

making her data available before publication. We are also indebted to Dr. William Movius for valuable discussions.

Registry No. (Benzoato)(NH₃)₅Co^{III}, 30931-77-2; (*o*-iodobenzoato)(NH₃)₅Co^{III}, 31060-39-6; (*o*-bromobenzoato)(NH₃)₅Co^{III}, 31060-38-5; (*o*-chlorobenzoato)(NH₃)₅Co^{III}, 52950-67-1; (*o*-fluorobenzoato)(NH₃)₅Co^{III}, 46503-45-1; (*p*-methoxybenzoato)(NH₃)₅Co^{III}, 52950-68-2; (*o*-methylbenzoato)(NH₃)₅Co^{III}, 30931-78-3; (5-sulfosalicylato)(NH₃)₅Co^{III}, 52950-70-6; (pentafluorobenzoato)(NH₃)₅Co^{III}, 52950-69-3; (*p*-sulfobenzoato)(NH₃)₅Co^{III}, 31060-43-2; (*o*-thiomethylbenzoato)(NH₃)₅Co^{III}, 51965-42-5; (*m*-sulfobenzoato)(NH₃)₅Co^{III}, 52950-71-7; (*o*-fluorophenylacetato)(NH₃)₅Co^{III}, 52950-72-8; (*o*-methoxybenzoato)(NH₃)₅Co^{III}, 31083-91-7; (*p*-fluorophenylacetato)(NH₃)₅Co^{III}, 52950-73-9; (*o*-sulfobenzoato)(NH₃)₅Co^{III}, 31060-45-4; (sulfoacetato)(NH₃)₅Co^{III}, 31083-92-8; (acrylato)(NH₃)₅Co^{III}, 44982-34-5; (*m*-methoxycinnamato)(NH₃)₅Co^{III}, 52993-09-6; (*o*-hydroxycinnamato)(NH₃)₅Co^{III}, 46913-88-6; (*p*-hydroxycinnamato)(NH₃)₅Co^{III}, 46922-32-1; (β -styrylacrylato)(NH₃)₅Co^{III}, 52950-74-0; europium(II), 16910-54-6; vanadium(II), 15121-26-3.

References and Notes

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- (13) The rationale invoked by several workers^{12,14} to account for the inverse relationship between basicity of oxidant-bound ligands and rate of outer-sphere electron transfer, to Co(III), which focuses on the energy of the d_{z²} orbital on cobalt into which the electron moves, should, in principle, apply to inner-sphere reactions as well. The Co(III)-Cr(II) inner-sphere case, however, is complicated by bonding of the bridge to both metal centers in the precursor complex, and any structural modification of the bridge that will stabilize the d_{z²} orbital on Co(III) should also stabilize the d_{z²} orbital on Cr(II), but to a lesser degree. Moreover, electron-withdrawing substituents on the bridging ligand would be expected to lower the formation constant of the precursor complex although increasing the specific rate of internal electron transfer.
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- (16) It is not unreasonable to relate the observed rate enhancement in Eu²⁺ reductions by the sulfonate group (which presents a "sulfate-like" exterior to outside species) to the relatively strong Eu(II)-sulfate interaction that is reflected in the large crystal energy (hence the limited solubility in water) of EuSO₄. Although such a relationship may be descriptively useful, it is obviously too rough to serve as a basis for a quantitative treatment.
- (17) Values of *k*_{Cr} for the unsaturated complexes reach maximum limiting values at (H⁺) near 0.02 M,⁶ thus ruling out a kinetically significant contribution involving the conjugate acid of Cr²⁺(aq) (p*K*_A > 9).¹⁸ The apparent kinetic saturation effect is likewise incompatible with the deprotonation of a Co(III)-Cr(II) binuclear precursor unless the formation constant for this precursor is large. In the latter event, however, the reduction would, contrary to experiment, no longer be first order in that reagent taken in excess.
- (18) Although p*K*_A of Cr(H₂O)₆²⁺ does not appear to have been recorded, we estimate a value near 11 from the known p*K*_A's of Mg(H₂O)₆²⁺ (11.4) and Mn(H₂O)₆²⁺ (10.6) [see, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 32]. "Referee 2" suggests a value 1-2 units lower, reflecting the tetragonal distortion of Cr(II).
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Trans Effect in Octahedral Complexes. I. Rates of Ligation of *trans*-(Sulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) Complexes in Methanol

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The rates of ligation of *trans*-(*p*-toluylsulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) and *trans*-(methylsulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) by thiourea, *p*-toluidine, pyridine, di(*n*-propyl) sulfide (*p*-toluyl complex only), triphenylphosphine, triphenylarsine, and triphenylstibine in methanol to produce the respective *trans*-ligated complexes have been investigated. Temperature dependencies for eight of these thirteen reactions are reported, as are solvent dependencies for selected systems. For all systems the reaction rate is first order in the cobalt complex, the net reaction proceeding to a measurable equilibrium state with entering ligands di(*n*-propyl) sulfide, triphenylarsine, and triphenylstibine. For ligand concentrations less than 0.06 *F*, the observed first-order rate parameter, *k*^{obsd}, depends upon [L] according to the relation *k*^{obsd} = *a* + *b*[L]. Nonzero values of *a* are only observed for systems which proceed to an equilibrium state, all values of *b* fall within the range (3.7-18.2) × 10⁻² *F*⁻¹ sec⁻¹ at 25°, and all measured values of Δ*H*_b^{*} fall within the range 20.0-25.5 kcal/mol. At higher concentrations of L the rate law takes the form *k*^{obsd} = (*a* + *b*[L])/(1 + *c*[L]) where for the *p*-toluyl complex *c* = 0.56 ± 0.05 and 0.40 ± 0.05 *F*⁻¹ for thiourea and *p*-toluidine, respectively. This and other evidence are interpreted in favor of the ligation reactions proceeding via a limiting SN1 mechanism, although a prior association mechanism cannot be ruled out. Comparisons with previously studied systems show that in the title complexes S-bonded sulfinate ligands produce a moderate *trans*-labilizing effect; the relative ordering of *trans*-labilizing ability is CH₃⁻ > SO₃²⁻ >> RSO₂⁻ >> I⁻ ≈ NO₂⁻. Evidence is presented which indicates that ligands which exert a kinetic *trans* effect in cobalt(III) complexes do so at least partially via a ground-state weakening of the *trans* bond.

Introduction

It is now well established that in cobalt(III) chemistry S-bonded sulfite produces a specific and dramatic labilization of the ligand situated *trans* to it.² Studies of several S-sulfitecobalt(III) systems have established that the mechanism

involved in this process is probably SN1 in character, but no comprehensive theory is yet available to rationalize the phenomenon.² In an effort to provide such a rationalization, we set out to determine whether *trans* labilization occurs in cobalt(III) complexes for S-bonded ligands other than SO₃²⁻.

S-bonded sulfinato ligands, RSO_2^- , which by variation of R can have a range of electronic and steric properties, provide suitable complexes for this endeavor. While the chemistry of octahedral complexes containing S-sulfinato ligands is relatively unknown,³ S-bonded benzenesulfinato has been shown to exhibit a trans-labilizing effect in Pd(II) complexes.⁴

One of the more interesting features of the substitution reactions of the S-sulfinitocobalt(III) systems studied thus far is the accumulated evidence that replacement of the trans ligand proceeds *via* a limiting $\text{S}_{\text{N}}1$ mechanism.^{2a} This evidence derives mainly from observations that as the concentration of the incoming ligand, L, is increased, the observed ligation rate becomes less than first order in L and eventually zero order in L at sufficiently high [L]. However, this dependence of observed rate on [L] is also consistent with mechanisms involving prior association between L and the metal complex. Such prior association is well documented in aqueous systems when L is negatively charged and the cobalt complex has a multipositive charge (*i.e.*, ion-pair formation),⁵ and more recently prior association between multinegatively charged ligands and neutral cobalt complexes⁶ and between 1+ cobalt complexes and neutral ligands⁷ has been reported in aqueous systems involving trans labilization of cobalt(III) by coordinated alkyl groups. The prime experimentally determinable difference between rate laws predicted by the limiting $\text{S}_{\text{N}}1$ and prior association mechanisms is that the former demands the limiting observed rate at high [L] to be independent of the chemical identity of L, while the latter allows this limiting rate to be a function of the nature of L. In order to minimize the electrostatic driving forces for prior association and also to eliminate the complications of protonation equilibria encountered in the sulfito studies,² we have chosen to investigate the ligation of neutral sulfinatobis(dimethylglyoximate)cobalt(III) complexes by neutral ligands in nonaqueous solvents (chiefly methanol). The class of bis(dimethylglyoximate)cobalt(III) complexes is of additional interest since *trans*-sulfito-aquobis(dimethylglyoximate)cobalt(III) is the only S-sulfinitocobalt(III) complex investigated to date which exhibits ligation reactions simply first order in [L] (up to ligand concentrations as high as 0.5 *F*).^{1d}

