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Trans Effect in Octahedral Complexes. 2. Correlation of Dissociative Rates of Ligation of Selected *trans*-Bis(dimethylglyoximato)cobalt(III) Complexes in Methanol[1]

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The rates of ligation of a series of trans-substituted methanolbis(dimethylglyoximato)cobalt(III) complexes of the type $R-Co(DH)_2HOCH_3$ ($R = CH_3$, C_6H_5, SO_3, $(CH_3O)_2P(O)$, DH^- = monoanion of dimethylglyoxime) by thiourea and *p*-toluidine in methanol have been studied at 25 °C and at various ionic strengths. R groups were chosen for their known, or suspected, trans-labilizing ability. The ligation rates are all first order in cobalt complex, and in general, observed first-order rate parameters, k^{obsd}, depend on the concentration of entering ligand, L, according to $k^{obsd} = (a + b[L])/(1 + c[L])$. In a few cases, the $c[L]$ denominator term is not experimentally detectable. These data are consistent with the supposition that the ligation reaction proceeds via a dissociative (S_N1) cleavage of the cobalt–methanol bond. Analysis of these results and similar data obtained for $R = CH_3C_6H_4SO_2$ show the specific rates of dissociation of methanol, k_1, to be correlated by a linear free energy relationship (LFER) with σ_p, the Hammett substituent parameter for the labilizing group R. In addition, the specific rates of dissociation, k_4, of thiourea from the ligated products, $R-Co(DH)_2SC(NH_2)_2$, are also correlated by a LFER with σ_p. The slopes and correlation coefficients of the k_1 and k_4 LFER plots are -3.33 ± 0.18, 0.996 and -3.68 ± 0.02, 1.000, respectively. These LFER's show that the relative trans-labilizing ability of the R groups studied (1) is simply determined by the electron-donating ability of R and (2) is independent of the leaving group. The results of this work quantitatively establish a specific kinetic trans effect order for the R groups investigated, i.e., CH_3 (900) > C_6H_5 (300) > SO_3 (100) > $(CH_3O)_2P(O)$ (50) >> $CH_3C_6H_4SO_2$ (1), where the numbers in parentheses represent relative rates for dissociation of coordinated methanol from $R-Co(DH)_2HOCH_3$.

Introduction

In part 1 of this series,[1] the kinetics and equilibria governing ligation of the S-bonded sulfinatocobalt(III) complexes *trans*-$CH_3SO_2Co(DH)_2HOCH_3$ and *trans*-$CH_3C_6H_4SO_2Co(DH)_2HOCH_3$ (DH^- = monoanion of dimethylglyoxime) by several neutral ligands in methanol were investigated. The S-bonded sulfinato groups were observed to produce a significant kinetic trans effect in these complexes. Earlier studies had also shown that S-bonded sulfite,[2] σ-bonded organo ligands,[3] and P-bonded phosphite ligands[4] effect trans labilization in cobalt(III) complexes. However, these studies were conducted on different cobalt(III) complexes under widely varying experimental conditions (solvent, temperature, ionic strength, leaving group, entering group, etc.), making it impossible to quantitatively compare the trans-labilizing abilities of various ligands. Also, these studies have not generally yielded limiting rate data (obtained at high concentration of entering ligand). In the context of the well-established[1-6] (especially by the work of Brown on alkylcobalt(III) complexes[5]) dissociative nature of the cobalt(III) trans-labilization phenomenon, such limiting rate data provide a measure of the first-order rate parameter governing dissociative cleavage of the cobalt–ligand bond. This first-order parameter, rather than the generally obtained second-order parameter which is a complex function of the labilizing, entering, and leaving groups, is needed in order to quantitatively evaluate the trans-labilizing ability of a given ligand.

Therefore, in order to quantitatively assess the trans-labilizing ability of various ligands we have extended our previous study[1] by investigating the ligation kinetics of a series of related trans-substituted methanolbis(dimethylglyoximato)cobalt(III) complexes, $R-Co(DH)_2-HOCH_3$, in which only the identity of the trans-labilizing group, R, is varied. Experimental conditions were the same as those used previously[1] (25 °C, methanol solvent, same entering ligands) and R groups were chosen for their known or suspected trans-labilizing ability. The entering ligands were chosen to be thiourea and *p*-toluidine since (1) our previous work[1] had shown these species to be sufficiently soluble in methanol to allow experimentation in the limiting rate region, (2) these neutral nucleophiles should be less prone to ion-pair formation and salt effects than anionic nucleophiles,[7] and (3) these two ligands provide considerably different properties (hard–soft character, nature of ligating atom, etc.) as attacking nucleophiles. This paper describes, correlates, and interprets the results of these extended studies.

Experimental Section

Materials. Unless otherwise specified, all chemicals were of reagent grade and used without further purification. **Thiourea** was twice recrystallized from methanol and dried in a vacuum desiccator for 48 h. In general, ***p*-toluidine** was twice sublimed under reduced pressure (30–35 °C, 2–5 Torr); in some cases, the material was purified by a literature procedure[8] before sublimation. **Methanol** was fractionally distilled using a 50-cm Vigreaux column, with the middle fraction, bp 64 °C, being retained and stored in dark bottles over Linde 4A molecular sieves.

Preparation of Complexes. In most cases, established literature procedures were used to synthesize the cobalt(III) complexes. The purification of these complexes for use in kinetic experiments and their analytical characterization are described below.

