Table V. Activation Energies for the Anation of *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ by Chloride Ion in DMA, TMS, and DMF

Reaction	$[Cl] \times 10^3$ *M*	E_a, kcal mole^{-1}	Solvent
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *trans*-$[CoCl_2(en)_2]^+$	4.1	26.5 ± 0.3	DMA
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *cis*-$[CoCl_2(en)_2]^+$	38.0	27.5 ± 0.3	DMA
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *trans*-$[CoCl_2(en)_2]^+$	4.0	26.5 ± 0.3	TMS
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *cis*-$[CoCl_2(en)_2]^+$	91.5	29.0 ± 0.3	TMS
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *trans*-$[CoCl_2(en)_2]^+$	7.1	27.5 ± 0.3	DMF
cis-$[CoCl(DMSO)(en)_2]^{2+} \longrightarrow$ *cis*-$[CoCl_2(en)_2]^+$	53.0	27.5 ± 0.3	DMF

$(DMSO)(en)_2]^{2+}$ does not fall off at low Cl^- concentrations, as in the other systems, is difficult to explain unless it is due to methanolysis competing favorably with anation under all conditions including in the ion pair.

Finally it can be said that anation reactions as exemplified by these systems require in general at least these 11 reactions for specification although under some conditions some are not relevant (*e.g.*, sequence 1), some can be slow enough to be ignored, and some can be unimportant (*e.g.*, reactions 4 and 11) because the concentration of the starting material (in this case the ion triplet) is exceedingly low.

In all systems in which the steric course has been followed without the interference of subsequent isomerization, *trans* product is favored in the reaction of the ion pair and *cis* product from the ion triplet. Thus as one expects, orientation effects in the solvation sphere are important in product determination. In most systems it seems that, once an ion is established in the inner solvation sphere, then its entry is preferred over solvent interchange or exchange.

Activation energies for those systems in which they were determined are collected in Table V. As the above discussion would predict they are found to be dependent on the degree of association and the dependence quite adequately accounts for the observed variation in rate of formation of the transition state in the assigned dissociative reaction.

Electron Transfer through Organic Structural Units. V. Reductions of Carboxamidopentaamminecobalt(III) Complexes[1a]

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Contribution from the Departments of Chemistry, San Francisco State College, San Francisco, California, and Kent State University, Kent, Ohio.
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Abstract: Pentaamminecobalt(III) complexes of seven N,N-disubstituted amides, and of the amide-like heterocycles 2- and 4-pyridone, have been prepared as their perchlorates, and the specific rates at which they are reduced with Cr(II) have been measured at 24.5°. In each of these, the amide is coordinated to Co(III) through oxygen rather than nitrogen. Ligand fields associated with coordinated acetamides and benzamides are weaker than those associated with formamides; the acetamido and benzamido complexes exhibit maxima near 520 mμ (as contrasted to 506 mμ for the formamido derivatives) and are labile to aquation in warm water. Separations, using cation-exchange chromatography, of the Cr(III)-containing products resulting from these reductions yielded $Cr(H_2O)_6^{3+}$, and, in all cases except that of the 4-pyridone complex, this aquo ion was the sole monomeric Cr(III) product, thus implying reduction through "outer-sphere" activated complexes for these amide derivatives. Unlike reduction of carboxylato derivatives *via* ligand transfer, which are retarded by steric crowding, reductions of the amide derivatives appear to be subject to steric assistance; reductions of the acetamido and benzamido complexes are more rapid than those of the formamido complexes. This suggests a partial relief of crowding during the activation process for these reductions. Reduction of Co(III) *via* ligand transfer was observed only for the complex of 4-pyridone. This mode of reduction, which yields an amide-bound Cr(III) species, competes here with outer-sphere reduction and proceeds about 1.5 times as rapidly as the latter.

