has a bonding or antibonding character and the magnitude of the conjugation between the p electrons of the substituents Y and the π system of the ring, depend strongly upon the nature of substituent Y,[18] expressible in the HMO calculations by the parameters h and k in the definition of Coulomb and resonance integrals (see, *e.g.*, ref 18). The difference in the behavior of L and Q^{2-} amounts to a stabilization of the $2b_{2g}$ level and an increased conjugation between Y and the ring. The organic ligand in I can thus be regarded as being more closely a ten-π-electron system than the hydroquinone which is regarded to be very close to a six-π-electron system.[19] This effect, which can be accounted for by ascribing a higher h parameter to the $-OCo(CN)_5$ groups than to oxygen itself, is connected with the increase of electron attraction of oxygen atoms due to their coordination to cobalt atoms (coordination effect) and to an interaction of the π levels of L with the π levels of the $Co(CN)_5$ groups. The $2b_{2g}$ level might be stabilized not only because of the coordination effect but also because of the interaction with π-antibonding orbitals of the $Co(CN)_5$ groups. The $3b_1$ orbital (vacant, antibonding) is able, on the other hand, to interact, probably only weakly, with the π levels of $Co(CN)_5$ groups. All of these effects are consistent not only with the observed stabilization toward the oxidation but also with the disappearance of the L–L transition in I (*vide ante*). The observed absorption band at 23,000 cm^{-1} is most probably a charge-transfer band from the $2b_{2g}$ level of L into the lowest σ-antibonding level of the complex localized to a great extent on the metal atoms.

According to this picture of the electron configuration of L in I, the oxygen–carbon bond would be left with some double-bond character but at the same time with electron density in π-antibonding orbitals. The infrared frequency of L which can be ascribed to the C–O stretch is in the single C–O bond region and is even lower that in H_2O. The force constant of the C–O bond in I is influenced by the electron density in π-bonding as well as antibonding orbitals and by the coordination of oxygen which might decrease the σ-bond contribution to the force constant of the C–O bond, as is also the case in some other complexes.

The organic ligand in species II, on the other hand, resembles very closely the free hydroquinone (in redox as well as in spectral properties). Obviously, the splitting off of one $Co(CN)_5$ group from I causes a decrease of the above-discussed influences and brings the electronic configuration of the ligand in II closer to that of hydroquinone.

The primary product of electrochemical oxidation of II is a species which is actually a σ-bonded quinone complex, $[Co(CN)_5(quinone)]^{2-}$. The stability of this species in aqueous solution is rather low, undergoing a simple hydrolysis without any further intramolecular redox process.

[18] C. A. Coulson, A. Streitwieser, Jr., M. D. Poole, and J. I. Brauman, "Dictionary of π-Electron Calculations," Pergamon Press, New York, N. Y., 1965.

[19] V. Gold, *Trans. Faraday Soc.*, **46**, 109 (1950).

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Kinetics of Some Substitution Reactions of *trans*-Bis(dimethylglyoximato)cobalt(III) Complexes[1]

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Kinetic measurements are reported for a number of anation reactions of *trans*-$Co(DH)_2(NO_2)OH_2$ and *trans*-$Co(DH)_2(I)OH_2$, where DH^- is the dimethylglyoximate ion, $HON{=}C(CH_3)C(CH_3){=}NO^-$. The reactions were found to exhibit second-order kinetics, the order of increasing reactivity of the anions examined being $Cl^- < Br^-$, $NO_2^- < N_3^-$, $NCS^- < HSO_3^-$. For a number of the reactions, activation parameters as well as equilibrium measurements also are reported. The results, which are consistent with either SN1 or SN2 substitution mechanisms, are discussed and compared with those for related substitution reactions of other cobalt(III) complexes including the cobalamins.