Sodium *trans*-Sulfitoaquobis(dimethylglyoximato)cobaltate(III). The method of Tsiang and Wilmarth[2c] was used to prepare the initial complex $Na[SO_3Co(DH)_2OH_2]\cdot 5H_2O$ (DH^- = monoanion of dimethylglyoxime). The pentahydrate was recrystallized three times from water. Subsequent drying of the complex, under reduced pressure at room temperature, gave a final product which analyzed as the dihydrate. Anal. Calcd for $Na[SO_3Co(C_4H_7N_2O_2)_2OH_2]\cdot 2H_2O$: C, 21.5; H, 4.5; N, 12.6; S, 7.2; Co, 13.2; Na, 5.2. Found: C, 21.5; H, 4.4; N, 12.4; S, 7.0; Co, 13.0; Na, 5.5. Replacement of coordinated water in the above complex by thiourea or *p*-toluidine was easily accomplished by addition of a slight excess of the ligand to a solution of the aquo complex in anhydrous methanol. The ligated product complexes precipitated from solution immediately and were washed once with cold methanol and then dried in a desiccator. Since the solid product complexes were required only for infrared analysis, they were not purified further.

***trans*-Methylaquobis(dimethylglyoximato)cobalt(III).** The procedure of Schrauzer and Windgassen[9a] was used to prepare *trans*-$CH_3Co(DH)_2(NC_5H_5)$. The pyridine complex was converted to the aquo complex by warming the former in a 95:5 methanol–water solution containing an excess of dimethyl sulfate. On partial removal of solvent and cooling, dark red-orange crystals of $CH_3Co(DH)_2OH_2$ were formed. The product was twice recrystallized from water and dried under reduced pressure at room temperature. Anal. Calcd for $CH_3Co(C_4H_7N_2O_2)_2OH_2$: C, 33.6; H, 6.0; N, 17.4; Co, 18.3. Found: C, 33.5; H, 6.1; N, 17.3; Co, 18.2.

***trans*-Phenylaquobis(dimethylglyoximato)cobalt(III).** The pyridine complex $C_6H_5Co(DH)_2(NC_5H_5)$ was prepared using the procedure of Schrauzer.[9b] Treatment of this complex with excess dimethyl sulfate in aqueous methanol, as above, gave the desired complex, C_6H_5-$Co(DH)_2OH_2$, which was then twice recrystallized from aqueous methanol. Anal. Calcd for $C_6H_5Co(C_4H_7N_2O_2)_2OH_2$: C, 43.8; H, 5.5; N, 14.6; Co, 15.3. Found: C, 43.6; H, 5.5; N, 14.8; Co, 15.1.

Other Cobalt(III) Complexes. In some cases, the ligated products were not isolated but were generated in solutions containing a specific concentration of the starting complexes by addition of an excess of the appropriate nucleophile. Ultraviolet and visible spectra of most of the ligated species were obtained in this manner. The sample of ***trans*-dimethylphosphonatoaquobis(dimethylglyoximato)cobalt(III)** used in this study was the gracious gift of Professor L. G. Marzilli, Johns Hopkins University.[4] This complex was dried for 48 h under vacuum at room temperature.

Equipment. Infrared spectra were obtained using a Beckman IR-12 spectrophotometer (Nujol, KBr disks). ^{1}H NMR spectra were obtained using a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. Visible and ultraviolet spectra were recorded on a Cary 14 spectrophotometer under ambient conditions. All kinetic experiments were performed on a Durrum D-150 stopped-flow spectrophotometer which was equipped with a Durrum D-131 photometric log amplifier. The Durrum unit was interfaced with a Lockheed MAC 16 computer for data acquisition. The thermostated cell compartment and mixing chamber of the stopped-flow system were maintained at 25.0 °C. In addition, equilibrium constants for selected reactions were determined from spectral data obtained using the stopped-flow unit.

Kinetic Procedures. Solutions of the starting complexes in anhydrous methanol were prepared approximately 0.5–1 h before use. Solutions of the nucleophiles in anhydrous methanol were prepared and used within 24 h. Both cobalt(III) and ligand solutions were handled in subdued light and purged for 15–20 min with dry nitrogen which had been passed through a 2-ft column of P_2O_5 and a column of anhydrous methanol. The concentration of nucleophiles was always greater than 20 times that of the cobalt complexes which was generally in the range of 10^{-3} to 10^{-5} M. For studies at 0.1 and 1.0 M ionic strengths, stock solutions of the complexes and nucleophiles were prepared and made up to contain the appropriate concentration of lithium perchlorate. Reagent solutions, at the same ionic strength as the stock solutions, were prepared by dilution of an appropriate volume of the stock solutions with a methanolic solution of lithium perchlorate at the same ionic strength. The reactions were followed by monitoring either the near-ultraviolet charge-transfer band or the visible d–d bands of the initial or product complex. Within experimental error, no wavelength dependency of the reaction rates was observed.