Although the reductions, with Cr(II), of well over 100 different carboxylatopentaamminecobalt(III) complexes (I) have been studied,[2] only a handful of carboxamide derivatives (II or III) in the $(NH_3)_5Co^{III}$ series have been reported.

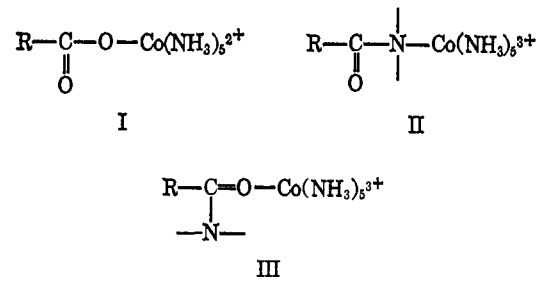
The reductions of complexes derived from N,N-dimethylformamide (IV, R = H) and 2-pyridone (VII)[3] are faster, by several orders of magnitude, than reductions of the hexaamminecobalt(III) complex[4] and the imidazolepentaammine complex,[2c] being,

(1) (a) This research was sponsored in part by the Faculty Development Fund at San Francisco State College. This support is gratefully acknowledged. (b) Department of Chemistry, Kent State University, Kent, Ohio.

(2) See, for example, (a) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); (b) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961); (c) E. S. Gould, *ibid.*, **87**, 4730 (1965); (d) R. T. M. Fraser, *ibid.*, **83**, 4921 (1961); (e) E. S. Gould, *ibid.*, **88**, 2983 (1966).

(3) E. S. Gould, *ibid.*, **89**, 5792 (1967).

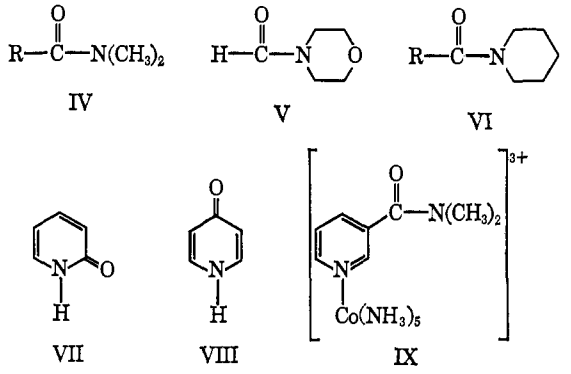
(4) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).



I II III

at the same time, less than one-tenth as rapid as reductions of the vast majority of the carboxylate derivatives (I). Since the very slow reductions are thought to proceed *via* "outer-sphere" activated complexes, whereas the carboxylato complexes are reduced *via* transfer of the carboxylato ligand from cobalt to chromium, there is a question as to which mechanism operates in reduction of the amide complexes, or whether both may perhaps operate together. This problem has become of greater interest in view of recent evidence[5] that a carboxamido group, if favorably situated, may transfer a reducing electron from one site to another within a ligand.

This report describes the preparation and reduction of $Co(NH_3)_5$ derivatives of amides of types IV–VI and adds further information concerning the reduction, with Cr(II), of the previously described[3] derivatives of pyridones VII and VIII and the ring-coordinated pyridine complex IX. Evidence is presented that each of these complexes is reduced through the "outer-sphere" route with, however, a substantial inner-sphere contribution to the Cr(II) reduction of the $Co(NH_3)_5$ complex of 4-pyridone (VIII).



IV V VI

VII VIII IX

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate, lithium perchlorate solutions (for kinetic runs), and chromous solutions were prepared as described.[2a] N-Acetyl- and N-benzoylpiperidine and N,N-dimethylbenzamide were prepared by acylation of the appropriate secondary amine with acetic anhydride or benzoyl chloride.[6] Other amides (Aldrich products) were used as received. Cation-exchange resin (Bio-Rad, 50W-X2, 200–400 mesh), used in separation of reaction products, was pretreated as described.[3]

Preparation of the Complexes. The complexes were prepared by treatment of aquopentaamminecobalt(III) perchlorate (2.0 g) with a large excess (4.0 g) of amide at 95° in a rotary evaporator. Heating periods were 10–20 min. The formamide derivatives could then be isolated simply by cooling the reaction mixture, adding 3 cc of water and 1.5 cc of 12 *N* $HClO_4$, then cooling to 0°. The formamide-substituted complex precipitated as its perchlorate and was recrystallized from hot water.

