sensitivity to the β effect between the two systems is very small, it seems necessary to conclude that hyperconjugation is the cause.

As a further confirmation of this assignment, we note that the tendency of the cobaloxime-chelated cobalt centers to undergo resonance interactions with aryl organic ligands (i.e., d–π or p–π delocalization) as measured by σ_R^0 values for these cobalt centers[1] does not correlate in any fashion with the β effect, a plot of $-\sigma_\beta$ vs. $-\sigma_R^0$ (not shown) showing no trends at all. To the extent that neighboring group participation (eq 1) in (1-carboxyalkyl)cobaloximes can be expected to resemble such d–π or p–π electron donation, this observation also argues against the involvement of neighboring group participation in the β effect. Hyperconjugation, on the other hand, is known to be insensitive to such π delocalization; there are no confirmed examples of π–σ–π cross conjugation.[14k]

It thus seems reasonable to attribute the feeble acidity of (carboxymethyl)cobalamin[3,4] to hyperconjugation as well. It is similarly tempting to attribute other known examples of the β effect in organocobalt chemistry to hyperconjugation including the anomalously low carbonyl stretching vibration ($\nu_{CO} = 1655$ cm^{-1}) of (formylmethyl)cobaloximes,[10c] the upfield shift of the ^{1}H NMR resonance of the aldehyde hydrogen of (formylmethyl)cobalamin,[40] and possibly the extreme acid lability of the latter compound as well,[40] and the anomalous ^{19}F NMR chemical shifts of (*p*-fluorobenzyl)- and (*m*-fluorobenzyl)cobaloximes.[1]

Structural and Electronic Effects on σ–π Conjugation. As pointed out above, there is a slight, but finite enhancement of the β effect in (1-carboxyethyl)cobaloximes relative to (carboxymethyl)cobaloximes. This may be viewed as a steric effect of α-methyl substitution on carbon–cobalt bond length. Available X-ray crystallographic data on the methyl esters of these two (carboxyalkyl)cobaloximes show an increase in C–Co length from 2.040 Å in the carboxymethyl system[24] to 2.067 Å in the 1-carboxyethyl system.[26] This increase in bond length should lead to increased polarizability and hence increased delocalizability of the electron pair.[14k] However, this effect could also be attributed to the increase in inductive donation to the α-carbon on changing the 2-substituent from H ($\sigma_I = 0$)[35] to CH_3 ($\sigma_I = -0.04$).[35] Hence, whether this effect is due to stretching bond strain or increased inductive donation to the α-carbon in the (1-carboxyethyl)coba-

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(37) f is the ratio of the root mean square of the deviations from the fit to the root mean square of the data values ($pK_a - pK_a^0$).[35] According to Topsom's criteria[38] values of f between 0.1 and 0.2 represent acceptable fits while $f < 0.1$ indicates an excellent fit.
(38) Topsom, R. T. *Prog. Phys. Org. Chem.* **1976**, *12*, 1–20.
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loximes or to some combination of these effects is not clear, but it must be concluded that at least in the current case the effect of σ-bond stretching strain on $\sigma-\pi$ conjugation is quite small.

Changes in axial ligation to the cobalt center would also be expected to alter the delocalizability of the carbon–cobalt electron pair to the extent that they affect the net electron density on the cobalt atom. In Traylor's terms[14k] increased electron donation to the cobalt atom should decrease its electronegativity and hence increase polarizability of the carbon–cobalt bond and enhance $\sigma-\pi$ conjugation. Inasmuch as changes in electron donation to cobalt via axial ligands affect the inductive ability of the cobaloxime-chelated cobalt centers,[29] we might, perhaps somewhat naively, expect a direct correlation of σ_β with σ_I for the cobaloxime-chelated cobalt centers, along the lines of eq 25. A plot of $-\sigma_\beta$ vs. $-\sigma_1$ is