Data Analysis. Observed pseudo-first-order rate constants (k^{obsd}) were obtained by a nonlinear treatment of the optical density (OD_t) vs. time data for 4–5 half-lives. The nonlinear treatment was employed because of the possibility of complications arising from slow photodecomposition of the product complexes, and the possibility of subsequent reaction of the initial product complexes to form the bis-substituted complexes. The raw kinetic data were fitted to the expression

$$\text{OD}_t = \text{OD}_\infty + (\text{OD}_0 - \text{OD}_\infty)\exp(-k^{\text{obsd}}t) \qquad (1)$$

by the LASL nonlinear least-squares program[10] which had been modified somewhat for these studies. Rate parameters calculated by using the standard log ($\text{OD}_t - \text{OD}_\infty$) vs. time method and/or the Kezdy time-lag method[11] were used as initial parameter estimates for the nonlinear routine. In general, the results from each method were the same within experimental error, as was the case for replicate experiments. Each reported value for k^{obsd} represents the mean value for 5–10 single determinations; the standard deviation from this mean, σ_k, is also recorded and is used as an estimate of the error in k^{obsd}. The k^{obsd}–[L] data (L = nucleophile) were treated by either of two methods. Data which reflected a linear dependence of k^{obsd} on the concentration of entering ligand were treated according to the two-term expression

$$k^{\text{obsd}} = a + b[\text{L}] \qquad (2)$$

by weighted linear least-squares analysis, with each k^{obsd} value being weighted by $1/\sigma_k^2$. For systems which exhibited nonlinear k^{obsd}–[L] plots, the data were fitted to the functional form

$$k^{\text{obsd}} = (A + BC[\text{L}])/(1 + C[\text{L}]) \qquad (3)$$

by the LASL program, each value of k^{obsd} again being weighted as $1/\sigma_k^2$. Initial parameter estimates for this analysis were obtained from double-reciprocal plots of $1/k^{\text{obsd}}$ vs. $1/[\text{L}]$. The functional form of eq 3 was also used to fit the spectrophotometric $\text{OD}_{[\text{L}]}$–[L] data for evaluation of equilibrium quotients for selected systems. All errors reported in this work are single standard deviations resulting from weighted least-squares treatment of the data.

Equilibrium Data. For selected systems, equilibrium quotients were determined from spectrophotometric data taken at 25 °C in methanol solutions containing a constant amount of the initial complex and varying excess concentrations of the entering ligand (L). The rapid approach to equilibrium was monitored using the stopped-flow apparatus, a technique which minimizes problems due to subsequent ligation of the R–Co(DH)$_2$–L product to give $[\text{L–Co(DH)}_2\text{–L}]^+$ complexes. The spectrophotometric data were treated according to the expression

$$\frac{\text{OD}_{[\text{L}]} - \text{OD}_0}{l[\text{Co}^{\text{III}}]_{\text{tot}}} = \frac{(\epsilon_{\text{L}} - \epsilon_{\text{S}})Q[\text{L}]}{1 + Q[\text{L}]}$$

where $\text{OD}_{[\text{L}]}$ and OD_0 represent the optical density of the solution in the presence and absence, respectively, of added L, ϵ_{L} and ϵ_{S} are extinction coefficients of product and starting complexes, respectively, l is the path length, $[\text{Co}^{\text{III}}]_{\text{tot}}$ is the total concentration of cobalt(III), and Q represents the equilibrium quotient.

Results and Discussion

Characterization of Complexes. For most cases, the initial cobalt(III) complexes used in this study have been well characterized in previous reports (see Experimental Section). The trans stereochemistry of the axial ligands and the planarity of the Co(DH)$_2$ moiety have been well established on the basis of ^{1}H NMR spectra which show only one type of dimethylglyoximato CH_3 resonance[1] and on the basis of infrared[2c,12] and x-ray[13] analyses which confirm the presence of the O–H- - -O bridging groups in the planar ligand system. Sulfur bonding by the sulfito and thiourea ligands and phosphorus bonding by the phosphonate ligands are established by ultraviolet,[14,15] infrared,[14,16] and kinetic[16b] evidence. The ^{1}H NMR spectra of our complexes[14] are entirely consistent with previously reported, and extensively correlated, spectra;[1,17-20] ^{1}H NMR data are given in Table I.[21]

Stoichiometry. The kinetic results presented below show that the ligand situated trans to the R groups used in this work is labile on the time scale of seconds. Therefore, when the trans-substituted aquobis(dimethylglyoximato)cobalt(III) starting complexes are dissolved in anhydrous methanol (total cobalt concentration 10^{-3} to 10^{-5} M), the coordinated water is rapidly and essentially completely replaced by methanol. The net ligation reactions studied in this work may therefore be described as an approach to the equilibrium

$$\text{R–Co(DH)}_2\text{–HOCH}_3 + \text{L} = \text{R–Co(DH)}_2\text{–L} + \text{CH}_3\text{OH} \qquad (4)$$

where L = thiourea or *p*-toluidine. Values of Q, the equilibrium quotient governing reaction 4, are calculated from the raw data given in Table IIb[21] and are listed in the last column of Table III. The discrepancies between Q values obtained in this fashion and those obtained from kinetic data (see below and Table III) may be ascribed to systematic errors in the two procedures which are not reflected in the calculated standard deviations; e.g. the values of Q from kinetic data are calculated as the ratio of two numbers that have a correlation coefficient of 1.00.[1] Such discrepancies between spectrophotometrically and kinetically derived equilibrium quotients are commonly encountered.[1,3e]

Kinetics and Mechanism of Ligation. Under conditions of large excesses of entering ligand, the ligation of RCo(DH)$_2$HOCH$_3$ (R = CH_3, C_6H_5, SO_3, $(CH_3O)_2P(O)$) by thiourea and *p*-toluidine in methanol at 25 °C is first order in cobalt complex for more than 4 half-lives. Table IIa[21] gives a compilation of observed rate parameters, k^{obsd}, for the ligation reactions as a function of R, entering ligand (L), and ionic strength. For a few cases k^{obsd} values exhibit a linear dependence on the concentration of entering ligand, [L], the data being adequately described by the relation $k^{\text{obsd}} = a + b[\text{L}]$