When this work-up procedure was applied to the reaction mixture from the preparations involving substituted acetamides and benzamides, the products formed were largely (although not entirely) mixtures of the parent aquo complex and the corresponding acetato or benzoato complex. For these preparations, the conditions during work-up were more gentle; at the conclusion of the heating period, the mixture was extracted with 300 cc of ether and the ether layer discarded. To the pasty material remaining was added 50 ml of warm methanol. The mixture was cooled and filtered to remove a large portion of the unreacted aquo complex. The methanol was removed by rotary evaporation, and 3 cc of water was added. The mixture was then cooled to 0°, and 3 cc of 12 *N* $HClO_4$ added dropwise with cooling. The precipitated material was quickly filtered off and the filtrate cooled at −10° for several hours, yielding the magenta amide complexes. Further purification, if necessary was carried out by dissolving the complex in water at 25°, adding $HClO_4$ as before, and recooling to −10°. (Aqueous solutions of acetamido or benzamido complexes were kept below 30° to minimize hydrolysis to the aquopentaamminecobalt(III) complex.) The above procedure for work-up, when applied to preparations of the complexes from 2- and 4-pyridone, gave superior products.

These procedures were not effective in preparing complexes from N-acetylmorpholine, 2-acetamidopyridine, picolinamide, N-maleylpiperidine, and N,N-dimethylmaleamide, from such high-melting amides as oxamic acid and benzanilide, or from such simple amides as formamide and acetamide.

Kinetic Experiments. Specific rates of reduction were determined by following the decrease in optical density at the high-wavelength visible absorption maximum of the cobalt(III) complex as previously described.[2c] For the acetamido- and benzamido-substituted complexes, hydrolysis of the Co(III) complex prior to addition of Cr(II) was minimized by adding the solid complex to the reaction cell, purging with prepurified N_2, then adding an oxygen-free solution of supporting electrolyte which had been preequilibrated to 24.5°, thus eliminating the period of bubbling to remove oxygen from solution. Rates were run under pseudo-first conditions with the ratio Cr(II)/Co(III) about 12. Temperatures were constant to within better than 0.1° during the entire series of experiments. Acidities were between 0.12 and 1.2 *M;* for runs at the lower acidities, ionic strengths were kept at 1.3 by addition of $LiClO_4$. Reactions were allowed to proceed for at least five half-lives. Specific rates did not vary systematically with acidity within the range studied, but values appeared to be considerably less reproducible at the lower acidities. The source of scatter is not clear, but the more reliable values are taken as those obtained in 1.2 *M* acid. Rate constants taken from several points in a single run agreed to better than 5%, and those from different runs at high acidities checked to better than 10%.

Ion-Exchange Experiments. Two series of reactions were carried out. In the first series, 0.06-mmole quantities of the Co(III) complexes were dissolved in 0.5–1.0 ml of oxygen-free water, using vials sealed by rubber serum caps. To these solutions were added 25 μl of 12 *M* $HClO_4$; then a quantity of 0.9 *M* Cr(II) equivalent to Co(III) was taken. Reactions were allowed to proceed 3.5 hr at 25°, after which the vial was opened and the reaction mixture subjected to cation-exchange chromatography.

The second series of reactions employed similar quantities of Co(III) complexes, water, and $HClO_4$, but Cr(II) was added in fourfold excess. After a reaction period corresponding to six half-lives, the solution was diluted with 5 ml of 0.02 *F* $HClO_4$ and air bubbled through for 10 min to oxidize the unreacted Cr(II) to dimeric Cr(III). The resulting solution was then absorbed onto the cation-exchange column.