Introduction

This paper describes some kinetic studies on a number of substitution reactions of *trans*-bis(dimethylglyoximato)cobalt(III) complexes, notably the anation reactions of nitroaquobis(dimethylglyoximato)cobalt(III) and iodoaquobis(dimethylglyoximato)cobalt(III)

$$trans\text{-}Co(DH)_2(X)OH_2 + Y^- \longrightarrow trans\text{-}Co(DH)_2(X)Y^- + H_2O \quad (1)$$

where $DH^- = HON{=}C(CH_3)C(CH_3){=}NO^-$, $X^- = NO_2^-$ or I^-, and $Y^- = NO_2^-$, Cl^-, Br^-, NCS^-, N_3^-, or HSO_3^-. These studies were undertaken in the context of the extensive continuing general interest, reflected in numerous recent investigations,[2–5] in the kinetics and mechanisms of the substitution reactions

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[1] Support of this research through grants from the National Science Foundation and the Advanced Research Projects Agency is gratefully acknowledged.

[2] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

[3] C. H. Langford, *ibid.*, **4**, 265 (1965).

[4] J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

[5] P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967).

of octahedral cobalt(III) complexes. Contributing to the selection of these systems for study was the recognition of the susceptibility of aquobis(dimethylglyoximato)cobalt(III) complex to anation by a variety of ligands and of the possibility of examining the kinetics of substitution as a function of the *trans* ligand. The present investigation is also of interest in the light of the striking parallels noted by Schrauzer[6,7] between various features of the chemistry of bis(dimethylglyoximato)cobalt complexes (cobaloximes) and those of the corresponding cobalamins (derivatives of vitamin B_{12}).

Some related measurements on the rates of substitution (notably hydrolysis) of bis(dimethylglyoximato)-cobalt(III) complexes have previously been reported by Ablov and his co-workers.[8-11]

Experimental Section

Materials.—The following compounds were prepared by the procedures described by Ablov in the references cited: [Co-$(DH)_2(NO_2)OH_2$],[12] [$Co(DH)_2(I)OH_2$],[13] Na[$Co(DH)_2(NO_2)Cl$],[12] and Na[$Co(DH)_2(NO_2)Br$].[12] Satisfactory analyses were obtained in every case for C, H, N, and, where applicable, halogen. Other chemicals were of reagent grade. Distilled water was used in the preparation of all solutions.

Kinetic and Equilibrium Measurements.—The rates of substitution were measured spectrophotometrically using a Cary 14 recording spectrophotometer with a thermostated ($\pm 0.5°$) cell compartment. The reactions were monitored at wavelengths in the range 320–360 mμ where the greatest absorbance change occurred. To increase the effective absorbance which could be measured, a neutral density filter of optical density about 1.4 was placed in the reference beam. The equilibrium data were also obtained spectrophotometrically using a Cary 14 recording spectrophotometer. To avoid problems associated with aquation of the iodobis(dimethylglyoximato)cobalt(III) complexes,[8,10] the solid compound was weighed out for each kinetic experiment. The ionic strength was maintained at the reported values with potassium nitrate.

Results and Discussion

Stoichiometry and Stereochemistry.—The preparation of salts of $Co(DH)_2(NO)_2Cl^-$, $Co(DH)_2(NO)_2$-Br^-, and $Co(DH)_2(NO_2)NCS^-$ by reaction of $Co(DH)_2$-$(NO)_2OH_2$ with Cl^-, Br^-, and NCS^-, respectively, has previously been described by Ablov.[12,14] The maintenance of *trans* stereochemistry (*i.e.*, coplanar arrangement of the dimethylglyoximate ligands) has been confirmed[12] for the cyclic sequence

$$Co(DH)_2(NO_2)_2^- \xrightarrow{H_2O} Co(DH)_2(NO_2)OH_2 \xrightarrow{Cl^-}$$
$$Co(DH)_2(NO_2)Cl^- \xrightarrow{NO_2^-} Co(DH)_2(NO)_2^-$$

This and subsequent observations[15] have led to the assignment of *trans* configurations to other bis(dimethylglyoximato)cobalt(III) complexes[16] and it is assumed that this configuration is maintained in all of the reactions studied here.