Table III. Calculated Rate and Equilibrium Parameters for Ligation of $RCo(DH)_2HOCH_3$ in Methanol at 25 °C as a Function of R, Entering Ligand (L), and Ionic Strength

R	L	μ,[a] M	A, s^{-1}	B, s^{-1}	BC, M^{-1} s^{-1}	C, M^{-1}	$10^{-2}Q$(kinetic),[b] M^{-1}	$10^{-2}Q$(spectral),[c] M^{-1}
CH_3	$SC(NH_2)_2$	0.0	0.21 ± 0.02	(2.1 ± 0.2) × 10^2		0.22 ± 0.02	2.3 ± 0.1	1.07 ± 0.01
		0.1	0.13 ± 0.03	(2.0 ± 0.2) × 10^2		0.24 ± 0.03	3.7 ± 0.9	
		1.0	0.14 ± 0.02	(3.5 ± 0.3) × 10^2		0.17 ± 0.02	4.4 ± 0.8	
CH_3	p-$CH_3C_6H_4NH_2$	0.0		(2.1 ± 0.2) × 10^2		0.13 ± 0.01		4.7 ± 0.2
		0.1		(5.4 ± 1.1) × 10^2		(5.1 ± 0.1) × 10^2		
		1.0		(3.0 ± 0.3) × 10^2		0.11 ± 0.01		
SO_3	$SC(NH_2)_2$	~0.0		24.6 ± 0.5[e]		4.7 ± 0.3		6.1 ± 0.1
		0.1		24.7 ± 0.8		2.8 ± 0.2		
		1.0		34.6 ± 1.7		0.75 ± 0.05		
SO_3	p-$CH_3C_6H_4NH_2$	~0.0			65.2 ± 0.7			8.5 ± 1.1
		0.1			36.6 ± 0.4			
C_6H_5	$SC(NH_2)_2$	0.0	(5.4 ± 1.6) × 10^{-2}	75.6 ± 5.8		0.20 ± 0.02	2.8 ± 0.9	1.06 ± 0.01
	p-$CH_3C_6H_4NH_2$	0.0	(4.4 ± 1.1) × 10^{-2}	(1.55 ± 0.34) × 10^2		(5.4 ± 1.1) × 10^{-2}		
$(CH_3O)_2PO$	$SC(NH_2)_2$	0.0	(5.5 ± 0.2) × 10^{-3}	12.0 ± 0.4		0.14 ± 0.01	3.0 ± 0.2	
	p-$CH_3C_6H_4NH_2$	0.0			(8.2 ± 0.1) × 10^{-1}			
p-$CH_3C_6H_4SO_2$[d]	$SC(NH_2)_2$	0.0		(2.22 ± 0.13) × 10^{-1}		(5.64 ± 0.49) × 10^{-1}		
	p-$CH_3C_6H_4NH_2$	0.0		(2.09 ± 0.19) × 10^{-1}		(4.00 ± 0.46) × 10^{-1}		

[a] Ionic strength ($LiClO_4$). [b] Calculated from $Q = BC/A$. [c] Calculated from spectral data. [d] Data from ref 1. [e] Replicate experiment yielded a value of 22.9 ± 0.7 s^{-1}.

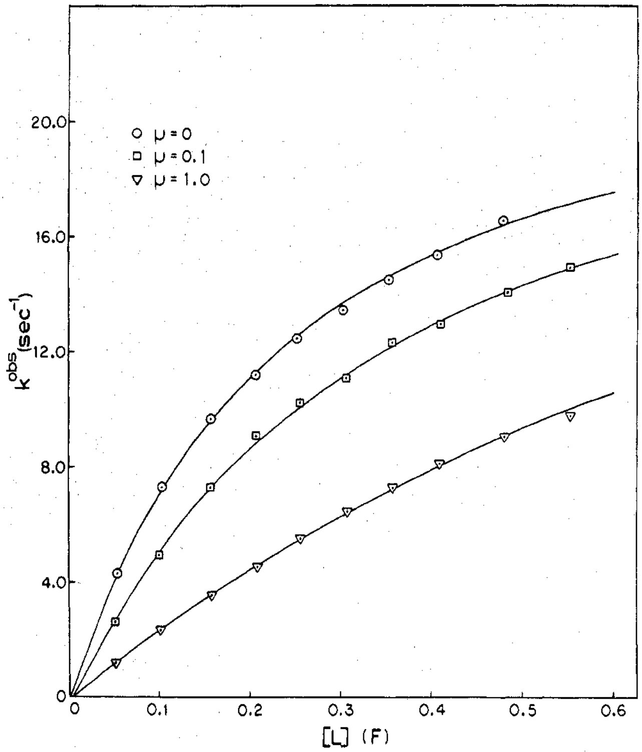

Figure 1. k^{obsd} vs. [L] for the reaction of thiourea with sodium *trans*-sulfito(methanol)bis(dimethylglyoximato)cobaltate(III) in methanol at 25.0 °C as a function of ionic strength (μ, $LiClO_4$). Indicated curves are calculated from eq 5 using the calculated parameters of Table III.