Cation-exchange separations were run at 2°, using 6 cc of resin comprising a 7-in. column; the elution rate was 0.5 cc/min. Initial stages of elution employed a solution 1.0 *M* in $NaClO_4$ and 0.02 *M* in $HClO_4$, but, as the elution proceeded, the $NaClO_4$ concentration of the eluent was gradually raised to 3.0 *M* while keeping the $HClO_4$ concentration near 0.02 *M*. Complete separations generally required less than 90 min; at the end of this period, only the green di- and polynuclear Cr(III) species remained on the column. These were not eluted.

Ion-exchange experiments were carried out with each of the Co(III) complexes in Table I except the substituted benzamide complexes (IV and VI, R = C_6H_5), which were available in insufficient quantity, and the N-formylpiperidine derivative (VI, R = H), which was not sufficiently soluble at or near room temperature. In all reactions, except for that involving the complex of 4-pyridone (VIII), the sole eluted Cr(III) product was the blue-violet $Cr(H_2O)_6^{3+}$

(5) F. R. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, 88, 4295 (1966).
(6) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 260.

Table I. Pentaamminecobalt(III) Perchlorates, $LCo(NH_3)_5(ClO_4)_3$

L	% Co Calcd	% Co Found[a]	λ_{max}, mμ	ϵ_1	λ_{max}, mμ	ϵ_2	$\nu_{C=O}$, cm^{-1} Complex[b]	$\nu_{C=O}$, cm^{-1} Free ligand	$k_{Cr(II)}$[c]
N,N-Dimethylformamide (IV, R = H)	11.4	11.4	505	76.0	347	62.5	1663	1674	0.0072[d]
N-Formylmorpholine (V)	10.6	10.5	507	72.0	347	66.0	1647	1667	0.0064
N-Formylpiperidine (VI, R = H)	10.6	10.5	506	71.2	346	64.6	1655	1667	0.0081
N,N-Dimethylacetamide (IV, R = CH_3)	11.1	11.1	520	66.5	340[e]	73	1612	1640	0.018
N,N-Dimethylbenzamide (IV, R = C_6H_5)			524				1598	1630	0.027
N-Acetylpiperidine (VI, R = CH_3)	10.3	10.1	523	78.2			1595	1641	0.025
N-Benzoylpiperidine (VI, R = C_6H_5)	9.3	9.4	523	75.0			1588	1622	0.062
2-Pyridone (VII)	11.0	11.0	523	105			1645	1659	0.012
4-Pyridone (VIII)	11.0	10.8	519	107	370[e]	96	1642	1647	0.024[d]
N,N-Dimethylnicotinamide (IX)	9.8	10.0	475	63.2	334	86.5	1632	1634	0.029[d]

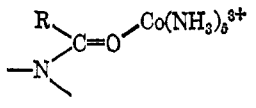
[a] See ref 2a. [b] KBr pellet. [c] Specific rate for reaction with Cr(II) (l. mole^{-1} sec^{-1} at 24.5°), 1.2 M $HClO_4$, μ = 1.3. [d] See ref 3. [e] Shoulder.

ion, which was recovered in quantity equivalent to 80–95% of the Co(III) taken.

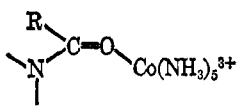
Reduction of the 4-pyridone complex yielded, in addition to $Cr(H_2O)_6^{3+}$, a blue-green ion having absorption maxima at 586 mμ (ε 25) and 415 mμ (ε 27), which was eluted slightly more slowly off the column than $Cr(H_2O)_6^{3+}$, and which was converted to $Cr(H_2O)_6^{3+}$ (ϵ_{max} 13.4 (574 mμ), 15.6 (408 mμ)[7]) when heated at 90° for 8 min in 0.02 M $HClO_4$. This species comprised 61% of the eluted Cr(III) recovered from the reaction of equivalent quantities of Cr(II) and Co(III) (reaction time 3.5 hr), and 59% of the eluted Cr(III) from the reaction using a fourfold excess of Cr(II) (reaction time 12 min). It was not formed when uncomplexed 4-pyridone was treated with Cr(II) in dilute $HClO_4$.