$$\sigma_\beta = m\sigma_I + b \qquad (25)$$

shown in Figure 3 in which a weak, if rather poor, positive trend is seen for the $-Co(D_2H_2)L$ substituents when L = RNH_2 or RS^- (a least-squares fit to eq 25 gives b = 1.637 ± 0.041 and m = 0.281 ± 0.205). A stronger, and more significant, but inverse, correlation is seen for L = 4-X-py, H_2O, and $RSCH_3$ (b = 1.554 ± 0.041, m = −2.011 ± 0.219) although it is not completely clear if the $RSCH_3$-ligand cobalt centers belong on the former or latter correlations. It is perhaps not unreasonable that a strictly linear σ_β–σ_I correlation for all the cobalt centers is not obtained since, if σ_β were a strictly linear function of σ_I, the dual substituent parameter equation (eq 20) would not be required to adequately fit all of the pK_a data. However, the grouping of the ligands into the two correlations seems strange, the neutral, strictly σ-donating primary amine ligands correlating (albeit roughly) with the anionic and probably π-accepting (as well as σ-donating) thiolate anions, while the neutral, π-accepting and σ-donating pyridine ligands correlate reasonably well with H_2O and possibly with the methyl sulfides which are probably primarily π acceptors in such complexes.[29] It should, however, be noted that trans axial π interactions should not directly affect $\sigma-\pi$ conjugation, there being no evidence for the occurrence of such $\pi-\sigma-\pi$ cross conjugation.[14k]

The single property which would seem to separate those ligands on the upper correlation of Figure 3 at least from the pyridine ligands on the lower correlation is the geometry of the ligand orbital carrying the donor electron pair. For all the ligands except the pyridines the donor pair is in a p or sp^n hybrid orbital which is substantially angularly displaced from the donor atom–R group bond axis. Consequently, there may be substantial steric interactions of such ligands with the underside of the equatorial ligand system. If the alkylcobaloximes tend to adopt a square-bipyramidal solution conformation with the cobalt atom somewhat displaced above the equatorial donor plane, such steric interactions with strongly binding axial ligands would tend to force the cobalt atom into the equatorial plane causing a lengthening of the carbon–cobalt bond and hence increased polarizability and delocalizability of the σ electron pair. Since the donor orbital of the pyridine ligands is on the ligand major symmetry axis, such geometrical distortion would not occur. Axial ligands like H_2O and $RSCH_3$, although belonging to the former class, may simply be too weakly bound (see Tables I and II and ref 29), and in the case of H_2O, too small to cause such distortion. Such an explanation gains some support from the fact that $-\sigma_\beta$ does show a rough, positive correlation with log K^{AH} (Figure 4) for L = RS^- and RNH_2, and possibly $RSCH_3$ as well, although again the correlation for L = X-py is inverse. While this line of reasoning may provide a reasonable explanation for the decreased $-\sigma_\beta$ values for the pyridine–liganded cobaloxime centers relative to those with primary amine and thiolate axial ligands, it does not appear to explain the inverse independence of $-\sigma_\beta$ on $-\sigma_I$ (or on log K_f^{AH}) for such chelates.

Effect of Hyperconjugation on Axial Ligation. Rate constants for axial ligand association and dissociation with the (carboxyalkyl)cobaloximes and their conjugate bases are shown in Table IV, and correlations of log K_f and log k_{on} or log k_{off} with pK_L, the pK_a of the conjugate acid of the axial ligand, are shown in Figures 5 and 6, respectively. The slopes and intercepts of these

Table IV. Forward and Reverse Rate Constants for Association of Various Ligands with the (Carboxyalkyl)cobaloximes and Their Conjugate Bases (25.0 ± 0.1 °C, Ionic Strength 1.0 M)