Experimental Section

Materials. Unless otherwise specified, all chemicals were of reagent grade. Triphenylarsine, triphenylstibine, and thiourea were twice crystallized from methanol, triphenylphosphine was twice crystallized from 95% ethanol, and *p*-toluidine was purified by a literature procedure⁸ and then vacuum sublimed; after purification, all five solids were dried under vacuum for 48 hr. Pyridine was purified by distillation from calcium hydride and was stored over molecular sieves; di(*n*-propyl) sulfide was purified by a literature procedure⁸ and then distilled from sodium (bp 143–144°). *trans*-Chloro-aquobis(dimethylglyoximate)cobalt(III),^{9a} *trans*-chloromethano-bis(dimethylglyoximate)cobalt(III),^{9b} and *trans*-methylo-aquobis(dimethylglyoximate)cobalt(III)^{9c} ($\text{Cl-Co}(\text{DH})_2\text{-OH}_2$, $\text{Cl-Co}(\text{DH})_2\text{-HOCH}_3$, and $\text{CH}_3\text{-Co}(\text{DH})_2\text{-OH}_2$, respectively, where DH represents the mono-anion of dimethylglyoxime) were prepared by previously reported procedures. *trans*-Phenyl(pyridine)bis(dimethylglyoximate)cobalt(III) was prepared by a literature procedure^{9c} and recrystallized in the dark from hot 1,1,1-trifluoroethanol.

Preparation of Complexes. Modification of existing procedures for the synthesis of sulfinatobis(dimethylglyoximate)cobalt(III) species^{3a,10} led to the following specific preparations and purifications of the aquo complexes.

trans-(*p*-Toluenesulfinato)aquobis(dimethylglyoximate)cobalt(III). A 50% molar excess of sodium *p*-toluenesulfinate was stirred with $\text{Cl-Co}(\text{DH})_2\text{-OH}_2$ in 1:1 ethanol-water at room temperature for 10 min; precipitation with water yielded a brown product which could be crystallized from 1,1,1-trifluoroethanol by slow addition of 5:1 hexane-acetone. *Anal.* Calcd for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{OH}_2\text{-OH}_2$: C, 37.50; H, 5.25; N, 11.66; S, 6.67. Found: C, 37.43; H, 5.38; N, 11.56; S, 6.60.

trans-Methanesulfinatoaquobis(dimethylglyoximate)cobalt(III).

Three grams of $\text{CH}_3\text{-Co}(\text{DH})_2\text{-OH}_2$ was dissolved in 50 ml of liquid SO_2 and the resulting solution was maintained at room temperature in a sealed tube for 24 hr; evaporation of the SO_2 yielded an orange-red precipitate which was dissolved in 25 ml of 1,1,1-trifluoroethanol, filtered, and diluted with an equal volume of 95% ethanol; addition of several volumes of ether, followed by refrigeration at 0°, yielded red-brown crystals of the desired product. *Anal.* Calcd for $\text{CH}_3\text{SO}_2\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)\text{OH}_2$: C, 27.98; H, 4.96; N, 14.50; S, 8.30. Found: C, 27.91; H, 5.02; N, 14.37; S, 8.10. Replacement of coordinated water in the above two sulfinato complexes by a variety of ligands may easily be accomplished by allowing the complex to react for 1 hr with an equimolar amount of ligand in methanol. Neutral product complexes either precipitate from the solution or may be precipitated by addition of water; charged product complexes may be precipitated by addition of ether. An example of this procedure is given by the following preparation.

trans-(*p*-Toluenesulfinato)(triphenylphosphine)bis(dimethylglyoximate)cobalt(III). A 0.315-g (1.20-mmol) sample of triphenylphosphine was added to 0.555 g (1.20 mmol) of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$ in 20 ml of methanol and the resulting solution was stirred for 1 hr at room temperature; the resulting brown crystals were recrystallized from dichloromethane-hexane. *Anal.* Calcd for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{P}(\text{C}_6\text{H}_5)_3$: C, 55.93; H, 5.12; N, 7.91; S, 4.52. Found: C, 55.84; H, 5.13; N, 7.96; S, 4.71. Complexes containing two coordinated sulfinato ligands can be prepared by analogous procedures, as in the following synthesis.

Sodium *trans*-Bis(*p*-toluenesulfinato)bis(dimethylglyoximate)cobaltate(III). A 2.0-g (5.6-mmol) amount of sodium *p*-toluenesulfinate was added to 2.0 g (2.8 mmol) of $\text{Cl-Co}(\text{DH})_2\text{-CH}_3\text{OH}$ in 30 ml of methanol to yield a clear orange-brown solution; after 30 min at room temperature, addition of 10 volumes of ether yielded a yellow precipitate which was recrystallized from 2-propanol-methanol. *Anal.* Calcd for $\text{Na}[(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2)_2\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2]\cdot\text{CH}_3\text{OH}$: C, 42.16; H, 4.89; N, 8.56; S, 9.80. Found: C, 42.13; H, 5.06; N, 8.86; S, 9.80. The coordinated water of the aquo complexes is also readily displaced by methanol, as in the following preparation.

trans-(*p*-Toluenesulfinato)methanolbis(dimethylglyoximate)cobalt(III). A 1.0-g sample of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$ was dissolved in 50 ml of methanol and the resulting solution stirred at room temperature for 2 hr. The yellow-brown crystals which formed were filtered and washed with ether. *Anal.* Calcd for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{CH}_3\text{OH}$: C, 40.39; H, 5.29; N, 11.76; S, 6.73. Found: C, 40.84; H, 5.29; N, 12.05; S, 6.72. Further characterization of the above complexes by ultraviolet, infrared, and pmr spectroscopy is described in the Results.

Equipment. Pmr spectra were recorded on a Varian A-60A at 37°; infrared spectra were recorded in Nujol mulls on a Beckman IR-10; visible-uv spectra were recorded on a Cary 14 at 25°. Kinetic experiments with half-lives greater than about 2 min were spectrophotometrically monitored using a Cary 16K equipped with a thermostated cell compartment which maintained the reaction solution to within $\pm 0.1^\circ$ of the working temperature. Kinetic experiments with half-lives less than about 2 min were spectrophotometrically monitored using either a Cary 14 or a Varian Techtron 635K at 24.8 \pm 0.3°.

Kinetic Procedures. Stock solutions of ligands and sulfinato-aquobis(dimethylglyoximate)cobalt(III) complexes were freshly prepared each day in reagent grade methanol and were allowed to equilibrate at the working temperature for at least 30 min prior to reaction. Reaction solutions were prepared so that the concentration of free ligand was at least 20 times greater than the concentration of the cobalt complex which was usually about 2.5×10^{-5} *F*. Equivalent rates were obtained by monitoring the near-ultraviolet charge-transfer band of either the starting complex or the product complex; most reactions were monitored by the latter procedure. Exclusion of oxygen from reaction solutions had no discernible effect on the observed rates and therefore most experiments were performed with air-saturated solutions. Unless otherwise specified, reactions were studied in methanol and no reagents were added to control ionic strength, pH, or solvent composition. Experiments on the effect of water in the methanol solvent (data presented later) showed that the presence of 0.5% water changed the observed rate by only 4%, and therefore no efforts were made to eliminate traces (<0.1%) of water from the solvent.