Kinetics.—All of the reactions were examined under pseudo-first-order kinetic conditions, these being achieved in the case of the anation reactions by maintaining a sufficiently large excess of the substituting anion. The initial concentration of $Co(DH)_2(X)OH_2$ ($X^- = NO_2^-$ or I^-) was generally about 2×10^{-4} *M* and the concentration of the substituting anion was in the range 0.03–1.4 *M*. Under these conditions reactions of $Co(DH)_2(NO_2)OH_2$ yielded first-order plots over at least 3 half-lives, whereas those of $Co(DH)_2(I)$-OH_2 exhibited somewhat earlier deviations, sometimes after only 1.5 half-lives. The cause of this is not conclusively established but is believed to be associated with hydrolysis of I^- from the product. Hydrolysis of $Co(DH)_2(I)OH_2$ itself was too slow[8] to interfere with the anation reactions. The aquation reactions that were examined all yielded excellent first-order plots.

In each case it proved possible to find a convenient pH range (Table I) below 7, in which the rate was independent of pH; at higher pH (>7) significant deviations from first-order kinetic behavior were observed. In the case of reactions of $Co(DH)_2(I)OH_2$ the pH was maintained below 6 because of the complications observed at higher pH.[17] In certain cases (*e.g.*, reactions involving N_3^- and HSO_3^-) the accessible pH range was determined by the p*K* of the incoming anion.

The effect of ionic strength was not investigated in detail. In most cases the ionic strength was maintained at 1.0 *M* with KNO_3. For a few reactions, namely, $Co(DH)_2(NO_2)OH_2 + Br^-$, $Co(DH)_2(NO_2)OH_2 + NCS^-$, and $Co(DH)_2(NO_2)Br^- + H_2O$, it was established that the rate was essentially independent of ionic strength and of whether the supporting medium was KNO_3 or Na_2SO_4.

The reactions studied fall conveniently into three classes which will be discussed separately.

(1) **Anation Reactions Which Attain a Measurable Equilibrium.**—The reactions of $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ with Br^- and Cl^- were found to attain a measurable equilibrium at Br^- or Cl^- concentrations up to 1.4 *M*. In each case the kinetics were found to be of the form

$$-d[Co(DH)_2(X)OH_2]/dt = k_1[Co(DH)_2(X)OH_2][Y^-] - k_{-1}[Co(DH)_2(X)Y^-] \quad (2)$$

The rate of approach to equilibrium under these conditions, with Y^- in large excess, thus exhibits pseudo-first-order behavior, *i.e.*

$$\ln\left[\frac{[Co(DH)_2(X)OH_2]_\infty - [Co(DH)_2(X)OH_2]_0}{[Co(DH)_2(X)OH_2]_\infty - [Co(DH)_2(X)OH_2]_t}\right] = k't \quad (3)$$

where

$$k' = k_1[Y^-] + k_{-1} \quad (4)$$

The plots of k' *vs.* $[Y^-]$ in Figure 1, typical of all these reactions, are in accord with this, yielding the values of

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(6) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964); G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966); **89**, 143, 1999 (1967).

(7) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

(8) A. V. Ablov and A. Y. Sychev, *Russ. J. Inorg. Chem.*, **4**, 1143 (1959).

(9) A. Y. Sychev and A. V. Ablov, *ibid.*, **6**, 1163 (1961).

(10) A. Y. Sychev, A. V. Ablov, and V. A. Zarinskii, *ibid.*, **6**, 421 (1961).

(11) A. V. Ablov and D. M. Palade, *Dokl. Akad. Nauk SSSR*, **144**, 414 (1962).

(12) A. V. Ablov, *ibid.*, **97**, 1019 (1954).

(13) A. V. Ablov and M. M. Samus, *Russ. J. Inorg. Chem.*, **5**, 410 (1960).

(14) A. V. Ablov, N. M. Samus, and M. S. Popov, *Dokl. Akad. Nauk SSSR*, **106**, 665 (1956).

(15) A. V. Ablov and G. P. Syrtsova, *Russ. J. Inorg. Chem.*, **5**, 588 (1960); see also A. Nakahara, *Bull. Chem. Soc. Japan*, **28**, 473 (1955).

(16) A possible exception to this generalization is to be found in the reported preparation of both *cis-* and *trans*-$Co(DH)_2(OH)_2^-$: A. V. Ablov, M. P. Filippov, and N. M. Samus, *Dokl. Akad. Nauk SSSR*, **133**, 575 (1960).