(eq 2). Values of a and b, calculated by a weighted least-squares analysis, are summarized in Table III as a function of R, L, and ionic strength. In most cases, the k^{obsd}–[L] data exhibit nonlinear, rate-limiting behavior at high [L] and are adequately described by the expression

$$k^{obsd} = \frac{A + BC[L]}{1 + C[L]} \qquad (5)$$

It can be seen that the linear relationship (eq 2) represents a special case of eq 5, for the condition $C[L] << 1$, and therefore $b = BC$ and $a = A$. Calculated values of A, B, and C, as a function of R, L, and ionic strength, are summarized in Table III. Figures 1 and 2[21] illustrate the rate-limiting behavior of the k^{obsd}–[L] data for ligation of the complexes where R = SO_3 and CH_3, respectively, by thiourea in methanol at 25 °C. A similar plot for L = p-toluidine and R = CH_3 is illustrated in Figure 3.[21]

The algebraic form of the general rate law expressed by eq 5 is consistent with either a limiting S_N1 mechanism or an outer-sphere association (I_d) process.[1,22] As indicated previously,[1] for substitution reactions of the nature presented in this work, only these two mechanisms are sufficiently plausible to warrant consideration. The S_N1 mechanism postulates the rapid and reversible dissociation of the initial six-coordinated complex to give a highly reactive five-coordinated species which is then attacked by the entering ligand to generate the product complex

$$R\text{-}Co(DH)_2\text{-}HOCH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R\text{-}Co(DH)_2 + CH_3OH$$

$$R\text{-}Co(DH)_2 + L \underset{k_4}{\overset{k_3}{\rightleftharpoons}} R\text{-}Co(DH)_2\text{-}L$$

Assuming a steady state for $RCo(DH)_2$, with pseudo-first-order excess of L, this mechanism leads to the expression

$$k^{\text{obsd}} = \frac{k_4 + k_1(k_3/k_2')[\text{L}]}{1 + (k_3/k_2')[\text{L}]} \tag{6}$$

$$k_2' = k_2[\text{CH}_3\text{OH}]$$

where, from eq 5, $A = k_4$, $B = k_1$, $C = k_3/k_2'$, and $Q = k_1k_3/k_2'k_4 = BC/A$. The outer-sphere I_d process involves the diffusion-controlled formation of an outer-sphere complex, followed by the rate-determining interchange of leaving and entering groups between the inner and outer coordination spheres of this complex

$$\text{R-Co(DH)}_2\text{-HOCH}_3 + \text{L} \overset{K_{\text{os}}}{\rightleftharpoons} \text{R-Co(DH)}_2\text{-HOCH}_3\text{, L}$$

$$\text{R-Co(DH)}_2\text{-HOCH}_3\text{, L} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \text{R-Co(DH)}_2\text{-L} + \text{CH}_3\text{OH}$$

When L is present in pseudo-first-order excess, this mechanism leads to the expression

$$k^{\text{obsd}} = \frac{k_6' + (k_5 + k_6')K_{\text{os}}[\text{L}]}{1 + K_{\text{os}}[\text{L}]} = k_6' + \frac{k_5K_{\text{os}}[\text{L}]}{1 + K_{\text{os}}[\text{L}]} \tag{7}$$

$$k_6' = k_6[\text{CH}_3\text{OH}]$$

where, from eq 5, $A = k_6'$, $B = (k_5 + k_6')$, $C = K_{\text{os}}$, and $Q - k_5k_{\text{os}}/k_6' = (B - A)C/A$. It is very difficult to definitively distinguish between these two mechanistic possibilities. However, the data of Table III may be used to construct indirect arguments which strongly indicate, but do not prove, the operation of the S_N1 mechanism in ligation of the $(\text{dmg})_2\text{Co}^{\text{III}}$ complexes studied in this, and our previous,[1] work.

(1) The limiting S_N1 formalism requires the limiting dissociation rates, k_1, to be independent of the nature of the entering group, L, whereas the I_d mechanism predicts a limiting rate, $k_5 + k_6'$, both terms of which could exhibit a dependency on the incoming ligand. The calculated limiting rates, B, of Table III are clearly independent of the nature of the entering ligand. While this equivalency of limiting rates could occur fortuitously within the I_d scheme, in recent reports on similar systems in which the outer-sphere mechanism was proposed, limiting rates varied significantly with the nature of the entering group.[23]

(2) In order to minimize the electrostatic driving forces for formation of outer-sphere complexes, the systems chosen for study in this work involve neutral ligands and, except for the sulfito complex, neutral substrates. In the case of the anionic sulfito complex, outer-sphere association between the complex and dipolar ligands is of course quite possible. However, if the I_d mechanism is operative, then the empirical parameter C (Table III) corresponds to K_{os}, a quantity which can be calculated on the basis of a simple ion–dipole interaction.[24] The value of K_{os} calculated from the interaction between the sulfito complex and thiourea (dipole moment 4.93 D[25]) at a distance of 4 Å in methanol (dielectric constant 32.6[26]) at 25 °C is 0.50 M^{-1}, an order of magnitude smaller than the observed value of $C = 4.7\ \text{M}^{-1}$ at $\mu = 0.0$ M. This difference is much larger than usually observed for similar association reactions.[27]

(3) Figures 1–3[21] and the data of Table III show that the ionic strength (μ) dependence for ligation of the anionic sulfito complex by thiourea is much greater than that for ligation of the neutral methyl complex. All of the ionic strength dependence for the anionic complex appears in the C parameter, the B term being essentially independent of μ. Within either mechanism, it is expected that the C parameter for the anionic complex would be more sensitive to μ than would be the C parameter for the neutral complex. However, the parameter B, which represents k_1 in the S_N1 process, or $(k_5 + k_6')$ in the I_d process, can only be reasonably anticipated to be independent of μ if the S_N1 mechanism is operative; the rate of dissociative cobalt–methanol bond fission, k_1, is expected to be independent of μ, whereas the rates of interchange between inner and outer coordination spheres, k_5 and k_6, would be expected to be strongly dependent on μ. Therefore, the detailed ionic strength dependence of ligation rates are in harmony with the predictions of the S_N1 mechanism but are difficult to rationalize within the I_d mechanism.