	$HOOCCH_2Co(D_2H_2)L$				$HOOCCH(CH_3)Co(D_2H_2)L$			
ligand	k_{on}^{AH}, M^{-1} s^{-1}	k_{off}^{AH}, s^{-1}	$k_{on}^{A^-}$, M^{-1} s^{-1}	$k_{off}^{A^-}$, s^{-1}	k_{on}^{AH}, M^{-1} s^{-1}	k_{off}^{AH}, s^{-1}	$k_{on}^{A^-}$, M^{-1} s^{-1}	$k_{off}^{A^-}$, s^{-1}
2,2,2-trifluoroethylamine	(2.34 ± 0.25) × 10^{-2}	(2.00 ± 0.16) × 10^{-4}	(5.29 ± 0.20) × 10^{-1}	(7.23 ± 0.19) × 10^{-3}				
2,2-dimethoxyethylamine	(3.95 ± 0.35) × 10^{-2}	(5.71 ± 0.30) × 10^{-6}	(8.21 ± 0.54) × 10^{-1}	(2.83 ± 0.03) × 10^{-4}	(7.07 ± 0.58) × 10^{-1}	(2.97 ± 0.20) × 10^{-4}	(2.18 ± 0.09) × 10	(2.16 ± 0.02) × 10^{-2}
2-methoxyethylamine	(5.22 ± 0.33) × 10^{-2}	(3.60 ± 0.08) × 10^{-6}	(7.18 ± 0.41) × 10^{-1}	(1.33 ± 0.04) × 10^{-4}	1.00 ± 0.09	(1.42 ± 0.10) × 10^{-4}	(3.15 ± 0.15) × 10	(1.25 ± 0.01) × 10^{-2}
n-propylamine					1.19 ± 0.06	(7.88 ± 0.06) × 10^{-5}	(3.52 ± 0.17) × 10	(7.12 ± 0.06) × 10^{-3}
4-cyanopyridine	(3.03 ± 0.04) × 10^{-1}	(7.84 ± 0.16) × 10^{-4}						
4-(carboxamido)pyridine	(5.58 ± 0.18) × 10^{-1}	(6.63 ± 0.22) × 10^{-4}						
pyridine	(5.64 ± 0.21) × 10^{-1}	(9.19 ± 0.22) × 10^{-5}						
4-methylpyridine	(5.95 ± 0.20) × 10^{-1}	(5.78 ± 0.22) × 10^{-5}						
methyl thioacetate	(7.05 ± 0.70) × 10^{2}	(9.00 ± 1.10) × 10^{-5}						
methyl thiopropionate	(3.30 ± 0.10) × 10^{4}	(1.14 ± 0.04) × 10^{-3}						
2 thioethanol	(3.68 ± 0.25) × 10^{4}	(1.80 ± 0.10) × 10^{-3}	(7.33 ± 0.10) × 10	(5.40 ± 0.40) × 10^{-5}				

Table V. Slopes and Intercepts of log K_f, log k_{on}, and log k_{off} vs. pK_L Correlations for the (Carboxyalkyl)cobaloximes ($RCo(D_2H_2)OH_2$) and Various Ligands[a]