(17) A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, **3**, 137 (1958).

TABLE I

KINETIC DATA[a] FOR THE ANATION REACTIONS

$$\mathrm{Co(DH)_2(X)OH_2 + Y^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(DH)_2(X)Y^- + H_2O}$$

X^-	Y^-	pH range	Temp, °C	10^4k_1, M^{-1} sec^{-1}	10^4k_{-1},[b] sec^{-1}
NO_2^-	Cl^-	3.3–4.7	25	0.8 ± 0.2	1.2 ± 0.1 (1.1)[c]
			30	1.5 ± 0.4	2.1 ± 0.2 (1.9)[c]
			35	3.2 ± 0.5	3.4 ± 0.3 (3.0)[c]
			40	...	... (4.4)[c]
NO_2^-	Br^-	3.0–4.7	20	...	... (0.67)[c]
			25	1.6 ± 0.2	1.2 ± 0.2 (1.16)[c]
			30	3.3 ± 0.3	2.0 ± 0.2 (1.88)[c]
			35	5.5 ± 0.5	3.5 ± 0.3 (3.25)[c]
NO_2^-	NO_2^-	6.1–6.4	30	(~3.5)[d]	
			35	7.4 ± 0.2	⩽0.1
			37.5	12.9 ± 0.5	
			40	18.6 ± 0.5	
			42.5	22.6 ± 0.1	
NO_2^-	N_3^-	5.1–5.9	25	5.7 ± 0.3	
			30	9.0 ± 0.4	
			35	14.2 ± 0.4	~0.3
			40	22.5 ± 1.1	
NO_2^-	NCS^-	3.7–6.0	25	5.8 ± 0.3	~0.05[e]
			30	9.9 ± 0.6	
			35	17.0 ± 0.8	
			40	28.6 ± 1.5	
NO_2^-	HSO_3^-	4.1–4.5	15	35 ± 2	
			20	63 ± 3	
			25	85 ± 4	~7[e]
			30	150 ± 7	
I^-	Cl^-	2.4–2.9	25	2.3 ± 0.7	0.6 ± 0.4
			30	4.5 ± 1.5	
			35	5.9 ± 1.2	2.7 ± 0.7
I^-	Br^-	2.5–2.9	25	3.0 ± 0.3	0.72 ± 0.2
			30	5.2 ± 1.1	1.4 ± 0.4
			35	7.9 ± 1.0	2.5 ± 0.2
I^-	NCS^-	2.2–2.9	20	6 ± 1	⩽0.6
			25	12 ± 2	
			30	24 ± 4	
I^-	HSO_3^-	2.7–3.1	15	14.0 ± 0.5	⩽0.05
			20	21.7 ± 0.9	
			25	33.8 ± 1.4	
			30	52 ± 2	

[a] The initial concentration of $Co(DH)_2(X)OH_2$ in these experiments was generally about 2×10^{-4} M and the concentration of Y^- was in the range 0.03–1.0 M. The ionic strength was generally maintained at 1.0 with KNO_3. [b] From intercept of plot of k' *vs.* $[Y^-]$. [c] Directly measured rate of hydrolysis. [d] Extrapolated from data at higher temperatures. [e] From k_1 and estimated equilibrium constant.

k_1 and k_{-1} reported in Table I. The values of k_{-1} for $Co(DH)_2(NO_2)Cl^-$ and $Co(DH)_2(NO_2)Br^-$ are in satisfactory agreement with the values of the corresponding hydrolysis rate constants, 1.03×10^{-4} and 1.15×10^{-4} sec^{-1} (at 25°), reported by Ablov and Palade,[11] and confirmed by us (Table I).

The equilibrium quotient for the reaction

$$\mathrm{Co(DH)_2(NO_2)H_2O + Br^- \rightleftharpoons Co(DH)_2(NO_2)Br^- + H_2O} \quad (5)$$

determined spectrophotometrically, at seven wavelengths in the range 330–390 mμ, was 1.58 M^{-1} at 25°, in reasonable accord with the value of 1.37 M^{-1} (for k_1/k_{-1}) derived from the kinetic measurements.