Results and Discussion

Spectral and kinetic data are summarized in Table I. Except for the nicotinamide derivative (IX), which has been shown to be coordinated through the ring nitrogen,[3] all complexes have visible maxima on the low-energy side of the aquopentaammine (492 mμ) and the many carboxylatopentaammine (501–504 mμ) complexes, strongly pointing to O coordination (III), rather than N coordination (II). This assignment is confirmed by the shift, to lower frequencies, of the carbonyl-stretching frequency when each of the amides is converted to its $Co(NH_3)_5$ complex.[8] Two stereoisomers are, in principle, possible for the first eight of these complexes, one with the $Co(NH_3)_5$ group *trans* to the amide nitrogen (X), the other *cis* (XI); present evidence does not allow a choice between these two



X



XI

forms. Rate curves for the reductions exhibit only a single kinetic component; thus it is probable that only one form is present in major quantity. If two are present, they are rapidly interconverted or (even less likely) are reduced at very nearly the same specific rates.

Among the derivatives of the N,N-disubstituted amides, the formamide complexes differ from the acetamido and benzamido in several respects. The formamido compounds absorb near 506 and 347 mμ, may be recrystallized unchanged from hot aqueous $HClO_4$, and are reduced at rate constants near 0.007 l. mole^{-1} sec^{-1} at 24.5°. The long-wavelength maxima for the acetamido and benzamido complexes have been shifted at 520–524 mμ, with the peak near 347 mμ either modified to a shoulder or completely obscured by strong ultraviolet bands lying below 300 mμ; moreover, these complexes undergo rapid aquation to $Co(NH_3)_5H_2O^{3+}$ in hot aqueous solution and, although more crowded than the formamido complexes, are reduced at specific rates greater than 10^{-2} l. mole^{-1} sec^{-1}. Finally, the changes in carbonyl stretching frequencies resulting from coordination of the acetamido and benzamido ligands with $Co(NH_3)_5$ are considerably greater than those for the formamides.

The pronounced shift of the high-wavelength visible maximum occasioned by acetamido or benzamido coordination reflects a weakening of the ligand field about Co(III). This is almost certainly a steric effect, for scale models of the complexes indicate much more serious nonbonded interference between the amide substitutents and coordinated ammonia in the acetamido and benzamido complexes than in the formamido. The greater labilities of the acetamido and benzamido derivatives are in accord with this picture, for assuming aquation to occur with Co–O bond breakage (rather than C–O breakage), any weakening of the cobalt–amide bond should facilitate reaction.[9]

The greater shifts in the carbonyl stretching frequencies upon coordination of the acetamido and benzamido ligands are unexpected. Such shifts are presumed to reflect a decrease in the double-bond character of the carbonyl group when O coordination occurs,[8a] and it would perhaps be anticipated that, contrary to observation, the lesser decrease would accompany the weaker coordination. Of the other effects which might come into play here, it is suggested here that the C=O double-bond character in the com-

(7) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(8) See, for example, (a) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *ibid.*, **79**, 1574 (1957); (b) C. D. Schulbach and R. S. Drago, *ibid.*, **82**, 4484 (1960).

(9) This should be the case whether aquation proceeds *via* preliminary dissociation or (less likely) *via* direct displacement.

plexes of the more bulky amides has been further decreased by nonbonded interferences between the amide substituents and the *cis*-coordinated ammonia ligands which make it difficult for the carbonyl group and the three groups attached to it to occupy a common plane. Examination of scale models of the complexes is consistent with this view.

