

to the value of aliphatic monoamines, whereas the value of pK_a for the ethyl analog, 6.91, corresponds to an acidity a hundred times greater and falls in the range of methyl-substituted, diprotonated ethylenediamines. Consequently, since the donor tendency of an amino group toward a metal ion can be expected, in the absence of steric hindrance, to run parallel to its basic strength, the propyl analog should be a better complexing agent than the ethyl analog. The electronic spectra of the nickel(II) complexes indicate that in fact the γ - L^+ ligand has a field strength very close to that of methylamine, whereas the β - L^+ ligand is much weaker and in the spectrochemical series occupies a position about halfway between a primary amine and water. That the propyl complexes were actually the more difficult to isolate may simply be explained by their greater solubility.

It might have been expected that the difference in ligating ability between β - L^+ and γ - L^+ would also be reflected in the frequency of the NH stretching and the

NH_2 rocking vibrations of the complexes, since these infrared modes are sensitive to the strength of the coordinate bond. Failure to observe this difference may be ascribed to the balancing effects of the increased strength of the coordinate bond and of the decreased withdrawal of electrons from the N-H bond, as the positive charge is farther removed from the donor amino group.

The results of this research show that the presence of a positive charge on a ligand does not in itself seriously prevent the formation of a coordinate bond to metal ions. It is therefore to be expected that, by an appropriate choice of multiple-charge cation ligands capable of chelation or π -bonding, a large variety of new complex metal cations can be formed, of higher charge and greater stability than those reported here.

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Electron Transfer through Mediators Coordinated to Cobalt by Nitrogen Atoms¹

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The chromium(II) reduction of a number of cobalt(III) ammine complexes containing ligands coordinated by nitrogen has been examined. The ligands studied include urethane, methyl glycinate, benzocaine, ethyl nicotinate and isonicotinate, and ethyl 4-aminobutyrate. The complexes are reduced at a rate fifty to a thousand times faster than complexes containing similar ligands attached to cobalt through oxygen. Since the possibility of adjacent attack no longer exists in the case of these substituted amines, reduction through ligands of low conductivity can be studied and is found to fall off rapidly as the number of $-CH_2-$ groups in the transfer path increases. The decrease is not related to the steric consequences of the increase in ligand size, a factor that has also been studied. The introduction of a group of low conductivity but containing atoms with electrons available for reductant bonding results in the lowering of the free energy of activation by 3 kcal./mole from that for the chromium(II) reduction of the parent hexaamminecobalt(III) ion.

Introduction

The use of carboxylic acids as mediators in electron-transfer reactions is limited by the fact that reduction by attack at some remote site on the ligand, to be measurable, must proceed at a rate equal to or greater than reaction *via* the adjacent carboxyl. Since the specific rate of adjacent attack is approximately $0.15 M^{-1} \text{ sec.}^{-1}$ at room temperature (taking the value of the chromium(II) reduction of acetatopentaamminecobalt(III) ion as an example³), this value effectively represents the lower limit of measurement, at least with chromium(II) ion as reductant. In contrast, the specific rate for the Cr(II) reduction of hexaamminecobalt(III) ion at 25° is $9 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$, fifteen

hundred times as slow.⁴ The possibility of substituted amines as mediators is immediately suggested, for just as electron transfer is slow through the coordinated NH_3 group because of the lack of unpaired electrons on the nitrogen, adjacent attack in the amine-N complexes should be negligible. This paper reports the study of the rates of reduction of some pentaammine complexes containing substituted amines in the sixth coordination position about the cobalt.

Experimental

Materials.—Methyl aminoacetate (methyl glycinate), ethyl 4-aminobutyrate, and the esters of the nicotinic acids were obtained from the acids *via* the respective acid chlorides. The ester hydrochlorides were freed from HCl by treating an ether suspension with either sodium hydroxide or barium hydroxide, drying the ether solution of the ester over magnesium sulfate, and removing the ether at a low temperature in the absence of

(1) This research was supported by grants from the Petroleum Research Fund administered by the American Chemical Society and from the National Science Foundation.