(2) **Anation Reactions Proceeding Essentially to Completion.**—Under the conditions employed, the anation of $Co(DH)_2(NO_2)OH_2$ by SCN^-, N_3^-, and HSO_3^- and the anation of $Co(DH)_2(I)OH_2$ by SCN^- and HSO_3^- proceeded essentially to completion. In these cases linear plots of k' *vs.* $[Y^-]$ passed through or very close to the origin, the value of k_{-1} being immeasurably small. This was confirmed by spectrophotometric equilibrium experiments which yielded equilibrium quotients of approximately 110 and 65 M^{-1}, respectively, at 25° for the reactions of $Co(DH)_2(NO_2)OH_2$ with NCS^- and HSO_3^-. The rates of sulfite anation of $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ in solutions containing a given total ($H_2SO_3 + HSO_3^- + SO_3^{2-}$) concentration were essentially independent of pH over the pH ranges 2.6–4.5 and 2.7–3.1, respectively, throughout which the concentration of the predominant species HSO_3^- is nearly constant, while the concentrations of the minor species H_2SO_3 and SO_3^{2-} vary considerably. The measured rate constants for these reactions are thus ascribed to anation by HSO_3^-.

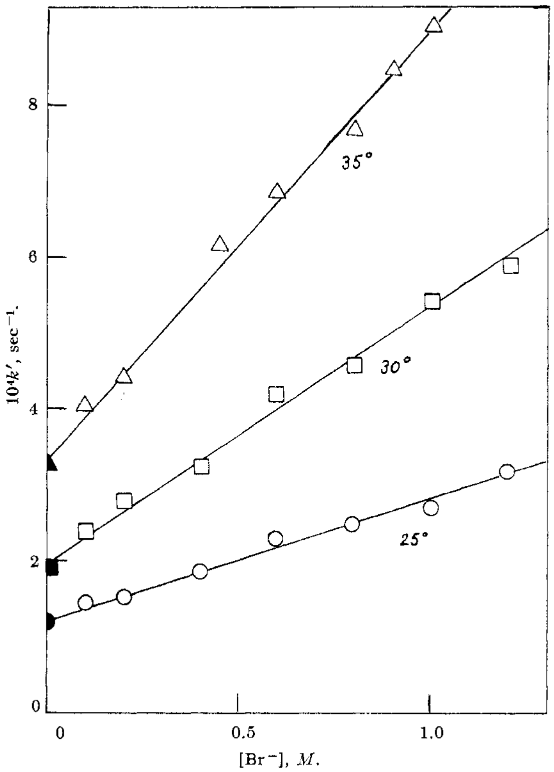

Figure 1.—Kinetic data for the reaction $Co(DH)_2(NO_2)OH_2 + Br^- \rightleftharpoons Co(DH)_2(NO_2)Br^- + H_2O$. Solid points are experimentally determined rate constants (k_{-1}) of hydrolysis of $Co(DH)_2(NO_2)Br^-$.

The anation of $Co(DH)_2(NO_2)OH_2$ by NO_2^- exhibited a pH dependence, depicted in Figure 2, in which contributions from a pH-independent path (predominant at high pH) and a pH-dependent path are apparent. The pH-independent path was found to be first order in NO_2^- and yielded the values of k_1 reported in Table I. The pH-dependent path was not investigated in detail but presumably reflects reaction of $Co(DH)_2(NO_2)OH_2$ with HNO_2, which apparently is a better nucleophile than NO_2^-. This somewhat unexpected observation is reminiscent of a similar conclusion reached by Margerum and Simandi[18] concerning the relative reactivities of HCN and CN^- as nucleophiles toward $Ni^{II}(EDTA)$.

The anation of $Co(DH)_2(I)OH_2$ by N_3^- could not be

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(18) D. W. Margerum and L. Simandi, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz, Switzerland, 1966, p 371.