When the amide complexes in the present study were reduced with Cr(II) and the products separated using cation-exchange chromatography, the $Cr(H_2O)_6^{3+}$ ion was obtained. Moreover, in all cases except that of the 4-pyridone complex (VIII), this *aquo ion was the sole monomeric Cr(III) product.* Although it is recognized that aquation of Cr(III) complexes having one or more organic ligands may occur on highly acidic sulfonate resins of the type used,[10] the observed stability on resin of the Cr(III) complex of 4-pyridone and the reported stability of the carboxamide-coordinated complexes of 3- and 4-pyridinecarboxamide[5] strongly indicate that these reductions (except for that of the 4-pyridone complex) yield $Cr(H_2O)_6^{3+}$, rather than amide-coordinated Cr(III), as the principal, and perhaps the sole, Cr(III) species. Thus, the observed products imply reduction through outer-sphere activated complexes for these amide derivatives.

The predominance of outer-sphere path for reduction of the N,N-dimethylnicotinamide complex (IX) is of some interest, for the reduction of the corresponding nonmethylated complex[5] has been reported to proceed through a combination of the inner- and the outer-sphere paths with the ratio of rates (at 25°) for the two paths being 0.032/0.013. If it is assumed that N methylation may retard electron transfer through the amide group to about the same degree that C methylation at C_α retards electron transfer through a bound carboxylato group[2e] (the steric situations are similar), then dimethylation should decrease the specific rate of reduction *via* ligand transfer approximately tenfold, *i.e.*, to about 0.003 l. mole^{-1} sec. This lower value constitutes only about 10% of the observed reduction rate (0.029) for the dimethyl compound, and the Cr(III) product resulting from this path might well be overlooked under the separation conditions used.

The suggestion made here that each of the carboxamide complexes is reduced through the outer-sphere path receives further support from the manner in which specific rates of reduction vary with structure. Unlike reduction *via* ligand transfer in the carboxylato series, which has been observed to be retarded by steric crowding,[2c] reduction of the carboxamido derivatives appears to be accelerated by crowding. Thus, substitution of the formyl hydrogen in the formamido complex with either the more electron-attracting phenyl group or the less electron-attracting methyl group speeds up reduction. Although the rate differences are small, the implication is that the transition states in these reductions are less crowded than the reactants, *i.e.*, that the activation process requires stretching of one or more cobalt-to-ligand bonds without compensating progress in bond-making.[11] In that sense, the reductions in the N,N-disubstituted carboxamido series constitute an example of steric assistance to electron transfer analogous to the well-recognized phenomena of steric assistance to homolysis and heterolysis.

The single clear example of reduction by ligand transfer in the present series involves the complex of 4-pyridone (VIII). As yet, it cannot be said whether the amide-bound Cr(III) product is formed by "adjacent attack" of Cr(II) on Co(III)-bound oxygen or by "remote attack" at the ring nitrogen, for the site at which Cr(III) is bound to the pyridone ligand is uncertain.[12] This reduction, irrespective of its stereochemical details, competes with reduction *via* the outer-sphere path. The amide-bound product constitutes very nearly 60% of the isolable Cr(III) product whether the reduction be carried out with equivalent quantities of reactants over a 3.5-hr period or with a fourfold excess of Cr(II) over a 12-min period. Since the ratio of bound to unbound Cr(III) in the product appears to be very nearly invariant over a range of conditions, it is probable that the ratio of rates for the two competing processes is very near 60/40.[13] The specific rate of outer-sphere reduction of this complex may then be taken as 40% of the observed rate, or 0.0096. This value is reasonable, for it is only slightly less than that for the outer-sphere reduction of the (slightly more crowded) isomeric complex of 2-pyridone (VII).