(2) Alfred P. Sloan Foundation Fellow.

(3) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).

(4) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

moisture. The ester ethyl 4-aminobenzoate (benzocaine) was obtained commercially. Cobalt(III) ammine complexes containing the sixth ligand coordinated through nitrogen were prepared by heating pentaammineaquocobalt(III) nitrate in the molten compound for periods of time ranging from 5 to 25 hr. Table I lists the times and temperatures used. The melt was cooled, the excess organic material removed by extraction with a suitable solvent, and the cobalt compound then recrystallized from perchloric acid solution. The carbamato complex was prepared by the method of Linhard.⁵ All other cobalt(III) pentaammine complexes were obtained by heating on a water bath a mixture of the aquo complex and the organic acid in a water solution adjusted to a pH of less than 5. The methods used to determine the purity of the complexes have been described previously.⁶ Pentaammine(methyl glycinate-N) was the only compound that did not give a good analysis, probably due to some induced hydrolysis of the ester followed by the formation of glycinatopentaamminecobalt(III) nitrate. The point of attachment of the ligands was checked by infrared examination of the complexes, run as Nujol mulls, and by titration with standard base. The presence of carbonyl absorption near 1700 cm^{-1} was taken as evidence for intact ester groups, so that coordination of the ligand was through the nitrogen, while replacement of the 1700 cm^{-1} absorption by peaks at 1600 and 1400 cm^{-1} showed coordination *via* the carboxyl group. Titration with base served to determine the amount (if any) of induced ester hydrolysis in the complexes.

TABLE I

PREPARATION OF N-COORDINATED PENTAAMMINE COMPLEXES

Ligand	M.p., °C.	Prep. temp., °C.	Time, hr.
Urethane	50	120	15
Methyl glycinate	Liquid	100	5
Benzocaine	90	120	20
Ethyl isonicotinate	Liquid	120	20
Ethyl nicotinate	Liquid	120	25
Ethyl 4-aminobutyrate	Liquid	110	15

Reagents.—The solution of sodium perchlorate used in adjusting ionic strengths of the solutions used in the kinetic measurements was prepared by neutralizing 70% perchloric acid (reagent grade) with electrolytic sodium hydroxide. Chromium(II) solutions were prepared by zinc reduction of chromium(III) perchlorate; after reduction the solution was transferred to a storage vessel. The reducing content of the solution was determined by titration with potassium permanganate.

Kinetic Measurements.—All rates were followed in a Beckman DK 1 spectrophotometer fitted with two time switches, one with a 1-hr. cycle, one with a 24-hr. cycle. The reacting solutions were placed in 10-cm. optical cells constructed with a double wall so that water from a constant temperature bath could be circulated continuously around the contents, maintaining temperature constant to $\pm 0.05^\circ$. The required amount of cobalt complex was dissolved in 20 or 24 ml. of the sodium perchlorate-perchloric acid solution and degassed in the cell by bubbling dry nitrogen through for 10 min.; the chromium(II) solution was then added through a serum cap from a gas-tight syringe. Measurements of the optical density at 410 $\text{m}\mu$ of the solutions as a function of time was continued until the absorbance remained constant for 5 min. Reactions were run under either first-order (with a large excess of Cr(II)) or second-order conditions. The order in all cases was established as first in Cr(II) concentration and first in complex concentration. Most of the reactions studied were acid independent, at least in the range of 0.2–0.6 *M*. For all reactions the ionic strength was maintained at 1.0; the complex concentration lay between 1×10^{-4} and 4×10^{-3} *M* and the chromium(II) concentration between 1×10^{-3} and $2 \times$

10^{-2} *M*. Specific rates obtained from duplicate runs agreed within $\pm 2\%$.