Data Analysis. Observed pseudo-first-order rate constants (k_{obsd}) were obtained from the slopes of $\ln(\text{OD}_t - \text{OD}_\infty)$ vs. time plots which

Table I. Charge-Transfer Peak Positions for $\text{RSO}_2\text{-Co(DH)}_2\text{-X}$ Species in Methanol as a Function of R and X^a

X	R = <i>p</i> -toluyl	R = methyl
Methanol	321 (3.45×10^4)	316
4- <i>tert</i> -Butylpyridine	320	
Pyridine	325	320
Bromide	331	
Di(<i>n</i> -propyl) sulfide	340	
Iodide	347	
Thiocyanate	348	
Thiourea	350	338
<i>p</i> -Toluidine	352	342
<i>p</i> -Toluylsulfinate	367	
Triphenylphosphine	369 (3.12×10^4)	358
Triphenylarsine	369	359
Triphenylstibine	375	363

^a Peak positions in nm. Extinction coefficients ($F^{-1} \text{ cm}^{-1}$) are given in parentheses.

were generally linear for more than 3 half-lives. Nonlinearity at long reaction times was especially bothersome in experiments with high ligand concentrations, the effect being ascribed to subsequent reaction of the initial ligation product, $\text{RSO}_2\text{-Co(DH)}_2\text{-L}$, with more ligand to form $\text{L-Co(DH)}_2\text{-L}^+$ which in some cases could be precipitated as a perchlorate salt. In those cases where an experimental value of OD_∞ could not be directly observed, the Kezdy time-lag procedure¹¹ was used to obtain k^{obsd} in the manner previously outlined.¹² Several experiments in which OD_∞ was directly observed were treated by both procedures and the calculated values of k^{obsd} always agreed to within 2%. In all cases data were collected and analyzed for a time period exceeding 2.5 reaction half-lives. For replicate experiments, values of k^{obsd} were reproducible to within $\pm 5\%$. For ligand concentrations less than 0.06 *F*, plots of k^{obsd} vs. [L] were treated by the linear least-squares procedure¹³ and in all cases the points were randomly distributed about the least-squares line. For the two systems extended to high concentrations of L (*ca.* 0.9 *F*), the k^{obsd} -[L] data were fit to the functional form

$$k^{\text{obsd}} = \frac{A + BC[L]}{1 + C[L]}$$

by the LASL nonlinear least-squares program;¹⁴ this same procedure and functional form were used to fit the spectrophotometric $\text{OD}_{[L]}\text{-[L]}$ data resulting from the determinations of equilibrium constants. Activation parameters were obtained from linear least-squares analyses of Eyring plots in which each rate parameter was weighted by the inverse square of its standard deviation. All errors reported in this work are standard deviations unless otherwise noted.

Results and Discussion

Characterization and Stoichiometry. The synthetic procedures and elemental analyses reported in the previous section suffice to establish that the complexes considered in this work are disubstituted bis(dimethylglyoximate)cobalt(III) species, XYCo(DH)_2 ; this conclusion is further confirmed by the observed characteristic infrared, ultraviolet, and pmr spectra resulting from this class of compounds. For all reactant and product complexes, the pmr spectra show only one type of dimethylglyoxime CH_3 resonance, indicating that the Co(DH)_2 moiety is planar and thus that X and Y are situated trans to one another, *i.e.*, $\text{X-Co(DH)}_2\text{-Y}$. This result is consistent with the generally observed trans stereochemistry of the Co(DH)_2 center^{15,16} and supports prior assumptions^{2d,17,18} that this stereochemistry is maintained during substitution reactions.

Our data also confirm earlier observations that the complexes considered in this work contain S-bonded and not O-bonded sulfinato ligands. First, both reactant and product complexes exhibit $\nu_{\text{as}}(\text{SO}_2)$ and $\nu_{\text{s}}(\text{SO}_2)$ infrared absorption bands at positions expected for *S*-sulfinato but incompatible with *O*-sulfinato ligands;^{3a} for those particular complexes also prepared by Johnson and Lewis,^{10a} we observe identical SO_2 band positions. Second, both reactant and product complexes exhibit an intense ($\epsilon \approx 10^4 \text{ F}^{-1} \text{ cm}^{-1}$) absorption band in the near-ultraviolet region. Previous work has shown that such

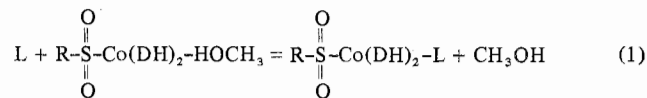
Table II. Selected Pmr τ Values for $\text{L-Co(DH)}_2\text{-X}$ Species

L	X^a	$\tau(\text{D-H}_{\text{Me}})$	$\tau(\text{C-H}_3)$	$\tau(\text{H}_\alpha)^a$	Solvent	Ref
CH_3	py	7.87	9.18	1.37	CDCl_3	21b
CH_3SO_2	py	7.75	7.34	1.59	CDCl_3	10a
CH_3SO_2	H_2O	7.70	7.37		CD_3OD	<i>b</i>
CH_3SO_2	$(\text{C}_6\text{H}_5)_3\text{P}$	8.03 ^c	7.43		CDCl_3	10a
CH_3	$(\text{C}_6\text{H}_5)_3\text{P}$	8.18 ^c	8.82		CDCl_3	21b
I	py	7.63		1.80	CDCl_3	21b
C_6H_5	py	7.97		<i>d</i>	CDCl_3	<i>b</i>
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	py	7.98	7.71	1.58	CDCl_3	<i>b</i>
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	$(\text{C}_6\text{H}_5)_3\text{P}$	8.24 ^c	7.71		CDCl_3	<i>b</i>
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	H_2O	7.81	7.64		$\text{CF}_3\text{CH}_2\text{OH}$	<i>b</i>
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	L^{e}	8.08	7.68		D_2O	<i>b, f</i>
SO_3^-	H_2O	7.63			D_2O	<i>b, g</i>

^a py = pyridine; H_α = α pyridine protons. ^b This work. ^c Doublet. ^d Sample solubility insufficient to determine accurately this value. ^e $\text{X} = \text{L} = \text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2$. ^f Sodium salt. ^g Ammonium salt.

bands arise when sulfur is coordinated to a potentially oxidizing center^{12,19,20} and they may be presumed to be ligand to metal charge transfer (LTMCT) bands. Table I lists the positions of these bands for several *trans*-(sulfinato-*S*)bis(dimethylglyoximate)cobalt(III) complexes, and it is seen that the band position is sensitive to the nature of the trans ligand in a fashion consistent with the LTMCT assignment. As described in the Experimental Section, the disappearances and appearances of these ligand-specific LTMCT bands were used to monitor the kinetics of ligation reactions. Third, in those sulfinato complexes where the LTMCT band is at a short enough wavelength (less than *ca.* 330 nm), the visible spectrum shows a shoulder at about 450 nm ($\epsilon \approx 10^2 \text{ F}^{-1} \text{ cm}^{-1}$) which is similar in intensity and position to the corresponding shoulder seen in *trans*-(sulfito-*S*)aquobis(dimethylglyoximate)cobalt(III).^{15b} For those complexes with LTMCT bands at longer wavelengths, it is probable that this shoulder is obscured by the more intense charge-transfer peak.

The preparative chemistry described previously and the kinetic results presented below show that the ligand situated trans to sulfur in the title complexes is labile on the time scale of minutes. Therefore when a *trans*-(sulfinato-*S*)aquobis(dimethylglyoximate)cobalt(III) complex is dissolved in a nonaqueous solvent and the resulting solution allowed to equilibrate for 30 min (our experimental procedure), the coordination site trans to sulfur no longer contains purely water but rather contains an equilibrium distribution of solvent molecules. For most of the kinetic experiments reported herein the solvent is essentially pure methanol, and therefore the net ligation reactions studied in this work may be described by



Pmr Spectra. Widespread interest in the chemistry of bis(dimethylglyoximate)cobalt(III) complexes, especially with regard to the trans influence, has led to extensive compilations of pmr data for these and closely related systems.²¹ Against this background it is useful to inspect the pmr spectral parameters of the *S*-sulfinato complexes investigated in this work. Table II lists these parameters, as well as those for some related Co(DH)_2 complexes, and four points relevant to this work may be noted. (1) On going from $\text{CH}_3\text{-Co(DH)}_2\text{-py}$ to $\text{CH}_3\text{SO}_2\text{-Co(DH)}_2\text{-py}$, the resonance of the dimethylglyoximate methyl peak, DH_{Me} , shifts to lower field. This is qualitatively in agreement with the correlation between $\tau(\text{DH}_{\text{Me}})$ and σ_{p} (the Hammett function of the axial ligand) found by Hill and Morallee;^{21b} CH_3 , with $\sigma_{\text{para}} = -0.17$, is a better electron donor than CH_3SO_2 , with $\sigma_{\text{p}} = 0.72$,²² and therefore the resulting greater electron density in the Co(DH)_2 center causes $\tau(\text{DH}_{\text{Me}})$ of the methyl compound to occur at

higher field.^{21b} (2) However, CH₃SO₂ does not quantitatively fit on Hill and Morallee's linear $\tau(\text{DH}_{\text{Me}}) - \sigma_{\text{p}}$ relationship which was obtained using the uninegative ligands O₂N, NC, Cl, Br, I, ONO, CH₃, and CH₃CH₂.^{21b} This implies that the overall electron-donating and -withdrawing properties of *S*-sulfinato ligands are manifested differently in σ_{para} from those of the ligands correlated by Hill and Morallee.^{21e} (3) For comparable complexes, $\tau(\text{DH}_{\text{Me}})$ observed for an alkylsulfinato ligand is less than that observed for an arylsulfinato ligand. This dependence of $\tau(\text{DH}_{\text{Me}})$ on the alkyl or aryl nature of R is opposite to that observed for planar ligand resonances in RSO₂-Co(salen) complexes (salen = bis(salicylaldehyde)ethylenediimine dianion)^{10b,22} but is in agreement with that observed for R-Co(DH)₂ complexes (see Table III) and for six-coordinated R-Co(BAE) complexes (BAE = bis(acetylacetonate)ethylenediimine dianion).²³ In these types of complexes the relative positioning of planar ligand resonances for axial ligands with R = alkyl or R = aryl may result from variable "through-space" shielding by the aryl ring current²⁴ and should not be taken as an indication of the relative electron-donating strength of the axial ligand. (4) Hill and Morallee^{21b} also noted that the τ values for the α pyridine protons, H _{α} , in py-Co(DH)₂-X complexes are sensitive to the nature of the trans ligand. This observation has been confirmed^{21e} and its significance will be discussed later.