In summary, the present study indicates that unstrained $Co(NH_3)_5$ derivatives of carboxamides are reduced by Cr(II) *via* the outer-sphere mechanism at specific rates near 0.006–0.008 l. mole^{-1} sec^{-1} at 25°, that rates higher than this minimum value may be observed (without a change of mechanism) by increasing the steric requirements of the amide, and that in extreme cases specific rates may become comparable to those of the slower reductions proceeding mainly by ligand transfer, *i.e.*, reduction of the trimethylacetato

(10) Resin-catalyzed aquation may be particularly troublesome in the case of carboxylatopentaaquochromium(III) complexes, and the extent of reaction appears to be strongly (and, at present, unaccountably) dependent on the nature of the carboxylato ligand. A number of carboxylatopentaamminecobalt(III) complexes, which, upon reduction with Cr(II), are presumed to yield very nearly pure carboxylatochromium(III) complexes, were so reduced and the resulting mixtures subjected to cation-exchange chromatography under conditions similar to those used for the amide complexes. With the pentaammineacrylato complex, 17% of the recovered Cr(III) product was $Cr(H_2O)_6^{3+}$; with the propionato complex the extent of aquation was 25%; with the pivalato complex, 43% of the recovered Cr(III) was in the hexaaquo form; and with the mesitoato, 4-methoxybenzoato, and 2-methylbenzoato complexes, over 90% of the recovered Cr(III) was the aquo ion. In addition to this difficulty, column-catalyzed dimerization may be significant; for example, with the final two benzoato complexes mentioned, less than 0.5 equiv of monomeric Cr(III) was recovered from reaction of 1.0 equiv of Co(III).

(11) A plot of the $\Delta\nu_{C=O}$ values associated with conversion of the various N,N-disubstituted amides to their $(NH_3)_5Co$ complexes (which, in the present communication, are suggested as being related to nonbonded interactions in the complex) *vs.* the log k values for Cr(II) reductions in this series gives a reasonable straight line with only the N-acetylpiperidine complex significantly "off." No attempt is made here to ascribe significance either to the observed linear relationship or to the departure of the one complex from it.

(12) The absorption maxima for the amide-bound product from the 4-pyridone complex (at 586 and 415 mμ) lie very close to those reported by Nordmeyer and Taube[5] for the amide-bound product formed from reduction of the $(NH_3)_5Co$ complex of 3-pyridinecarboxamide. These authors suggest that the positions of these maxima imply Cr(III) coordination to a weakly basic amide oxygen, but in the present case they may also be consistent with coordination to a weakly basic amide-like nitrogen. (The difficulty here is that no spectra of N-bound Cr(III) complexes of N-substituted amides appear to have been reported.) More important, the infrared criteria used by Nordmeyer and Taube to establish O coordination for 3-pyridinecarboxamide do not appear to be applicable to the 4-pyridone case since useful spectra of the (relatively dilute) solutions resulting from this reduction could not be obtained in the C=O stretching region.

(13) This value is a lower limit for the ratio of amide-bound to unbound Cr(III) in the reduction product. Conversion of aquochromium(III) to amide-bound complex is thermodynamically unfavorable; hence any interconversion between species subsequent to the reaction must increase the hexaaquo at the expense of the amide bound.

and trifluoroacetato complexes in the carboxylate series. Warning has already been issued against use of specific rates alone as criteria for judging the position of attack in reductions involving ligand transfer.[2a] In the same way, caution must be exercised in using reaction rates to choose between the outer- and inner-sphere mechanisms for reduction. Examination of reaction products generally tells a more reliable story, provided that observations are speedy and separation methods are gentle.

Acknowledgments. The author is grateful to Professors Henry Taube and Francis Nordmeyer and Mrs. Marti Barrett for making known their experimental data before publication. He is also indebted to Miss Joan Clarke for help in monitoring temperature control in the kinetic experiments.