R	σ^*[b]	parameter correlatd	L	slope	intercept	N[c]
$^-OOCCH(CH_3)$	−0.25	K_f	RNH_2	0.40 ± 0.04	−0.55 ± 0.34	5
$^-OOCCH(CH_3)$	−0.25	K_f	X-py	0.23 ± 0.02	1.87 ± 0.11	5
$^-OOCCH(CH_3)$	−0.25	K_f	RS^-	0.23 ± 0.06	3.49 ± 0.50	3
$^-OOCCH_2$	0.06	K_f	RNH_2	0.45 ± 0.03	−0.59 ± 0.25	5
$^-OOCCH_2$	0.06	K_f	X-py	0.26 ± 0.03	2.03 ± 0.15	5
$^-OOCCH_2$	0.06	K_f	RS^-	0.19 ± 0.04	4.48 ± 0.36	3
$HOOCCH(CH_3)$	0.75	K_f	RNH_2	0.48 ± 0.05	−0.83 ± 0.45	5
$HOOCCH(CH_3)$	0.75	K_f	X-py	0.30 ± 0.02	1.73 ± 0.11	5
$HOOCCH(CH_3)$	0.75	K_f	RS^-	0.32 ± 0.05	4.02 ± 0.47	3
$HOOCCH_2$	1.05[d]	K_f	RNH_2	0.50 ± 0.03	−0.69 ± 0.27	5
$HOOCCH_2$	1.05[d]	K_f	X-py	0.31 ± 0.03	1.97 ± 0.16	5
$HOOCCH_2$	1.05[d]	K_f	RS^-	0.31 ± 0.06	4.45 ± 0.50	3
$^-OOCCH(CH_3)$	−0.25	k_{on}	RNH_2	0.10 ± 0.04	0.44 ± 0.41	3
$^-OOCCH(CH_3)$	−0.25	k_{off}	RNH_2	−0.25 ± 0.02	0.51 ± 0.19	3
$^-OOCCH_2$	0.06	k_{on}	RNH_2	0.04 ± 0.02	−0.50 ± 0.18	3
$^-OOCCH_2$	0.06	k_{off}	RNH_2	−0.44 ± 0.01	0.33 ± 0.06	3
$HOOCCH(CH_3)$	0.75	k_{on}	RNH_2	0.11 ± 0.03	−1.14 ± 0.32	3
$HOOCCH(CH_3)$	0.75	k_{off}	RNH_2	−0.29 ± 0.05	−0.96 ± 0.45	3
$HOOCCH_2$	1.05[d]	k_{on}	RNH_2	0.08 ± 0.01	−2.11 ± 0.11	3
$HOOCCH_2$	1.05[d]	k_{off}	RNH_2	−0.45 ± 0.04	−1.16 ± 0.34	3
$HOOCCH_2$	1.05[d]	k_{on}	X-py	0.08 ± 0.03	−0.64 ± 0.12	4
$HOOCCH_2$	1.05[d]	k_{off}	X-py	−0.30 ± 0.07	−2.29 ± 0.31	4
$HOOCCH_2$	1.05[d]	k_{on}	RS^-	1.07 ± 0.12	−5.52 ± 1.04	3
$HOOCCH_2$	1.05[d]	k_{off}	RS^-	0.77 ± 0.01	−10.09 ± 0.06	3

[a] All data at 25.0 ± 0.1 °C, ionic strength 1.0 M. [b] Inductive substituent parameter of the organic ligand calculated or taken from ref 36 except as noted. [c] Number of points in the correlation. [d] Reference 41.

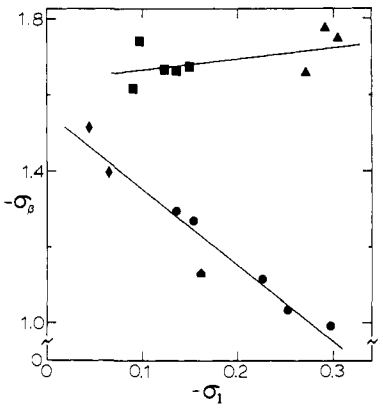

Figure 3. Plot of $-\sigma_\beta$ vs. $-\sigma_I$ (Table I) for cobaloxime-chelated cobalt centers, $-Co(D_2H_2)L$: L = 4-X-py (●), L = R–NH_2 (■), L = RS^- (▲), L = R–S–CH_3 (◆), L = H_2O (▲). The solid lines are least-squares fits according to eq 25: upper line, $m = 0.281 \pm 0.205$, $b = 1.637 \pm 0.041$; lower line, $m = -2.011 \pm 0.219$, $b = 1.554 \pm 0.041$.