Equilibrium Data. Spectrophotometric titration of RSO₂-Co(DH)₂-S complexes in methanol shows that for certain ligands reaction 1 proceeds to an equilibrium situation. Slow formation of L-Co(DH)₂-L⁺ species at high [L] precludes accurate determination of the equilibrium quotient, *Q*, by this method. By ignoring this complication and directly analyzing the OD-[L] data *via* the equation appropriate for a single ligation equilibrium^{2d}

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

(subscripts on OD refer to concentration of added ligand, ϵ_{S} and ϵ_{L} are extinction coefficients of the solvated and ligated forms of the complex respectively, *l* is the path length, and [Co_{tot}] is the total concentration of complexes in all forms) one can calculate values of *Q* which in this situation should be regarded as only order of magnitude estimates of the true values. For the methylsulfinato complex and L = triphenylarsine, triphenylstibine, and di(*n*-propyl) sulfide, this procedure leads to $Q(24.8^\circ) = 48, 34,$ and $14 F^{-1}$, respectively.

Kinetics and Mechanism of Ligation. Linearity of the $\ln |\text{OD}_t - \text{OD}_\infty|$ vs. time plots described in the Experimental Section indicates that, under conditions of pseudo-first-order excesses of ligand, the rate of the ligation reaction



where S represents a solvent molecule, obeys simple first-order kinetics, *i.e.*

$$\frac{-d(\ln \{[\text{Co-S}] - [\text{Co-S}]_{\text{eq}}\})}{dt} = \frac{d(\ln \{[\text{Co-L}] - [\text{Co-L}]_{\text{eq}}\})}{dt} = k^{\text{obsd}}$$

Table III²⁵ lists values of k^{obsd} for reaction 1 as a function of L, R, [L], and temperature when [L] < 0.06 *F*. The 224 kinetic experiments summarized in this table show that for all cases the dependence of k^{obsd} on [L] is adequately described by the relation

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

Figure 1 shows three representative plots of k^{obsd} vs. [L]. Table IV summarizes the values of *a* and *b* calculated from the raw data of Table III. For those ligands with $a \neq 0$ (tri-

Table IV. Calculated Reaction Parameters *a*, *b*, and *Q* at 24.8° for Reaction 1 as a Function of R and L^a

Ligand ^b	R	10 ² <i>a</i> , sec ⁻¹	10 ² <i>b</i> , F ⁻¹ sec ⁻¹	<i>Q</i> , ^b F ⁻¹
Thiourea	<i>p</i> -ToluyI		18.2 ± 0.4	>10 ³
Thiourea	Methyl		14.0 ± 0.3	>10 ⁴
<i>p</i> -Toluidine	<i>p</i> -ToluyI		8.68 ± 0.04	>10 ⁴
<i>p</i> -Toluidine	Methyl		6.67 ± 0.01	>10 ⁴
Pyridine	<i>p</i> -ToluyI		4.79 ± 0.07	>10 ⁴
Pyridine	Methyl		3.56 ± 0.11	>10 ⁴
(<i>n</i> -C ₃ H ₇) ₂ S	<i>p</i> -ToluyI	0.17 ± 0.08	5.25 ± 0.34	30 ± 14
(C ₆ H ₅) ₃ P	<i>p</i> -ToluyI		5.22 ± 0.06	>10 ⁴
(C ₆ H ₅) ₃ P	Methyl		3.72 ± 0.02	>10 ⁴
(C ₆ H ₅) ₃ As	<i>p</i> -ToluyI	0.086 ± 0.003	5.12 ± 0.13	59.5 ± 2.5
(C ₆ H ₅) ₃ As	Methyl	0.096 ± 0.001	3.72 ± 0.07	38.8 ± 0.8
(C ₆ H ₅) ₃ Sb	<i>p</i> -ToluyI	0.143 ± 0.002	8.67 ± 0.13	60.6 ± 1.2
(C ₆ H ₅) ₃ Sb	Methyl	0.187 ± 0.002	4.28 ± 0.10	22.9 ± 0.6

^a $k^{\text{obsd}} = a + b[\text{L}]$; $Q = b/a$. ^b Standard deviation in *Q* calculated by the usual propagation relationship; however, since the correlation coefficient between *b* and *a* is 1.00, the true error in *Q* is larger than this calculated value.

phenylarsine, triphenylstibine, and di(*n*-propyl) sulfide), reaction 1 proceeds to a measurable equilibrium state and the kinetically derived values of *Q* are just *b/a*. For those ligands with *a* indistinguishable from zero (thiourea, *p*-toluidine, pyridine, and triphenylphosphine), the equilibrium expressed by reaction 1 lies far to the right and estimated lower limits of *Q* are given in Table IV.

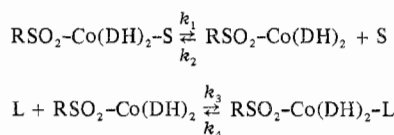
Both thiourea and *p*-toluidine have sufficient solubility in methanol so that the dependence of k^{obsd} on [L] may be extended to higher [L]. These dependencies are shown in Figure 2 wherein the smooth curves represent nonlinear least-squares¹⁴ fits of the k^{obsd} -[L] data to the functional form

$$k^{\text{obsd}} = \frac{A + BC[\text{L}]}{1 + C[\text{L}]} = \frac{a + b[\text{L}]}{1 + c[\text{L}]} \quad (3)$$

where $b = BC$, $A = a$, and $C = c$. As in studies at low [L], for these two ligands *a* is indistinguishable from zero. It is reasonable to assume that eq 2 is a special case of eq 3 that is observed when [L] is insufficient to make *c*[L] significant with respect to 1.

Of the mechanisms consistent with the general rate law expressed by eq 3, only two seem sufficiently plausible to warrant discussion.⁵⁻⁷

I. Limiting S_N1 Mechanism. The reactions to be considered are

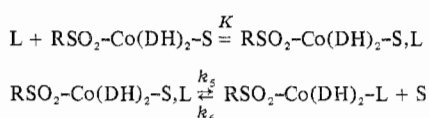


Assuming a steady state for RSO₂-Co(DH)₂ and letting $k_2' = k_2[\text{S}]$, where S represents solvent, leads to

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

and therefore $a = k_4$, $b = k_1 k_3 / k_2'$, $c = k_3 / k_2'$, and $Q = k_1 k_3 / k_2' k_4$.