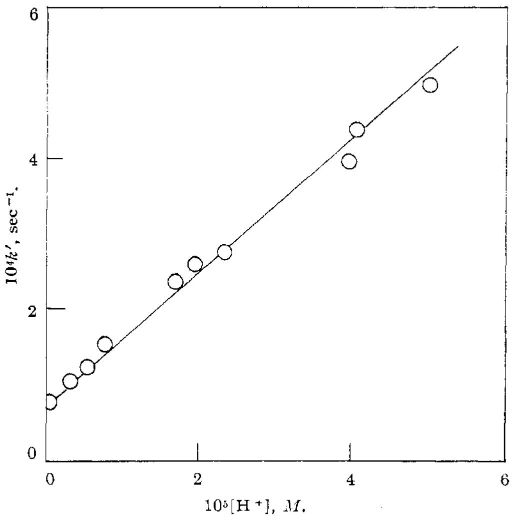

Figure 2.—pH dependence of the rate of the reaction $Co(DH)_2(NO_2)OH_2 + NO_2^- \rightarrow Co(DH)_2(NO_2)_2^- + H_2O$, at 35° and 1.0 *M* NO_2^-.

studied because of the instability of $Co(DH)_2(I)OH_2$ at the high pH demanded by N_3^-.

(3) Replacement Reactions.—To establish whether any direct replacement of one anion by another occurred with these complexes, the replacement reactions

$$Co(DH)_2(NO_2)Cl^- + Y^- \longrightarrow Co(DH)_2(NO_2)Y^- + Cl^- \quad (6)$$

were examined for $Y^- = NCS^-$ and N_3^-. It was found that the absorbance changes during the course of both reactions could be accounted for quantitatively in terms of the sequence of steps

$$Co(DH)_2(NO_2)Cl^- + H_2O \xrightarrow{k_{-1}^{Cl^-}} Co(DH)_2(NO_2)OH_2 + Cl^- \quad (7)$$

$$Co(DH)_2(NO_2)OH_2 + Y^- \xrightarrow{k_1^{Y^-}} Co(DH)_2(NO_2)Y^- \quad (8)$$

using the separately determined values of $k_1^{Y^-}$ and $k_{-1}^{Cl^-}$ from Table I. A typical comparison of the observed and calculated absorbance changes for such a reaction is depicted in Figure 3. There is thus no evidence for direct replacement of Cl^- by NCS^- or N_3^-.

Activation parameters are reported in Table II for those reactions in which the precision of the kinetic measurements was considered to warrant such determinations.

Discussion of Trends and Mechanism.—The order of reactivity of various anions for the anation of $Co(DH)_2(NO_2)OH_2$ at 30° was found to be: $Cl^- < Br^-, NO_2^- < N_3^-, NCS^- < HSO_3^-$. The corresponding order for the anation of $Co(DH)_2(I)OH_2$ is: $Cl^- < Br^- < NCS^- < HSO_3^-$. The rates of anation of $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ by a given anion are similar, the spread being somewhat smaller for the latter complex. Our results do not support Ablov's suggestion[13] that I^- exerts a much stronger *trans* effect than NO_2^-.

Although comparative kinetic data for anation reactions of other complexes are sparse, the following comparisons may be noted. The order of nucleophilicity of anions toward $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$, cited above, parallels the general order of nucleophilicity (n_{Pt}) toward platinum(II) complexes[19] and, to some degree, the order of nucleophilicity toward $Co(CN)_5^{2-}$ ($Br^- < NCS^- < N_3^-$)[20] and toward $Co(NH_3)_4(SO_3)^+$ ($NCS^- < NO_2^- < SO_3^{2-}$)[5,21] in the SN1 anations of $Co(CN)_5OH_2^{2-}$ and $Co(NH_3)_4(SO)_3OH$, respectively. This order and the relatively favorable equilibria for the replacement of water by some of the anions cited (in comparison with $Co(NH_3)_5OH_2^{3+}$) reflect considerably greater class "B" character of the cobalt in the bis(dimethylglyoximato)cobalt(III) complexes. This is also reflected in the very low reactivity toward aquobis(dimethylglyoximato)cobalt(III) complexes exhibited by oxyanions such as NO_3^- and SO_4^{2-} which are relatively reactive toward $Co(NH_3)_5OH_2^{3+}$.