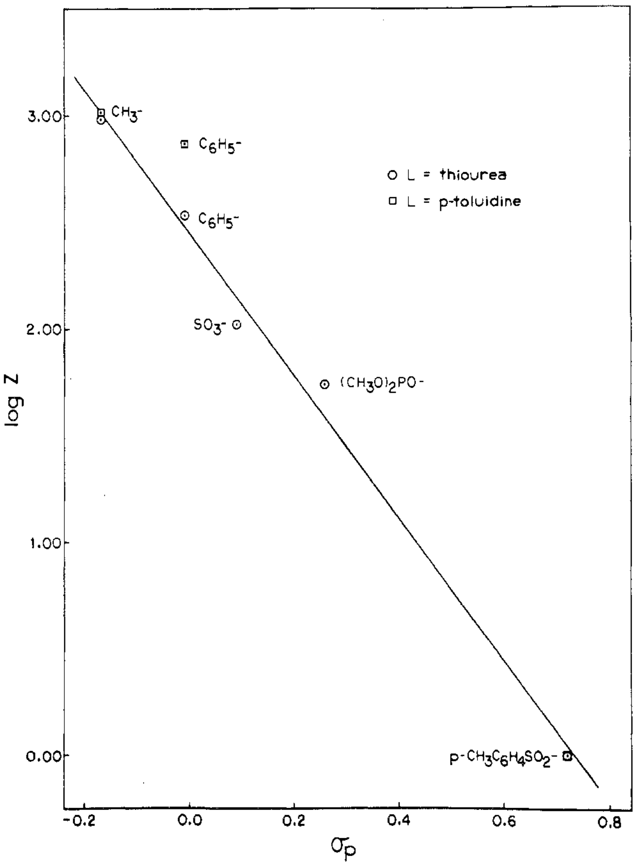

Figure 4. log Z vs. σ_p for the R group in $\text{R-Co(DH)}_2\text{HOCH}_3$, where Z is the relative dissociation rate, $k_{1(\text{R})}/k_{1(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2)}$, for dissociative ($S_N1$) cleavage of the cobalt–methanol bond in methanol at 25.0 °C; R = CH_3, C_6H_5, SO_3, $(\text{CH}_3\text{O})_2\text{PO}$, $p\text{-CH}_3\text{C}_6\text{H}_5\text{SO}_2$. Entering ligands are thiourea and p-toluidine. Calculated line is log $Z = (2.45 \pm 0.06) - (3.33 \pm 0.18)\sigma_p$. Data are from Table V.

Correlation of Trans Labilization in *trans*-Bis(dimethylglyoximato)cobalt(III) Complexes. After an extensive review, Pratt and Thorp[28] have concluded that in cobalt(III) complexes the influence of a ligand on its complex is primarily determined by the amount of electron density donated to the cobalt "via the σ bond". While this conclusion is commonly accepted on a qualitative level, its quantitative assessment in terms of trans labilization, requires rate data which accurately reflect the influence of the labilizing ligand on substitution rates. For a dissociative (S_N1) process the appropriate parameter is k_1, the specific rate of cobalt–ligand bond cleavage. Table IV[21] lists calculated k_1 values for $\text{RCo(DH)}_2\text{HOCH}_3$ in methanol at 25 °C, along with Hammett substituent parameters,[29] σ_p and σ_p^-, for the R group (R = CH_3, C_6H_5, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$, SO_3, and $(\text{CH}_3\text{O})_2\text{P(O)}$). The σ_p values for R = $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ and $(\text{CH}_3\text{O})_2\text{P(O)}$ have been approximated as those determined for CH_3SO_2 and HPO_3, respectively. A plot of relative trans-labilizing ability, in terms of log Z ($Z = k_{1(\text{R})}/k_{1(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2)}$), vs. σ_p for the R group is shown in Figure 4. The observed correlation of rates is quite good considering the two approximations involved. The weighted linear least-squares analysis of this plot gives