Results

The specific rates for the chromium(II) reduction of a series of cobalt(III) complexes containing ligands attached through oxygen and through nitrogen are listed in Table II. In all cases the ligand was transferred from cobalt to chromium, at least as shown by ion-exchange experiments, so that the over-all reaction can be written as

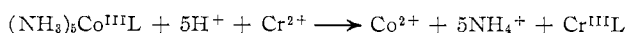


Table III lists the rates for the reduction of a series of pentaamminecobalt(III) complexes where reductant attack must take place at the carboxyl group adjacent to the cobalt

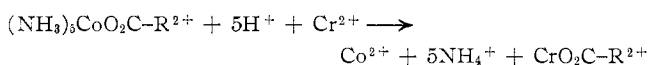


Table IV lists the activation parameters for a number of the reactions.

TABLE II

SPECIFIC RATES FOR THE CHROMIUM(II) REDUCTION OF COBALT(III) COMPLEXES CONTAINING O- AND N-COORDINATED LIGANDS

Complex	k , $M^{-1} \text{sec}^{-1}$	Temp., °C.
(i) Pentaammines		
Carbamato	$9.1 + 107[\text{H}^+]^a$	25.0
Urethane-N-	160	9.9
Benzocaine-N-	180	10.0
4-Aminobutyrate	0.122	25.0
	0.23	35.4
Ethyl 4-aminobutyrate-N-	0.017	24.1
	0.04	35.5
Nicotinato	0.0655	17.0
	0.134	30.0
Ethyl nicotinate-N-	0.0135	25.0
	0.037	35.5
Glycinato	0.53	24.0
Methyl glycinate-N-	4	24.0
(ii) Tetraammine		
Glycinato	0.071	15.0
	0.151	25.0

^a Each specific rate reported is the average of three or more experimental runs.

TABLE III

SPECIFIC RATES OF THE CHROMIUM(II) REDUCTION OF SOME PENTAAMMINECOBALT(III) COMPLEXES

Ligand	k , $M^{-1} \text{sec}^{-1}$	Temp., °C.
Cyclopropanecarboxylato	0.125	25.0
	0.187	35.0
Cyclobutanecarboxylato	0.05	25.0
	0.112	35.0
Cyclopentanecarboxylato	0.072	25.0
	0.127	35.0
Cyclohexanecarboxylato	0.040	24.2
	0.096	35.0

Discussion

Equivalence of Carboxyl Oxygens.—The infrared spectra of ammine complexes containing monocarboxylic acids as ligands show a strong absorption band

(5) M. Linhard and H. Flygare, *Z. anorg. Chem.*, **251**, 25 (1943).

(6) R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

TABLE IV
ACTIVATION PARAMETERS FOR CHROMIUM(II) REDUCTIONS
AT 25°

Ligand	ΔH^* , kcal./mole	ΔS^* , e.u.	ΔG^* , kcal./mole
4-Aminobutyrate	9.9	-30	19
Ethyl 4-aminobutyrate-N-Nicotinato	13.5	-21	20
Ethyl nicotinate-N-	4.7	-48	19
Cyclopropanecarboxylato	17.5	-9	20
Cyclobutanecarboxylato	7.3	-38	19
Cyclopentanecarboxylato	10.3	-29	19
Cyclohexanecarboxylato	9.2	-33	19
Glycinato ^a	12.4	-23	19
	12.2	-21	19

^a Tetraammineglycinatocobalt(III).

at 1600 cm^{-1} . This coupled with the absence⁷ of any absorption at 1720 cm^{-1} is indicative of ionic carboxyl and appears to be quite general. The only important exception is the pentaamminecarbonatocobalt(III) complex, where there is infrared evidence for a covalent Co-O bond^{8,9} and where tracer studies have shown¹⁰ that the liberation of carbon dioxide occurs without rupture of the Co-O bond. Structures of the com-

plexes should perhaps be written as $(\text{NH}_3)_5\text{Co} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \text{C}-\text{R}$

rather than $(\text{NH}_3)_5\text{Co}-\text{O}-\text{C}-\text{R}$, emphasizing the equivalence of the two carboxyl oxygens.¹¹ The nature of the metal-ligand bond is not clear and may in fact differ in the solid and in solution, for tracer experiments seem to indicate two different types of oxygen in the formatopentaamminecobalt(III) complex.¹²