II. Prior Association Mechanism. The reactions to be considered are



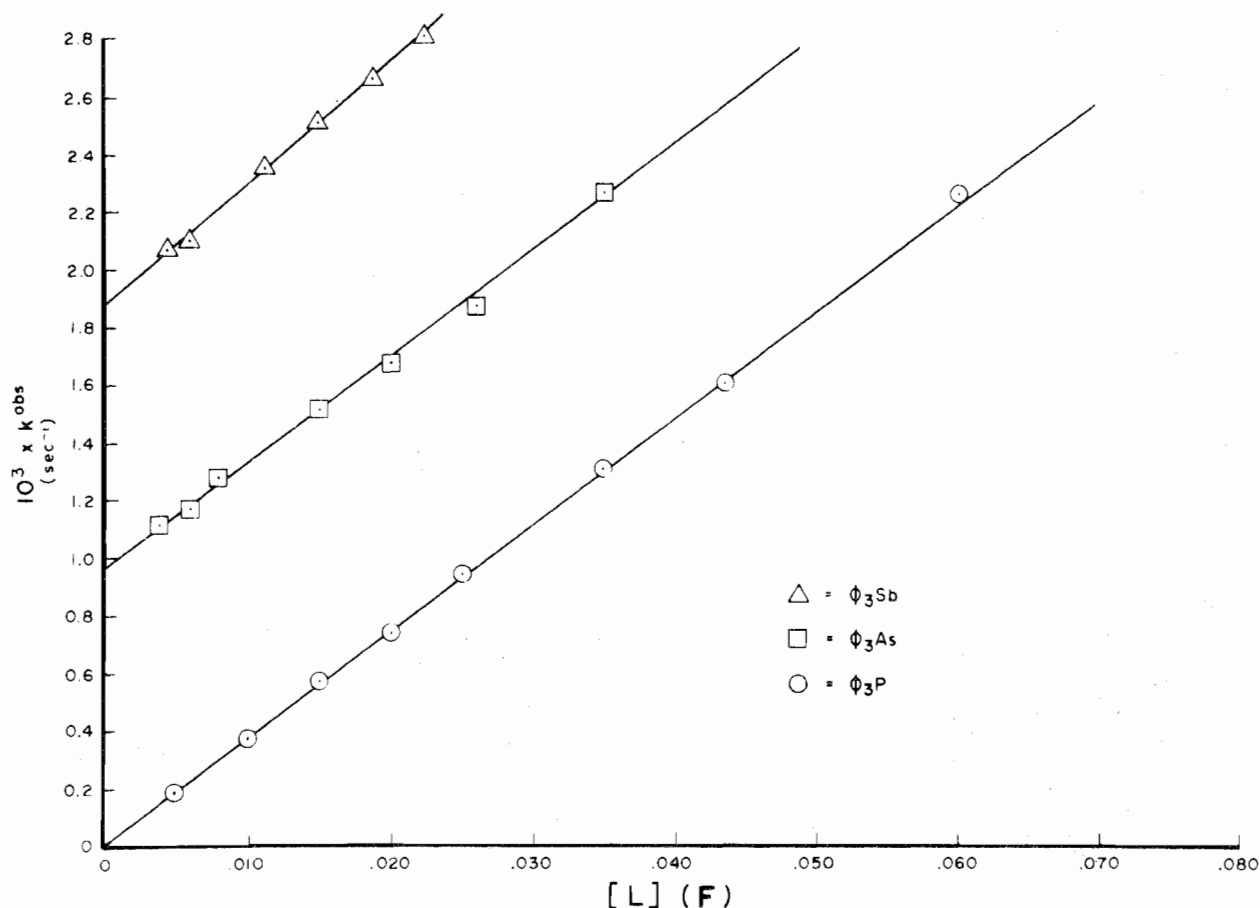


Figure 1. k^{obs} vs. $[L]$ for the reaction of triphenylphosphine, triphenylarsine, and triphenylstibine with *trans*-(methylsulfinato-*S*)methanol-bis(dimethylglyoximate)cobalt(III) in methanol at 24.8°. Data are from Table III.²⁵ Indicated lines are calculated from the least-squares parameters given in Table IV.

Letting $k_6' = k_6[S]$ leads to

$$k^{\text{obs}} = \frac{k_6' + (k_5 + k_6')K[L]}{1 + K[L]} = k_6' + \frac{k_5K[L]}{1 + K[L]}$$

and therefore $a = k_6'$, $b = (k_5 + k_6')K$, $c = K$, and $Q = k_5K/k_6'$.

While we are not able to distinguish between these two possibilities, the following four lines of evidence are consistent with the demands of the limiting SN1 mechanism and taken together they form a circumstantial argument in favor of its operation in the ligation of $\text{RSO}_2\text{-Co}(\text{DH})_2\text{-S}$ complexes.

(1) The limiting SN1 formalism demands that the limiting rate at high $[L]$, k_1 , be independent of the chemical identity of L . Contrariwise, the prior association mechanism allows the limiting rate, $k_5 + k_6'$, to be a function of the nature of L . Nonlinear least-squares analysis¹⁴ of the data in Figure 2 leads to limiting rates at high $[L]$ of 0.22 ± 0.01 and $0.21 \pm 0.02 \text{ sec}^{-1}$ for thiourea and *p*-toluidine, respectively. The equivalency of these limiting rates is consistent with the demands of the limiting SN1 formalism, but within the prior association mechanism this would have to occur by happenchance. This is unlikely since two recent reports on similar systems^{6,7} have noted large variations of limiting rates with the nature of L (which therefore implies operation of the prior association mechanism).

(2) The data in Table IV show that b , the second-order rate parameter governing reaction in the forward direction, is insensitive to the nature of L . For the *p*-toluylsulfinato complex, six out of the seven ligands investigated have b values that fall within a factor of 2 of one another; inclusion of the seventh ligand, thiourea, expands this range to only a factor

Table V. Temperature Dependencies of the Reaction Parameters a , b , and Q for Reaction 1 as a Function of R and L^a

Ligand	R	Term	$\Delta H,^b$		
			kcal/mol	$\Delta S,^b$ eu	$\Delta F(298^\circ),^b$ kcal/mol
Thiourea	<i>p</i> -Toluyyl	b	20.7 ± 0.4	7.6 ± 1.4	18.4 ± 0.6
<i>p</i> -Toluidine	<i>p</i> -Toluyyl	b	18.8 ± 0.3	-0.4 ± 1.1	18.9 ± 0.4
$(\text{C}_6\text{H}_5)_3\text{P}$	<i>p</i> -Toluyyl	b	21.4 ± 0.3	7.5 ± 1.1	19.2 ± 0.4
$(\text{C}_6\text{H}_5)_3\text{P}$	Methyl	b	20.0 ± 0.4	1.9 ± 1.3	19.4 ± 0.6
$(\text{C}_6\text{H}_5)_3\text{As}$	<i>p</i> -Toluyyl	a	23.0 ± 0.1	4.6 ± 0.2	21.6 ± 0.1
$(\text{C}_6\text{H}_5)_3\text{As}$	<i>p</i> -Toluyyl	b	24.3 ± 1.2	17 ± 4	19.2 ± 1.7
$(\text{C}_6\text{H}_5)_3\text{As}$	<i>p</i> -Toluyyl	Q	1.3 ± 1.2	12 ± 4	-2.4 ± 1.7
$(\text{C}_6\text{H}_5)_3\text{As}$	Methyl	a	23.4 ± 1.7	6 ± 6	21.6 ± 2.5
$(\text{C}_6\text{H}_5)_3\text{As}$	Methyl	b	20.7 ± 1.9	4 ± 7	19.5 ± 2.8
$(\text{C}_6\text{H}_5)_3\text{As}$	Methyl	Q	-2.7 ± 2.5	-2 ± 9	-2.1 ± 3.7
$(\text{C}_6\text{H}_5)_3\text{Sb}$	<i>p</i> -Toluyyl	a	19.6 ± 1.4	-6 ± 5	21.4 ± 2.0
$(\text{C}_6\text{H}_5)_3\text{Sb}$	<i>p</i> -Toluyyl	b	25.5 ± 1.8	22 ± 6	18.9 ± 2.5
$(\text{C}_6\text{H}_5)_3\text{Sb}$	<i>p</i> -Toluyyl	Q	5.9 ± 2.3	28 ± 8	-2.5 ± 3.2
$(\text{C}_6\text{H}_5)_3\text{Sb}$	Methyl	a	21.5 ± 0.6	1 ± 2	21.2 ± 0.8
$(\text{C}_6\text{H}_5)_3\text{Sb}$	Methyl	b	20.2 ± 0.6	3 ± 2	19.3 ± 0.8
$(\text{C}_6\text{H}_5)_3\text{Sb}$	Methyl	Q	-1.3 ± 0.8	2 ± 3	-1.9 ± 1.2

^a For explanation of symbols see footnotes of Table IV. ^b Activation parameters ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger for terms a and b . Thermodynamic parameters for Q calculated as $\Delta X_Q^\circ = \Delta X_b^\ddagger - \Delta X_a^\ddagger$.

of 4. Equivalent results are seen for the methylsulfinato complex. This insensitivity of b to large variations in the nature of L (five different attacking atoms) is consistent with the limiting SN1 mechanism and indicates that breaking of the Co-S bond is the most important factor determining the rate in the forward direction. Correspondingly, a , the rate parameter governing reaction in the reverse direction, primarily reflects breaking of the Co-L bond. Values of a are therefore more sensitive to the nature of L (see Table IV) and, after division by the concentration of solvent to convert to