Diastereoisomeric Four-Coordinate Complexes. IV.[1] Zinc(II) Complexes with Three Asymmetric Centers and Ligand Racemization in Bis[N-(alkoxycarbonylalkyl)-salicylaldimino]metal(II) Complexes

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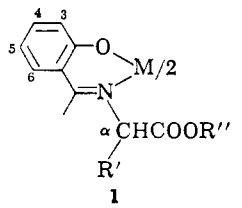
Abstract: An earlier report of the formation of optically inactive bis[N-(alkoxycarbonylalkyl)salicylaldimino]-copper(II) complexes in the reaction of the bis(salicylaldehydo) complex with an optically active amino acid ester has been confirmed and found also to occur in the preparation of Co(II), Pd(II), and Zn(II) complexes. The results of deuterium labeling and exchange experiments, which were followed by proton resonance, have revealed that loss of optical activity proceeds by racemization at the α-carbon of the N-alkoxycarbonylalkyl group and that a previously proposed tautomeric exchange path cannot be significant in the over-all racemization reaction. A transient carbanion intermediate produced by loss of the α-hydrogen is concluded to be the probable intermediate through which racemization proceeds in all cases. The pmr spectrum of optically inactive bis[N-(1-ethoxycarbonylethyl)salicylaldimino]zinc(II) revealed the presence of active and *meso* diastereoisomeric complexes produced in nonstatistical amounts in the racemization reaction. The analogous nickel(II) complex has been prepared for the first time. The two active isomers ((+,+) and (−,−)) of bis[N-(α-phenethyl)salicylaldimino]zinc(II) have been prepared and have been shown to undergo ligand exchange in chloroform to yield the *meso* complex. Pmr studies have demonstrated that the spectra of the active and *meso* forms of this complex are resolvably different and that the *meso* form is somewhat more stable in chloroform solution. Probable conformations of the phenethyl groups in the *meso* and active isomers have been deduced by steric arguments. From a comparison of the pmr spectra of the two forms, it is proposed that the synthesis of the (+,+) or (−,−) form from the active amine is nearly or totally stereospecific with respect to the absolute configuration at the metal (Δ,Λ), the more stable active isomers being $\Delta(-,-)$ and $\Lambda(+,+)$.

Schiff base complexes derived from salicylaldehyde and amino acids and their derivatives are commonly of two structural types, **1** and **2**. Of the tremendous number and variety of salicylaldimine complexes known,[4] these complexes are of particular significance because of a number of reactions undergone by the coordinated ligands, which are well defined in terms of product characterization although not necessarily completely specified mechanistically. The nitrogen substituents in the bis[N-(alkoxycarbonylalkyl)salicylaldimino]metal(II) complexes **1** (R′, R″ = alkyl), originally prepared by Pfeiffer, Offermann, and Werner,[5] may be transesterified,[5-8] amidated,[6] hydrolyzed (to yield **2**),[7] and racemized.[5] The N-(α-substituted acetato)salicylaldiminometal(II) complexes **2** (L = H_2O, py, etc.), and the recently synthesized anionic bischelate metal(III) analogs,[9] are structurally closely related to N-substituted pyridoxylideneamino, hydroxypyridinealdimino, and certain ring-substituted salicylaldimine complexes whose intermediacy in the



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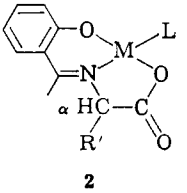

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(1) Part III: R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967).
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(4) For a recent general review of Schiff base complexes, *cf.* R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966).
(5) P. Pfeiffer, W. Offermann, and H. Werner, *J. Prakt. Chem.*, **159**, 313 (1942).
(6) H. S. Verter and A. E. Frost, *J. Am. Chem. Soc.*, **82**, **85** (1960).
(7) R. P. Houghton and D. J. Pointer, *J. Chem. Soc.*, 3302 (1964).
(8) G. A. Auld and A. Davison, *Inorg. Chem.*, 7, 306 (1968).
(9) R. C. Burrows and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 4150 (1966); *J. Inorg. Nucl. Chem.*, **29**, 709 (1967).