Ligand Size and Reduction Rate.—The results of Tables III and IV show that the size of the substituent R in the complex $(\text{NH}_3)_5\text{CoO}_2\text{C}-\text{R}^{2+}$ does not affect the rate of reduction through the adjacent carboxyl very much: as the size increases, the entropy of activation becomes less negative (-38 e.u. for the reduction of cyclopropanecarboxylato to -23 e.u. for the cyclohexanecarboxylato complex), reflecting the increased order in the original cobalt complex. Cyclopentanecarboxylato does not fit the pattern, and the reasons for this are not immediately clear. The changes in the entropy of activation are partly offset by changes in the enthalpy, so that the net result is a lowering of the rate by a factor of 3 at 25°. As the temperature increases, the difference becomes smaller and the isokinetic temperature is calculated as 72°. The results do suggest that any complete theory of electron transfer through bridging groups must take into account the steric properties of each group, even those not involved directly in the electron-transfer process, and allowance must be made for the temperature factor.¹³

The specific rate of the reduction of the glycinato-

(7) D. N. Sen, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 211 (1955).

(8) M. Drouin, J. Mathieu, and H. Poulet, *J. chim. Phys.*, **58**, 322 (1961).

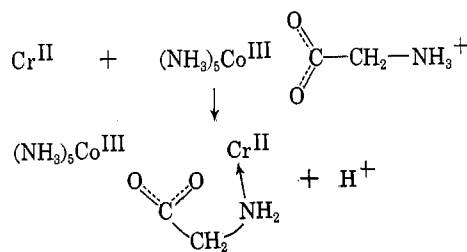
(9) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959).

(10) J. P. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, **74**, 268 (1952).

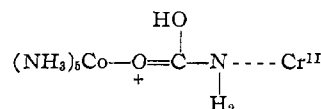
(11) R. T. M. Fraser, *Nature*, **202**, 691 (1964).

(12) H. Taube, private communication.

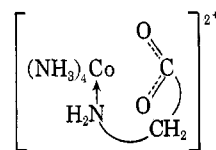
pentaammine complex is 0.53 $M^{-1} \text{sec}^{-1}$ and is acid-independent over the range $0.2 M \leq [\text{H}^+] \leq 0.6 M$, while that of the glycinatotetraammine is 0.15 $M^{-1} \text{sec}^{-1}$ at 25°. The rate constant recorded for the pentaammine complex does not agree with that in the literature (0.06 $M^{-1} \text{sec}^{-1}$),¹⁴ but the new value has been checked on two different samples, prepared by different workers. The difference in rates between the pentaammine and the tetraammine complexes suggests that the greater rate of the former is not due to any inductomeric affect, but rather to coordination of the reductant by the terminal amine group during the transfer process.



This results in the formation of the chelated chromium(III) complex, in a manner similar to that found in the reduction of the pyridine 2-carboxylatopentaamminecobalt(III) ion.¹⁵ The electron that is transferred probably uses both the OCO path and the NCCO since the acid-dependent term in the rate law for the reduction of the carbamate complex indicates that attack by the reductant does take place at the lone pair electrons of the nitrogen, with electron transfer through the conjugated path

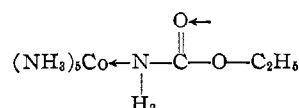


The tetraammine complex itself is interesting, since the chelation of the glycine forms a five-membered ring with very little flexibility.



Extensive rearrangement cannot take place in the activated complex, and this is reflected in the activation entropy of only -21 e.u.

Electron Transmission through Nitrogen Coordinated to Cobalt(III).—When ethyl carbamate (urethane) is bonded to the pentaamminecobalt(III) residue through the nitrogen, the only path for electron transfer is OCN


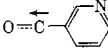


(13) Compare J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960), and P. V. Manning, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, **68**, 265 (1964).

(14) K. D. Kopple and G. F. Svartos, *J. Am. Chem. Soc.*, **82**, 3227 (1960).