$$\log Z = (2.45 \pm 0.06) - (3.33 \pm 0.18)\sigma_p \tag{8}$$

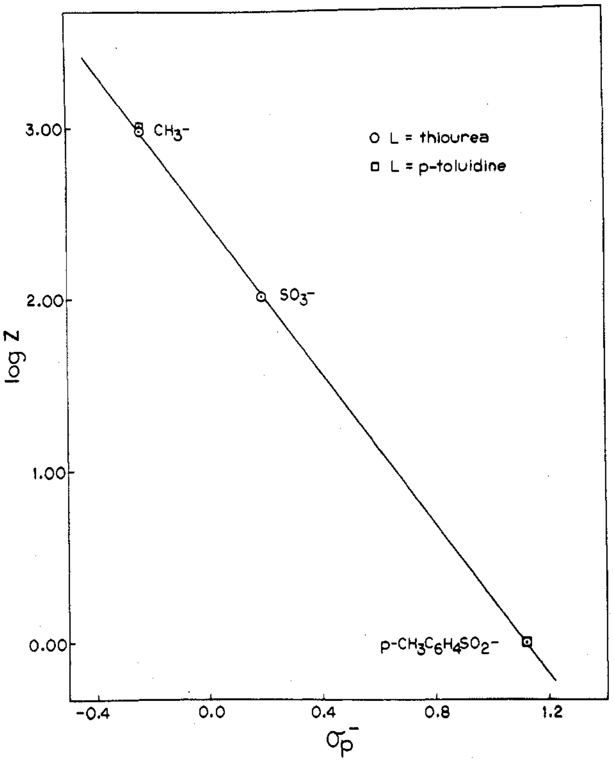

Figure 5. log Z vs. σ_p^- for the R group in R–Co(DH)$_2$HOCH$_3$, where Z is the relative dissociation rate, $k_{1(R)}/k_{1(p\text{-}CH_3C_6H_4SO_2)}$, for dissociative ($S_N1$) cleavage of the Co–methanol bond in methanol at 25.0 °C; R = CH_3, SO_3, p-$CH_3C_6H_4SO_2$. Entering ligands are thiourea and p-toluidine. Calculated line is log Z = (2.45 ± 0.01) – (2.19 ± 0.02)σ_p^-. Data are from Table V.

with a correlation coefficient of 0.996. This analysis is based only on data for reactions with thiourea as entering ligand, since this represents a complete series. However, the adequate fit of the p-toluidine data, where available, is clear. A slightly improved correlation is obtained when log Z is plotted vs. σ_p^- for the R group, as illustrated in Figure 5. The weighted linear least-squares analysis of this plot yields

$$\log Z = (2.45 \pm 0.01) - (2.19 \pm 0.02)\sigma_p^- \qquad (9)$$

with a correlation coefficient of 1.000. Unfortunately, σ_p^- values are not available for all R groups. The linear free energy correlations (LFER) of Figures 4 and 5 illustrate quite dramatically that relative trans labilization in the cobalt(III) complexes studied is determined by the electron-donating ability of the labilizing group. This becomes even more apparent when the rate constants for dissociation, k_4, of thiourea from RCo(DH)$_2$SC(NH$_2$)$_2$ (R = CH_3, C_6H_5, and $(CH_3O)_2P(O)$) are plotted as log Z' ($Z' = k_{4(R)}/k_{4((CH_3O)_2PO)}$ vs. σ_p, as illustrated in Figure 6. The weighted linear least-squares analysis of this plot yields

$$\log Z' = (0.96 \pm 0.03) - (3.68 \pm 0.02)\sigma_p \qquad (10)$$

with a correlation coefficient of 1.000. The similarity of the slopes of the plots of Figures 4 and 6 (3.33 ± 0.18 and 3.68 ± 0.02, respectively) indicate that the relative trans-labilizing ability of the R group is independent of the nature of the leaving group.

In summary, a specific kinetic trans-effect order, R = CH_3 (900) > C_6H_5 (300) > SO_3 (100) > $(CH_3O)_2P(O)$ (50) >> p-$CH_3C_6H_4SO_2$ (1), where the numbers in parentheses represent relative dissociation rates, has been obtained from a quantitative evaluation of the limiting S_N1 rates of dissociation of coordinated methanol from the complexes RCo(DH)$_2$HOCH$_3$ in methanol at 25 °C. This order encompasses a range of almost 10^3 in dissociation rates and involves ligands with three different atoms bonded to cobalt but yet is quantitatively correlated with the simple Hammett substituent parameters of the various R groups.

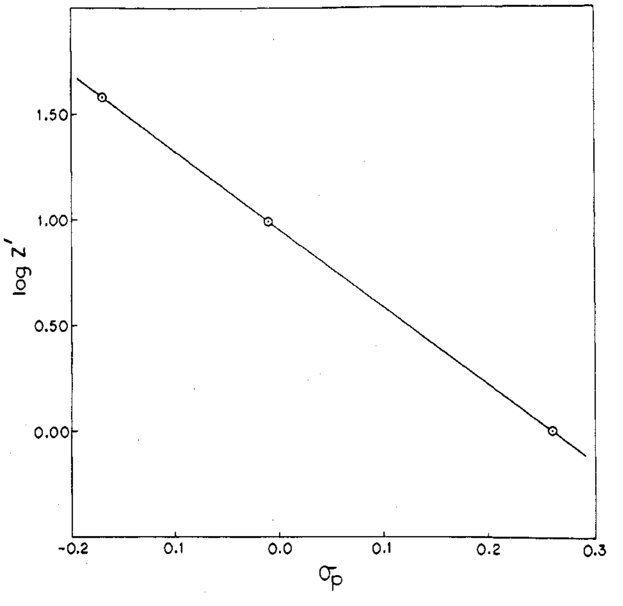

Figure 6. log Z' vs. σ_p for the R group in R–Co(DH)$_2$SC(NH$_2$)$_2$, where Z' is the relative dissociation rate, $k_{4(R)}/k_{4((CH_3O)_2PO)}$, for dissociative ($S_N1$) cleavage of the cobalt–thiourea bond in methanol at 25.0 °C; R = CH_3, C_6H_5, $(CH_3O)_2PO$. Calculated line is log Z' = (0.96 ± 0.03) – (3.68 ± 0.02)σ_p. Data are from Table V.