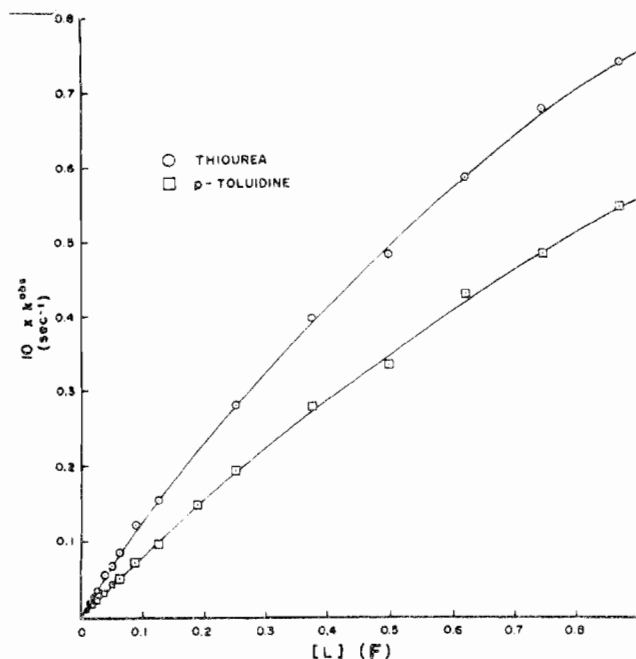


Figure 2. k^{obsd} vs. $[L]$ for the reaction of thiourea and *p*-toluidine with *trans*-(*p*-toluylsulfonato-*S*)methanolbis(dimethylglyoximate)-cobalt(III) in methanol at 24.8°. Indicated curves are calculated from eq 3 using the following nonlinear least-squares best-fit parameters for thiourea and *p*-toluidine, respectively: A taken to be 0.0 sec^{-1} (best-fit values are $(6.9 \pm 3.0) \times 10^{-4}$ and $(-0.2 \pm 2.4) \times 10^{-4}$ sec^{-1}); $B = 0.222 \pm 0.013$ and 0.209 ± 0.019 sec^{-1} ; $C = 0.564 \pm 0.049$ and 0.400 ± 0.046 F^{-1} .

Table VII. Dependence of the Rate of Ligation of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-S}$ and $\text{NO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$ on the Solvent

A. Ligation of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-S}$ by Pyridine ^a			
Solvent	μ, F	$b, F^{-1} \text{sec}^{-1}$	a, sec^{-1}
Ethanol	0.0	$(1.121 \pm 0.002) \times 10^{-1}$	
Methanol	0.0	$(4.79 \pm 0.07) \times 10^{-2}$	
Water	0.0	$(4.16 \pm 0.10) \times 10^{-3}$	$(7.4 \pm 0.5) \times 10^{-5}$
Water	1.0 (LiClO_4)	$(8.60 \pm 0.24) \times 10^{-3}$	$(6.6 \pm 0.7) \times 10^{-5}$
B. Ligation of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-S}$ by Triphenylphosphine ^b			
Solvent	$k^{\text{obsd}}/[(\text{C}_6\text{H}_5)_3\text{P}], F^{-1} \text{sec}^{-1}$		
Ethanol	0.112		
Methanol	0.052		
0.5% Water in methanol	0.050		
1.25% Water in methanol	0.048		
2.5% Water in methanol	0.044		
C. Ligation by Thiourea in Methanol ^a			
Complex	$b, F^{-1} \text{sec}^{-1}$	a, sec^{-1}	
$\text{NO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$	$(1.75 \pm 0.05) \times 10^{-3}$	$(6.0 \pm 1.2) \times 10^{-5}$	
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-S}$	$(1.82 \pm 0.04) \times 10^{-1}$		

^a 25°; $k^{\text{obsd}} = a + b[L]$. ^b 25°, $\mu = 0.0 F$, $[(\text{C}_6\text{H}_5)_3\text{P}] = 0.020 F$. Each entry represents one kinetic experiment. Estimated error in $k^{\text{obsd}} \pm 5\%$.

Table VIII. Calculated Rate Parameters a and b for Selected Ligation Reactions of the Type $\text{X-Co}(\text{DH})_2\text{-OH}_2 + \text{L} = \text{X-Co}(\text{DH})_2\text{-L} + \text{H}_2\text{O}$, in Water at 25°, $\mu = 1.0 F$ ($k^{\text{obsd}} = a + b[L]$)

X	L	$b, F^{-1} \text{sec}^{-1}$	a, sec^{-1}	Medium	Ref
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$	py ^a	$(8.60 \pm 0.24) \times 10^{-3}$	$(6.6 \pm 0.7) \times 10^{-5}$	LiClO_4	<i>b</i>
SO_3^{2-}	py	5		NaClO_4	2d
CH_3^-	py	114	5.6×10^{-2}	KCl	<i>c</i>
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$	Br^-	$(1.46 \pm 0.02) \times 10^{-3}$	$(5.5 \pm 0.2) \times 10^{-3}$	KNO_3	<i>b</i>
NO_2^-	Br^-	1.6×10^{-4}	1.2×10^{-4}	KNO_3	17
I^-	Br^-	3.0×10^{-4}	7.2×10^{-5}	KNO_3	17

^a The plot of k^{obsd} vs. $[\text{py}]$ is linear only below $[\text{py}] = 0.05 F$. Above this concentration the slope begins to decrease. This effect has been noted for other systems involving pyridines in water and has been ascribed to ligand self-association at high concentrations: A. J. Firby and W. P. Jencks, *J. Amer. Chem. Soc.*, **87**, 3209 (1965), and references therein. ^b This work. ^c K. L. Brown and R. G. Kallen, *J. Amer. Chem. Soc.*, **94**, 1894 (1972); K. L. Brown, D. Chernoff, D. J. Keljo, and R. G. Kallen, *ibid.*, **94**, 6697 (1972).

second-order units, about 10^4 times smaller than typical b values which reflect breaking of the weaker Co-S bond.

(3) Activation parameters for several of the reactions considered herein are given in Table V. These parameters are consistent with the limiting $\text{S}_{\text{N}}1$ mechanism in that ΔH_b^* values are relatively insensitive to the nature of L, and all ΔS_b^* and ΔS_a^* values fall within the range (-10 to +34 eu) considered normal for this mechanism in nonaqueous solvents.²⁶ All ΔF_b^* values are of course equal within experimental error.

(4) If breaking of the Co-S bond, where S represents a solvent molecule, is the most important factor governing the rate in the forward direction, then varying the nature of the solvent should have a strong effect on b . Values of k^{obsd} for the ligation of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-S}$ as a function of solvent, entering ligand, and $[L]$, are listed in Table VI.²⁵ These and related data are summarized in Table VII wherein it is seen that changing S from methanol to the more strongly coordinating water decreases b by about an order of magnitude; changing methanol to the less strongly coordinating ethanol increases b by about a factor of 2. Likewise, addition of increasing amounts of water to methanol progressively decreases the observed rate. This variation of b with the coordinating ability of the solvent is therefore in harmony with the limiting $\text{S}_{\text{N}}1$ formalism, but the magnitude of the effect would seem to be too large to be easily rationalized within the prior association mechanism.

By assuming that reaction 1 proceeds *via* the limiting $\text{S}_{\text{N}}1$ mechanism, relative reactivities of ligands toward the reactive intermediate $\text{RSO}_2\text{-Co}(\text{DH})_2$ may be calculated. Thus, the values of c obtained by nonlinear least-squares analysis of the data of Figure 2, multiplied by the concentration of solvent (*ca.* 25 F for methanol), give relative reactivities of ligand and solvent for the reactive intermediate $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Co}(\text{DH})_2$; specifically, $k_{\text{thiourea}}/k_{\text{methanol}} = 14$ and $k_{p\text{-toluidine}}/k_{\text{methanol}} = 10$. These values may be compared to $k_{\text{SO}_3^{2-}}/k_{\text{H}_2\text{O}} = 650$ and 9000, respectively for the $\text{S}_{\text{N}}1$ intermediates $\text{SO}_3\text{-Co}(\text{DH})_2^{2-}$ and $\text{SO}_3\text{-Co}(\text{en})_2^{2-}$ in water. The considerably smaller $k_{\text{ligand}}/k_{\text{solvent}}$ ratios observed for the sulfinate relative to the sulfito $\text{Co}(\text{DH})_2$ intermediates could indicate that the former are considerably more reactive (less discriminating), especially considering the fact that water is a better nucleophile than methanol. However, the opposite conclusion would be reached from the observation that $k_{\text{thiourea}}/k_{\text{pyridine}}$ in methanol is 4.2 for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Co}(\text{DH})_2$ and 3.9 for $\text{CH}_3\text{SO}_2\text{Co}(\text{DH})_2$ (see Table IV) but only 1.7 for $\text{SO}_3\text{Co}(\text{DH})_2^{2-}$ in water.^{2d} These comparisons demonstrate the difficulties involved in drawing conclusions from relative reactivities measured for different systems and reemphasize the current lack of fundamental understanding of the dependence of relative reactivities on solvent properties, ionic charge, ligand polarizability, etc.^{2a,27}