(15) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

TABLE V
 RATES OF Co(III) REDUCTION THROUGH LIGANDS OF LOW CONDUCTIVITY AT 25°

Ligand	Transfer path	Specific rate, $M^{-1} \text{ sec.}^{-1}$	
Acetato	$\text{O}=\text{C}=\text{O}$	0.16	
Carbamato	$\text{O}=\text{C}-\text{N}$	8	
Ethyl carbamate-N	$\text{N}-\text{C}=\text{O}$	168 ^a	400
Methyl glycinate-N	$\text{N}-\text{C}-\text{C}=\text{O}$	3.8	
Glycinato	$\text{O}=\text{C}-\text{C}-\text{N}$		$1.6 \times 10^{-3} < k < 8 \times 10^{-2}$
Ethyl nicotinate-N		1.5×10^{-2}	
Nicotinato			$6.7 \times 10^{-3} < k < 3 \times 10^{-4}$
Ethyl 4-aminobutyrate-N	$\text{N}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O}$	1.7×10^{-2}	
4-Aminobutyrate	$\text{O}=\text{C}-\text{C}-\text{C}-\text{C}-\text{N}$		$7 \times 10^{-6} < k < 3.5 \times 10^{-4}$

^a At 9.9°.

for there is as little possibility for transmission of the electron directly through the nitrogen here as there is in the hexaamminecobalt(III) ion. In spite of the increased charge on the complex, the rate of reduction is at least 10^3 times more rapid than the reduction of the pentaammineacetato, and this is also the case for reduction through the aromatic system in the benzocaine complex. In the same way, the rate of reduction of the ethyl isonicotinate-N- complex appears too rapid to be measured easily, and this is not unexpected since the rate of reduction of the isonicotinato complex *via* the basic path¹² is $1.5 \times 10^3 M^{-1} \text{ sec.}^{-1}$. A reasonable estimate for the reduction rate of the N-bonded complex might therefore be $1.5 \times 10^6 M^{-1} \text{ sec.}^{-1}$ at 25°.

The contrast (of the rapid transfer *through* adjacent nitrogen with that *to* the tetravalent atom directly) creates a situation favorable for the detection of electron transfer through nonconjugated ligands. Thus, while transfer through the $-(\text{CH}_2)_2-$ chain in the levulinato-pentaamminecobalt(III) ion cannot be studied because of the relatively high rate of attack at the adjacent carboxyl ($0.15 M^{-1} \text{ sec.}^{-1}$ at 25°),¹² it can be in the $-(\text{CH}_2)_3-$ system in the 4-aminobutyrate-N complex. Similarly, electron transfer through the nicotinate ligand can be demonstrated in the reduction of the ethyl nicotinate-N- complex but not the nicotinato. The values for these reduction rates can be calculated from a comparison of the rates for the acetato, carba-

mato, and ethyl carbamate-N, since reductant coordination to nitrogen in a ligand bound to cobalt through oxygen leads to reduction 50 to 2500 times slower than coordination to oxygen in a ligand coordinated to cobalt through nitrogen. The ratio is 50 ($= k_{\text{ethyl carbamate-N}}/k_{\text{carbamato}}$) if most of the reduction of the carbamato complex takes place *via* the NCO path, that is, if the high rate observed is due to the conductivity of the nitrogen and not to an electromeric effect. If, on the other hand, the conductivity of a remote nitrogen approximates to that of an oxygen, the ratio becomes 2500 ($= k_{\text{ethyl carbamate-N}}/k_{\text{acetato}}$). Using these two figures as the upper and lower limits and the experimental values for the reduction of the ethyl nicotinate-N and ethyl 4-aminobutyrate-N complexes, the reaction rates for the corresponding carboxy complexes are obtained (Table V).

It is clear that transmission through the carboxy ligands containing CH_2 chains is too low to be observed experimentally. In the case of the glycinato complex, however, the NCCO path may be as effective as the OCO for electron transfer, especially as chelation in the transition state simultaneously makes the adjacent oxygen and the nitrogen equally accessible to the reductant.

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