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Registry No. CH$_3$Co(DH)$_2$HOCH$_3$, 50600-25-4; SO$_3$Co(DH)$_2$HOCH$_3$, 63122-49-6; C$_6$H$_5$Co(DH)$_2$HOCH$_3$, 63122-93-0; (CH$_3$O)$_2$POCo(DH)$_2$HOCH$_3$, 63122-94-1; C$_6$H$_5$Co(DH)$_2$DMSO-d_6, 63148-37-8; CH$_3$Co(DH)$_2$DMSO-d_6, 63148-38-9; SO$_3$Co(DH)$_2$DMSO-d_6, 63122-50-9; (CH$_3$O)$_2$POCo(DH)$_2$DMSO-d_6, 63122-51-0; C$_6$H$_5$Co(DH)$_2$SC(NH$_2$)$_2$, 63122-95-2; CH$_3$Co(DH)$_2$SC(NH$_2$)$_2$, 63122-96-3; SO$_3$Co(DH)$_2$SC(NH$_2$)$_2$, 23329-61-5; (CH$_3$O)$_2$POCo(DH)$_2$SC(NH$_2$)$_2$, 63122-97-4; C$_6$H$_5$Co(DH)$_2$-p-CH$_3$C$_6$H$_4$NH$_2$, 63122-98-5; CH$_3$Co(DH)$_2$-p-CH$_3$C$_6$H$_4$NH$_2$, 30975-00-9; SO$_3$Co(DH)$_2$-p-CH$_3$C$_6$H$_4$NH$_2$, 63122-52-1; (CH$_3$O)$_2$POCo(DH)$_2$-p-CH$_3$C$_6$H$_4$NH$_2$, 63122-99-6; SC(NH$_2$)$_2$, 62-56-6; p-CH$_3$C$_6$H$_4$NH$_2$, 106-49-0; Na[SO$_3$Co(DH)$_2$OH$_2$], 23490-08-6; *trans*-CH$_3$Co(DH)$_2$(NC$_5$H$_5$), 23642-14-0; CH$_3$Co(DH)$_2$OH$_2$, 25360-55-8; C$_6$H$_5$Co(DH)$_2$OH$_2$, 29156-99-8; C$_6$H$_5$Co(DH)$_2$(NC$_5$H$_5$), 29130-85-6.

Supplementary Material Available: Table I giving ^{1}H NMR spectral data, Table IIa which gives observed first-order rate parameters for reaction 4 as a function of L, R, [L], and ionic strength, Table IIb which gives equilibrium optical densities as a function of L, R, and [L], Table IV summarizing S_N1 dissociation rates as a function of Hammett substituent parameters, and Figures 2 and 3 showing plots of k^{obsd} vs. [L] for the ligation of *trans*-methyl(methanol)bis(dimethylglyoximato)cobalt(III) at 25.0 °C as a function of ionic strength (13 pages). Ordering information is given on any current masthead page.

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Alkoxyfluorophosphoranes. 3. Synthesis and Characterization of Some Di-, Tri-, and Tetraalkoxyfluorophosphoranes

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Several dialkoxyfluorophosphoranes $PhPF_2(OR)_2$ (R = CH_2CCl_3, CH_2CHCl_2, $CH(CH_3)(CN)$, CH_2CF_3) and $MePF_2(OCH_2CF_3)_2$ have been isolated and characterized by NMR, IR, and mass spectrometry and elemental analysis. Their formation can be facilitated by the disproportionation reaction $2R'PF_3(OR) \rightarrow R'PF_2(OR)_2 + R'PF_4$. These compounds are stable with respect to both further disproportionation and decomposition into phosphonates. The tetraalkoxyphosphorane $PhP(OCH_2CF_3)_4$ has also been isolated. Trialkoxyfluorophosphoranes $PhPF(OR)_3$ (R = CH_2CCl_3, CH_2CHCl_2, $CH(CH_3)(CN)$, CH_2CF_3) and $MePF(OCH_2CF_3)_3$ have been identified in mixtures but could not be separated from the other members of the $R'PF_{4-n}(OR)_n$ series.

Introduction

Phosphoranes containing simultaneously fluorine atoms and alkoxy groups were generally found to be unstable with respect to their decomposition into phosphoryl compounds according to[1,2]

$$R'PF_3(OR) \rightarrow R'P(O)F_2 + RF \tag{1}$$

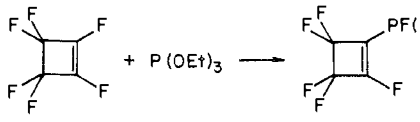
We have shown[3] that they could be stabilized by introducing electron-withdrawing substituents in the alkoxy moiety, and we have recently reported the preparation of a series of stable monoalkoxyfluorophosphoranes[4] through the general reaction[5]

$$R'PF_4 + (CH_3)_3SiOR \rightarrow R'PF_3(OR) + (CH_3)_3SiF \tag{2}$$

We now wish to report the preparation and isolation of several stable dialkoxydifluorophosphoranes of type $R'PF_2(OR)_2$ and of the tetraalkoxyphosphorane $PhP(OCH_2CF_3)_4$ as well as the identification of several trialkoxyfluorophosphoranes of type $R'PF(OR)_3$ which, although they could not be isolated in a pure form, were unambiguously characterized both by spectral determinations and by their transformation into the corresponding dialkoxydifluorophosphoranes.

Previous studies in the literature which produced nonionic multialkoxyfluorophosphoranes stable at room temperature appear to be limited to[6,7]

$$PF_3Cl_2 + 2\,t\text{-}C_4F_9OCl \longrightarrow (t\text{-}C_4F_9O)_2PF_3 + 2Cl_2$$



On the other hand, the related aryloxyfluorophosphoranes were found to be more stable than their alkoxy analogues.[8,9]

Experimental Section

All manipulations of fluorophosphoranes were carried out under a dry nitrogen atmosphere. Reactions involving CH_3PF_4 were carried