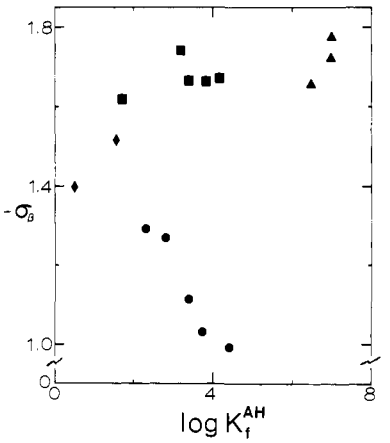

Figure 4. Plot of $-\sigma_\beta$ for cobaloxime-chelated cobalt centers vs. log K_f^{AH} for association of axial ligands with $HOOCCH_2Co(D_2H_2)OH_2$. Symbols are given in legend to Figure 3.

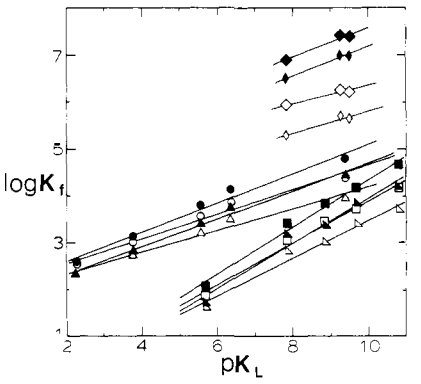

Figure 5. Plots of log K_f^{AH} (solid symbols) and log $K_f^{A^-}$ (open symbols) vs. pK_L, the pK_a of the conjugate acid of the ligand, for association of axial ligands with (carboxyalkyl)cobaloximes: (carboxymethyl)cobaloxime, L = 4-X-py (○, ●), L = R–NH_2 (□, ■), L = RS^- (◇, ◆); (1-carboxyethyl)cobaloxime, L = 4-X-py (△, ▲), L = R–NH_2 (◺, ◣), L = $R–S^-$ (◊, ♦). The solid lines are least-squares fits; slopes and intercepts are given in Table V.

correlations are collected in Table V.

Since the β effect in (1-carboxyalkyl)cobaloximes has been attributed to σ–π conjugation, such complexes might be expected to behave irregularly with respect to reactivity (and other chemical properties) of the cobalt atom. In particular, to the extent that σ–π conjugation depletes electron density on the cobalt atom, it might be expected to enhance the interaction of the cobalt atom with axial ligands, particularly those which are solely σ donors. The effect upon the interaction with those ligands which can act as π acceptors as well as σ donors is more complex since depletion of electron density on cobalt would decrease such π interactions possibly cancelling out the increased σ donation.

Inspection of the slopes and intercepts of the axial ligation rate and equilibrium constant correlations in Table V shows that such an effect can be found. As previously pointed out (see ref 29 and references therein), the slopes of correlations of log K_f with pK_L for primary amines show little or no variation over a wide variety of trans organic ligand ($\sigma^* = 0$ to +0.90), the average value being 0.394 ± 0.016. Although the slopes for the conjugate bases of the (1-carboxyalkyl)cobaloximes (for which σ–π conjugation must surely be diminished relative to the conjugate acids) fall quite close

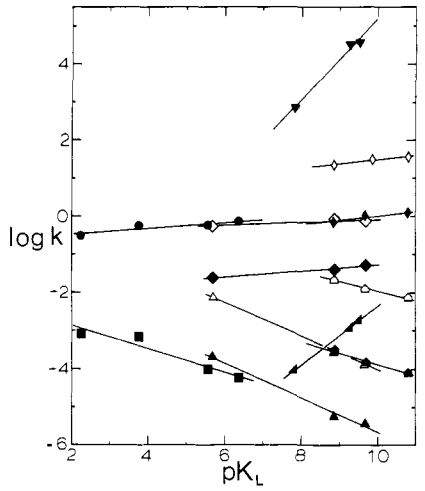

Figure 6. Plots of the logarithms of the rate constants for ligand association and dissociation with (carboxyalkyl)cobaloximes (solid symbols) and their conjugate bases (open symbols) vs. pK_L, the pK_a of the conjugate acid of the ligand: (carboxymethyl)cobaloximes, k_{on}, 4-X-py (●), R–NH_2 (◇, ◆), RS^- (▼), k_{off}, 4-X-py (■), R–NH_2 (△, ▲), RS^- (◢); (1-carboxyethyl)cobaloxime, k_{on}, R–NH_2 (◊, ♦), k_{off}, R–NH_2 (□, ■). The solid lines are least-squares fits; slopes and intercepts are given in Table V.