Trans Labilization by RSO_2^- . Although most of the kinetics of $\text{RSO}_2\text{-Co}(\text{DH})_2\text{-S}$ ligation were studied in methanol, some reactions were carried out in water in order to be able to compare directly ligation rates with those of other $\text{L-Co}(\text{DH})_2\text{-OH}_2$ complexes. Table VIII lists these rates as well

Table IX. Relative Trans-Labilizing Ability of the Ligand X Compared to Various Properties of X

X	$\log(b_X/b_{NO_2})^a$	σ_p^b	$\sigma_p^-^c$	σ_1^d	F^e	χ^f	$\tau(DH_{Me})^g$	$\tau(H_\alpha)^h$
NO ₂ ⁻	0.00	0.78	1.27	0.60	1.11	3.65	7.71	1.68
I ⁻	0.28	0.18	0.32	0.39	0.67	2.65	8.02	1.80
CH ₃ SO ₂ ⁻	1.86	0.72	1.05	0.62	0.90		8.03	1.59
CH ₃ C ₆ H ₄ SO ₂ ⁻	1.97		1.12				8.24	1.58
SO ₃ ²⁻	4.74	0.09	0.19	0.25	0.06			
CH ₃ ⁻	6.10	-0.17	-0.24	-0.08	-0.05	2.60	8.18	1.37

^a Relative trans-labilizing ability of X, calculated as described in text. ^b Hammett substituent parameter; data from ref 37. ^c Hammett substituent parameter; data from ref 37; data are for reactions of 1-Cl-2-NO₂-4-X-benzenes with CH₃O⁻ in methanol at 50°, except for X = CH₃C₆H₄SO₂⁻ which is estimated as that observed for X = C₆H₅SO₂⁻ in methanol-benzene. ^d Derived Hammett parameter purportedly reflecting only the nonresonance portion of the substituent effect; data from ref 38. ^e Derived Hammett parameter purportedly reflecting only the nonresonance portion of the substituent effect; data from ref 39. ^f Group electronegativity; data from ref 40. ^g Pmr resonance of dimethylglyoxime methyl group in the complexes X-Co(DH)₂-P(C₆H₅)₃; data from ref 10a and 21b and this work. ^h Pmr resonance of the pyridine α proton in the complexes X-Co(DH)₂-py; data from ref 21b and this work.

as some related parameters obtained in both methanol and water (also see Table VII) and it is seen that changing the solvent from methanol to water decreases the ligation rates of both *S*-sulfinato and nitro complexes by about an order of magnitude. More importantly, these data show that the *S*-bonded sulfinato ligands produce a significant kinetic trans effect; the comparable rates of substitution trans to RSO₂⁻ are about 10² faster than that trans to NO₂⁻. However, RSO₂⁻ is not as effective a trans-labilizing ligand as *S*-bonded sulfite since substitution trans to SO₃²⁻ is almost 10⁵ times faster than that trans to NO₂⁻.

The data of Table IV show that the rate of ligation of RSO₂-Co(DH)₂-S is about 25% greater when R is *p*-toluyl rather than methyl; this is true for all ligands except triphenylstibine where the difference is about 50%. This difference may be rationalized completely on steric grounds since the larger *p*-toluyl group should favor formation of the SN1 intermediate,²⁸ or there may also be a contribution from the greater σ -electron-donating ability of CH₃C₆H₄SO₂⁻ over CH₃SO₂⁻ (see next section). That CH₃C₆H₄SO₂⁻ is a better σ donor than CH₃SO₂⁻ in this particular system is inferred from the consistently lower energy of the CH₃C₆H₄SO₂-Co(DH)₂-L LTMCT peaks (see Table I) since this transition must terminate on the σ^* (eg) level in a cobalt(III) d⁶ system.²⁹

Possible Origins of Trans Labilization in Cobalt(III) Complexes. The data of Tables VII and VIII may be used to rank semiquantitatively the trans-labilizing ability of X in the reaction (25°, aqueous solution of ionic strength 1.0 *F*) X-Co(DH)₂-OH₂ + py → X-Co(DH)₂-py + H₂O

by correcting some table entries for differences in reaction conditions and attacking ligand. In no case is this correction larger than a factor of 2, which is not significant with respect to the large rate differences involved. The resulting relative trans-labilizing ability of X is listed in the first column of Table IX as $\log(b_X/b_{NO_2})$ where it is seen that the relative ordering is CH₃⁻ > SO₃²⁻ >> RSO₂⁻ >> I⁻ ≈ NO₂⁻. Establishment of *S*-bonded sulfinate as a moderate trans-labilizing ligand allows an assessment to be made of some of the theories that have been proposed regarding trans labilization in cobalt(III) complexes.

For instance, by comparing activation enthalpies, Stranks and Yandell^{2e} concluded that coordinated SO₃²⁻ affects labilization by stabilization of the SN1 intermediate and proposed the unusual bonding



to account for this stabilization. However, ΔH_b^* values for ligation of RSO₂-Co(DH)₂-S are no lower than for comparable reactions of O₂N-Co(DH)₂-OH₂¹⁷ while RSO₂⁻ is capable of the same type of unusual bonding proposed for SO₃²⁻. Therefore it seems unlikely that the rationalization offered by Stranks and Yandell^{2e} is correct.

After an extensive review of cis and trans effects in cobalt(III) complexes, Pratt and Thorp³⁰ summarized spectral data (infrared, nmr, and electronic), bond lengths, solution equilibrium constants, and ligation kinetic parameters, to conclude that 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." This is an intuitively pleasing generalization, reminiscent of the well-established σ trans effect in platinum(II) chemistry,³¹ and several authors have alluded to the paramount importance of the σ -donating properties of ligands when rationalizing the trans labilization induced by these ligands in cobalt(III) complexes.^{21a,32-35} One of the problems with this generalization is that it cannot be quantitatively assessed because of the difficulty in obtaining direct measures of electron density donation along the Co-L σ bond. For example, in Table IX are listed some properties³⁶⁻⁴⁰ of the ligand X which might reasonably be expected to be related to the σ -electron-donating power of X, and it is seen that none of them correlate well with $\log(b_X/b_{NO_2})$, the relative trans-labilizing ability of X. All but the last parameter predict that iodide should be an effective trans-labilizing group, but Hague and Halpern¹⁷ have shown that this is not the case.⁴¹ (Brown and coworkers³⁴ have also recently shown that in R-Co(DH)₂-P(OCH₃)₃ complexes, the rate of substitution trans to R is not directly related to the electronegativity of R.) However, since none of the ligand parameters of Table IX directly measures isolated donation of negative charge along the Co-L σ bond, their lack of correlation with $\log(b_X/b_{NO_2})$ cannot be definitely ascribed to a failure of the σ -donation generalization.

Qualitatively, the σ -donation generalization accounts for trans labilization by *S*-sulfinato ligands since in platinum(II) complexes RSO₂⁻ has been shown to be as strong a σ donor as a tertiary phosphine.⁴² Coupled with a recent study demonstrating that σ -bonding effects are similar in "soft" cobalt(III) and platinum(II) complexes,²⁴ this result implies that RSO₂⁻ probably functions as an effective σ donor in the complexes investigated in this work.

Elder and Trkula⁴³ have recently determined the crystal structure of [(NH₃)₅CoSO₃]Cl·H₂O and reported a significant lengthening (0.089 ± 0.004 Å) of the trans Co-N bond relative to the cis Co-N bonds. Since this structure compares cis and trans bonds to identical ligands, it provides a better probe of the ground-state trans effect than does the previously reported structure of *trans*-SO₃-Co(en)₂-NCS which shows no significant difference between the trans Co-N (to NCS) and cis Co-N (to en) bond lengths.⁴⁴ Therefore it may be concluded that *S*-bonded sulfite does induce a significant ground-state structural trans effect in cobalt(III) complexes, and previous kinetic arguments based on the absence of this effect must be discounted.^{2a,c} In this context the $\tau(H_\alpha)$ data given in the last column of Table IX are especially interesting. Hill and Morallee^{21b} have noted that $\tau(H_\alpha)$, the resonance of the pyridine α protons in the complexes X-Co(DH)₂-py, is de-

pendent on the nature of X, shifting toward the free-ligand value as X is changed from iodide to methyl. They also pointed out that this shift could be caused by a ground-state lengthening of the Co-py bond^{21b,f} (ground-state trans effect bringing $\tau(H_{\alpha})$ closer to the free-ligand value). Thus those ligands which exert a strong trans-labilizing influence seem to be just those which cause a ground-state lengthening of the trans bond, and the intermediate kinetic trans effect induced by coordinated RSO_2^- is consistent with its intermediate $\tau(H_{\alpha})$ value (see Table IX).