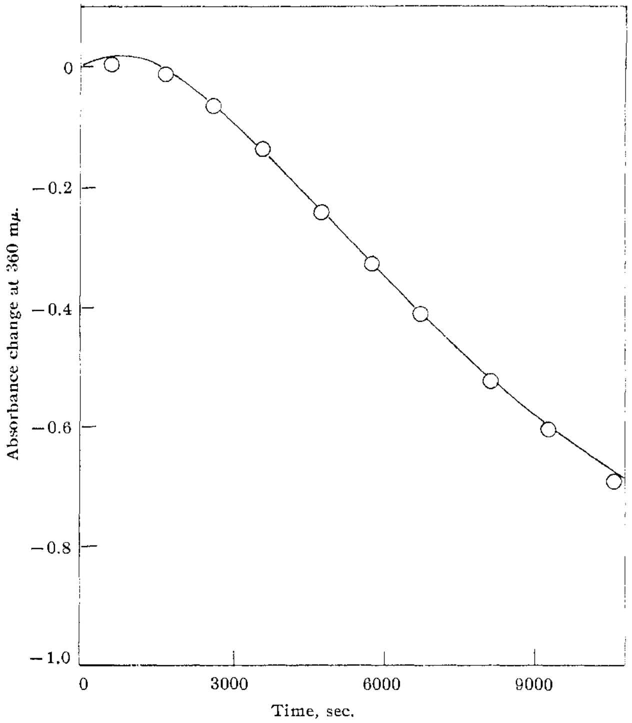

Figure 3.—Absorbance change accompanying the reaction between $Co(DH)_2(NO_2)Cl^-$ and NCS^- at 35° and 0.085 *M* NCS^-. The circles represent experimental points; the solid curve represents the absorbance change calculated according to the stepwise mechanism described by eq 7 and 8.

Table II

Activation Parameters[a] for Anation Reactions in Table I

X^-	Y^-	$\Delta H_1^{\ddagger}$, kcal/mole	$\Delta S_1^{\ddagger}$, eu
NO_2^-	Br^-	22.5 ± 3.9	0 ± 13
NO_2^-	NCS^-	19.1 ± 1.2	−9 ± 4
NO_2^-	N_3^-	16.2 ± 1.3	−19 ± 4
NO_2^-	HSO_3^-	15.0 ± 1.6	−17 ± 6
I^-	Br^-	17.8 ± 4.2	−14 ± 14
I^-	HSO_3^-	14.4 ± 0.8	−21 ± 3

[a] From temperature coefficients of k_1.

The results do not suffice to establish the mechanisms of these anation reactions, the kinetics of which are consistent with either SN1 or SN2 substitution paths.

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(19) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(20) A. Haim, R. J. Grossi, and W. K. Wilmarth, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.

(21) R. A. Palmer, Ph.D. Dissertation, The University of Chicago, 1966.

In contrast, a preliminary observation by Wilmarth and Tsiang[22] suggests that the related anation reaction

$$\mathrm{Co(DH)_2(SO_3)OH_2^- + NCS^- \longrightarrow Co(DH)_2(SO_3)(NCS)^{2-} + H_2O} \quad (9)$$

proceeds by the limiting SN1 mechanism

$$\mathrm{Co(DH)_2(SO_3)OH_2^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Co(DH)_2(SO_3)^- + H_2O} \quad (10)$$

$$\mathrm{Co(DH)_2(SO_3)^- + NCS^- \xrightarrow{k_3} Co(DH)_2(SO_3)NCS^{2-}} \quad (11)$$