to this average value (Table V), those for the (1-carboxyalkyl)-cobaloximes themselves are significantly higher. Hence an enhancement of the interaction of β-effect cobalt centers with purely σ-donating primary amine ligands may indeed be operating, at least for the more basic members of the amine series. A similar, but more striking effect can be seen in the k_{off} correlations for the primary amine ligands. In this case, the slopes of the correlations for all the β-effect cobaloximes are quite similar in sign and magntiude to those previously determined for other organocobaloximes but the intercepts for the (1-carboxyalkyl)cobaloximes (and *not* their conjugate bases) are at least 1.5 log units lower. This would tend to indicate a substantial effect of σ–π conjugation on the kinetic stability of the primary amine complexes, although it is not completely clear how much of this effect should be attributed to the inductive effect of the organic ligands involved.[42,43]

We conclude, then, that there appears to be an effect of depletion of cobalt electron density by σ–π conjugation in (1-carboxyalkyl)cobaloximes on reactivity of the cobalt center, but it is difficult to accurately assess its extent with the current data.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, TX (Grant Y-749), and the Organized Research Fund of The University of Texas at Arlington.

Registry No. $HOOCCH_2Co(D_2H_2)(OH_2)$, 60193-28-4; $HOOCCH_2Co(D_2H_2)$((2-methylthio)ethanol), 81956-62-9; $HOOCCH_2Co(D_2H_2)$(methyl (methylthio)acetate), 82010-07-9; $HOOCCH_2Co(D_2H_2)$(4-cyanopyridine), 81970-32-3; $HOOCCH_2Co(D_2H_2)$(4-(carboxamido)pyridine), 81956-63-0; $HOOCCH_2Co(D_2H_2)$(pyridine), 14641-02-2; $HOOCCH_2Co(D_2H_2)$(4-methylpyridine), 81956-64-1; $HOOCCH_2Co(D_2H_2)$(4-aminopyridine), 81970-33-4; $HOOCCH_2Co(D_2H_2)$(2,2,2-trifluoroethylamine), 81956-65-2; $HOOCCH_2Co(D_2H_2)$(glycine ethyl ester), 81956-66-3; $HOOCCH_2Co(D_2H_2)$(2,2-dimethoxyethylamine), 81956-67-4; $HOOCCH_2Co(D_2H_2)$(2-methoxyethylamine), 81956-68-5; $HOOCCH_2Co(D_2H_2)$(*n*-propylamine), 81956-69-6; $HOOCCH_2Co(D_2H_2)$(methyl thioacetate), 81956-70-9; $HOOCCH_2(Co(D_2H_2)$(methyl thiopropionate), 81956-71-0; $HOOCCH_2Co(D_2H_2)$(2-thioethanol), 81956-72-1; $HOOCCH(CH_3)Co(D_2H_2)(OH_2)$, 14637-38-8; $HOOCCH(CH_3)Co(D_2H_2)$((2-methylthio)ethanol), 81956-73-2; $HOOCCH(CH_3)Co(D_2H_2)$(methyl (methylthio)acetate), 81956-74-3; $HOOCCH(CH_3)Co(D_2H_2)$(4-cyanopyridine), 81956-75-4; $HOOCCH(CH_3)Co(D_2H_2)$(4-(carboxamido)pyridine), 81956-76-5; $HOOCCH(CH_3)Co(D_2H_2)$(pyridine), 14643-12-0; $HOOCCH(CH_3)Co(D_2H_2)$(4-methylpyridine), 