A recent report⁴⁵ on the trans effect in substituted phosphonobis(dimethylglyoximate)cobalt(III) complexes implicitly ascribes the substitution reactivity of these compounds to a ground-state trans effect induced by coordinated $RR'-P(O)^-$. While this rationale is consistent with the above argument, it should be noted that a ground-state trans effect has not yet been demonstrated for phosphonate ligands in octahedral complexes, and the reported small effect⁴⁶ in digonal Hg(II) complexes may be ascribed to a variety of factors.

In summary, on the basis of currently available data it would appear that ligands which exert a kinetic trans effect do so at least partially *via* a ground-state weakening of the trans bond, and the extent of labilization may to some extent be correlated with a measure of this bond weakening. There is no evidence for labilizing ligands functioning *via* stabilization of a reactive intermediate or a transition state. The ability of a ligand to donate electron density into the σ orbital shared by the trans ligand seems to be a very important factor in determining its trans-labilizing effect, but since it is difficult to measure specifically this ligand property, π interactions in the ground and transition state cannot be completely ruled out.

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Registry No. $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$, 52843-22-8; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$, 52843-23-9; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-HOCH}_3$, 52843-24-0; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-4-tert-butylpyridine}$, 52843-25-1; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-py}$, 52882-40-3; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-Br}$, 52843-26-2; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-(}n\text{-C}_3\text{H}_7\text{)}_2\text{S}$, 52843-27-3; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-I}$, 52843-28-4; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-thiocyanate}$, 52843-48-8; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-thiourea}$, 52843-49-9; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-}p\text{-toluidine}$, 52843-50-2; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$, 52843-51-3; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-P}(\text{C}_6\text{H}_5)_3$, 52882-45-8; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-As}(\text{C}_6\text{H}_5)_3$, 52882-46-9; $\text{CH}_3\text{SO}_2\text{-Co}(\text{DH})_2\text{-Sb}(\text{C}_6\text{H}_5)_3$, 52843-52-4; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-HOCH}_3$, 52843-53-5; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-py}$, 52882-47-0; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-thiourea}$, 52843-54-6; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-}p\text{-toluidine}$, 52843-55-7; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-P}(\text{C}_6\text{H}_5)_3$, 52843-56-8; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-As}(\text{C}_6\text{H}_5)_3$, 52843-57-9; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-Sb}(\text{C}_6\text{H}_5)_3$, 52843-58-0; $\text{C}_6\text{H}_5\text{-Co}(\text{DH})_2\text{-py}$, 29130-85-6; $\text{Na}[(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2)_2\text{Co}(\text{DH})_2]$, 52843-59-1; $\text{NH}_4[\text{SO}_3\text{-Co}(\text{DH})_2\text{-OH}_2]$, 52843-60-4; thiourea, 62-56-6; $p\text{-toluidine}$, 106-49-0; pyridine, 110-86-1; $(n\text{-C}_3\text{H}_7)_2\text{S}$, 111-47-7; $(\text{C}_6\text{H}_5)_3\text{P}$, 603-35-0; $(\text{C}_6\text{H}_5)_3\text{As}$, 603-32-7; $(\text{C}_6\text{H}_5)_3\text{Sb}$, 603-36-1; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{-ethanol}$, 52843-61-5; $\text{NO}_2\text{-Co}(\text{DH})_2\text{-OH}_2$, 15697-44-6.

Supplementary Material Available. Tables III and VI, giving observed first-order rate parameters for reaction 1 as a function of L, R, [L], and temperature and for the ligation of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-Co}(\text{DH})_2\text{S}$ and $\text{NO}_2\text{Co}(\text{DH})_2\text{OH}_2$ as a function of ligand, solvent, and [L], will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40395+.

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Photochemistry of Macrocyclic Coordination Compounds. I. A Cobalt(III) Complex Containing a Tetradentate Equatorial Ligand, PnAO¹

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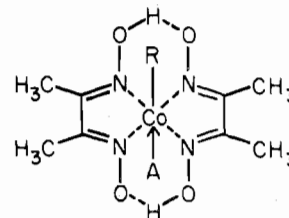
AIC40393P

Photochemical studies are reported on the complexes $\text{Co}(\text{PnAO})\text{X}_2$, $[\text{Co}(\text{PnAO})(\text{H}_2\text{O})\text{X}]^+$, and $[\text{Co}(\text{PnAO})(\text{H}_2\text{O})_2]^{2+}$ where $\text{X} = \text{N}_3$ or NO_2 and PnAO is 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime), which coordinates as a macrocyclic tetradentate equatorial ligand. Photoaquation of an axial X group is the dominant reaction for all wavelengths studied, 254, 366, and either 515 or 550 nm; quantum yields are a few thousandths at the longer wavelengths, the region of the first ligand field band, and increase to values of the order of 0.01 and then 0.1 at the shorter wavelengths, which correspond to charge-transfer absorptions. Photoredox decomposition to Co(II) also occurs, but in low yields; it is proposed that part of the time $[\text{Co}^{\text{II}}(\text{PnAO})(\text{H}_2\text{O})_2]^+$ results and that this species catalyzes aquation if $\text{X} = \text{N}_3$ but not if $\text{X} = \text{NO}_2$; kinetic studies on the catalyzed and noncatalyzed reactions were made and an atom-transfer type mechanism is suggested for the former. The spectra are normal relative to analogous cobalt(III)-acidoammine complexes and the photolysis mechanism is thought also to be similar, namely, heterolytic bond fission at the longer wavelengths and homolytic bond fission followed by cage reactions at the shorter wavelengths. The results are also compared to the behavior of cobaloxime complexes.

Introduction

The photochemistry of Co(III) complexes has been widely studied,² and for the present purpose it is useful to make three classifications of behavior. Irradiation in the wavelength region of the first charge-transfer, CT, absorption band generally leads to redox decomposition in good quantum yields; the ligand substitution (usually aquation) which may also occur has been attributed to a cage reaction following homolytic bond fission (see ref 2b). Except where intrusion of CT character seems evident from their intensity, the first and second, L₁ and L₂, absorption bands have not appeared to be sufficiently photoactive to warrant detailed study. The use of a laser-microcell technique has recently made it possible to measure low quantum yields even with complexes whose dark reaction times are of the order of minutes, and it is now evident that irradiation of the L₁ or L₂ bands of cobalt(III) ammines and acidoammines leads to stereospecific substitutional types of processes which can be accounted for by heterolytic bond fission according to rules developed for the analogous Cr(III) complexes.³⁻⁶ The low quantum yields (relative to Cr(III) complexes) were tentatively attributed to more rapid radiationless deactivation rather than to smaller reactivity of the thermally equilibrated excited (thexi³) state. The term *thexi* was coined in response to the felt need to distinguish between thermally equilibrated excited states and Franck-Condon states. These last are those produced following light absorption, have the approximate geometry of the ground state, and are the states treated in conventional ligand field theory.

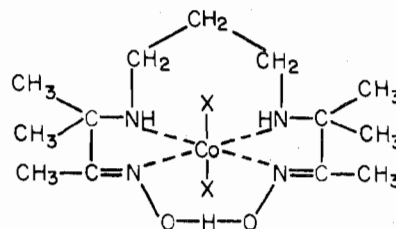
A third behavior pattern may be followed by Co(III) complexes of the glyoxime and corrin types, characterized by having a planar arrangement of four secondary or tertiary nitrogens held in a macrocyclic framework and one whose bonding may be partially delocalized. The axial coordination of these complexes typically includes one ligand making a cobalt-carbon bond. The structure for bis(dimethylglyoximate)cobalt(III) complexes is, for example



A number of variants, with $\text{R} = \text{CN}$, CH_3 , C_2H_5 , etc., and $\text{A} = \text{H}_2\text{O}$, pyridine, NH_3 , etc., have been prepared.⁷

These complexes and also those which constitute models of vitamin B₁₂ coenzyme⁸ show intense absorptions throughout the visible and uv regions; irradiation in the 400-450-nm region typically leads to homolytic fission of the cobalt-carbon bond⁹ in quantum yield of the order of 0.01.^{7,8} The complexes may be photoinert below 500 nm,⁷ although the laser-microcell technique may perhaps reveal substitutional photochemistry of the A ligand in low yields.

The present investigation was undertaken following a report of crystallographic and kinetic studies on a new type of Co(III) complex, $\text{Co}(\text{PnAO})\text{X}_2$.^{10,11} The ligand PnAO (an alternative designation is $\text{Co}(\text{PnAO}-\text{H})_2\text{X}_2$)^{10,12} is 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime);¹¹ when it coordinates, it loses one oxime hydrogen and the structural appearance of the complex is



In this series, the X groups are halogens, pseudohalogen, or other bases of moderately strong acids.

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