with $k_2 = 11$ sec^{-1} and $k_{-2}/k_3 = 0.85$ M at 25°. If the corresponding reactions of NCS$^-$ with Co(DH)$_2$(NO$_2$)OH$_2$ and Co(DH)$_2$(I)OH$_2$ are assumed to proceed by analogous mechanisms, then the measured values of k_1 for these reactions, *i.e.*, 5.8×10^{-4} and 12×10^{-4} M^{-1} sec^{-1}, respectively, can be equated with k_2k_3/k_{-2}. These values are about 10^4 times lower than the corresponding value (13 M^{-1} sec^{-1}) for the reaction of Co(DH)$_2$(SO$_3$)OH$_2^-$ with NCS$^-$. The marked *trans*-labilizing effect of SO$_3^{2-}$ and the limiting SN1 kinetic behavior exhibited by the sulfito complex parallel the effects of SO$_3^{2-}$ on the anation reactions of Co(NH$_3$)$_4$(SO$_3$)OH$_2^+$ and Co(CN)$_4$(SO$_3$)OH$_2^{3-}$.[4,5]

It is also of interest to compare the present results with a recent determination of Randall and Alberty[23] of the kinetics of the replacement of water in aquocobalamin by NCS$^-$. The kinetics were found to be similar to those of the anation reactions reported here, with $k_1 = 7.1 \times 10^3$ M^{-1} sec^{-1} (*i.e.*, about 10^7 times the corresponding value for Co(DH)$_2$(NO$_2$)OH$_2$ or Co(DH)$_2$(I)OH$_2$)[24] and $k_{-1} = 1.8$. The much higher substitution rates exhibited by this and other cobalamin complexes,[25] in comparison with the corresponding bis(dimethylglyoximato)cobalt(III) complexes, are of interest in the light of the striking parallels between other aspects of the chemistry of the two series of complexes, noted by Schrauzer.[7] The origin and significance of these differences in substitution lability are not clear and merit further investigation.

[22] Cited in ref 5.

[23] W. C. Randall and R. A. Alberty, *Biochemistry*, **5**, 3189 (1966).

[24] A paper which appeared subsequent to the submission of this article [W. C. Randall and R. A. Alberty, *ibid.*, **6**, 1520 (1967)] reports similarly high values of k_1 for the replacement of water in aquocobalamin by other ligands, *i.e.*, N$_3^-$, 1.7×10^3; NCO$^-$, 7.3×10^2; imidazole, 27; CN$^-$, 1.5×10^3, all in M^{-1} sec^{-1} at 25°.

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The Synthesis and Characterization of the Geometrical Isomers of Tris(β-alaninato)cobalt(III) Complexes

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Two geometrical isomers (red and violet) of the tris(β-alaninato)cobalt(III) complex have been prepared. Their electronic absorption spectra show the red isomer to be facial and violet isomer to be peripheral. The infrared spectra in the region 4000–400 cm^{-1} are reported, and the partial resolution of peripheral isomer by selective adsorption on quartz has been achieved.

It is well known that the coordination compounds of trivalent cobalt with amino acids of the type Co(am)$_3$ (where am = anion of an amino acid) can exist in two geometrical isomeric forms, *i.e.*, a violet α form and a red β form, having the peripheral (1,2,6) and facial (1,2,3) configurations, respectively. These compounds have been prepared by the following methods.

(1) Dissolving cobalt(III) hydroxide in the solution of the corresponding amino acid gives a product in which the peripheral isomer predominates. In this way the complexes with glycine,[1,2] DL-alanine,[2,3] L-alanine,[4-6] D-alanine,[5] DL-valine,[7] L-leucine,[2,6,7] and DL-phenylalanine[7] were prepared.

(2) The reaction of alkali salts of amino acids with hexaamminecobalt(III) chloride favors formation of the facial isomer of the corresponding tris(aminoacido)cobalt(III) complex. The method was applied[2] to the complexes of glycine, DL-alanine, and L-leucine.

(3) Using the reaction between alkali tricarbonatocobaltates(III) and amino acids—glycine, DL-alanine, and L-leucine—in the presence of acetic acid, Mori and co-workers[2] obtained both isomers in approximately equal amounts.

(4) Finally, the tris(aminoacido)cobalt(III) complexes were prepared by direct synthesis, namely, by the oxidation of cobalt(II) acetate in the presence of an amino acid.[8] Thus the complexes with DL-alanine and DL-valine have been prepared.

The above results show that the tris(aminoacido)cobalt(III) complexes studied up to now were prepared

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