81956-77-6; $HOOCCH(CH_3)Co(D_2H_2)$(4-aminopyridine), 81956-78-7; $HOOCCH(CH_3)Co(D_2H_2)$(2,2,2-trifluoroethylamine), 81956-79-8; $HOOCCH(CH_3)Co(D_2H_2)$(glycine ethyl ester), 81956-80-1; $HOOCCH(CH_3)Co(D_2H_2)$(2,2-dimethoxyethylamine), 81956-81-2; $HOOCCH(CH_3)Co(D_2H_2)$(2-methoxyethylamine), 81956-82-3; $HOOCCH(CH_3)Co(D_2H_2)$(*n*-propylamine), 81956-83-4; $HOOCCH(CH_3)Co(D_2H_2)$(methyl thioacetate), 81956-84-5; $HOOCCH(CH_3)Co(D_2H_2)$(methyl thiopropionate), 81956-85-6; $HOOCCH(CH_3)Co(D_2H_2)$(2-thioethanol), 81956-86-7; $HOOCCH_2CO_2^-$, 1000-88-0; CH_3COOH, 64-19-7; $C_6H_5CH_2COOH$, 103-82-2; CH_3SCH_2COOH, 2444-37-3; CH_3OCH_2COOH, 625-45-6; $C_6H_5OCH_2COOH$, 122-59-8; ICH_2COOH, 64-69-7; $BrCH_2COOH$, 79-08-3; $ClCH_2COOH$, 79-11-8; $NCCH_2COOH$, 372-09-8; $CH_3CH(CO_2^-)COOH$, 69858-36-2; $CH_3CH(CH_3)COOH$, 79-31-2; $CH_3CH(C_6H_5)COOH$, 492-37-5; $CH_3CH(CH_3S)COOH$, 58809-73-7; $CH_3CH(C_6H_5O)COOH$, 1701-77-5; $CH_3CH(Br)COOH$, 598-72-1; $CH_3CH(Cl)COOH$, 598-78-7; $CH_3CH(H_3N)COOH^+$, 17806-36-9.

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Reactions of B_{12r} with Aliphatic Free Radicals: A Pulse-Radiolysis Study[1]

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Abstract: The spectra of the intermediates formed in the reactions of B_{12r} with the free radicals Br_2^{-}·, CO_2^{-}·, ·$CH_2C(CH_3)_2OH$, ·$C(CH_3)_2OH$, ·CH_2CHO, and ·$CH(OH)CH_2OH$ are reported. The results indicate that Br_2^{-}· oxidizes B_{12r} to B_{12a}, via an inner-sphere mechanism, and CO_2^{-}· reduces B_{12r} to B_{12s}. All the aliphatic free radicals studied, ·R, react with B_{12r}, yielding as the first product a pseudocoenzyme denoted Co^{III}–R. Co^{III}–$CH_2C(CH_3)_2OH$ is stable for over a second in the pH range 3–10 as is Co^{III}–CH_2CHO. The latter compound hydrolyzes in acid solutions to yield B_{12a} and CH_3CHO. Co^{III}–$C(CH_3)_2OH$ and Co^{III}–$CH(OH)CH_2OH$ decompose heterolytically to yield mainly B_{12s}; a side reaction that probably yields Co^{III}–H via a β-hydride shift is also observed. The kinetics of decomposition of Co^{III}–$CH(OH)CH_2OH$ in neutral solutions are reported. No water elimination from the latter intermediate occurs. The reasons for the latter observation are discussed.

There is growing evidence that the mechanism of reaction of enzymes containing the coenzyme derivative of vitamin B_{12} involves free-radical reactions. The mechanism of reaction seems[3-6] to involve first the homolytic Co–C bond cleavage in the coenzyme

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