

the same. The observed values of E_a for rhodium(III) are in fact about 2 kcal. greater than for corresponding cobalt(III) complexes. Since many other energy terms contribute to the activation energy, this suggests that, apart from crystal field effects, rhodium(III) would react faster than cobalt(III).²⁶ This could either imply that the rhodium-chlorine bond energy is weaker, or that the larger size of rhodium(III) allows more nucleophilic assistance from the entering water molecule. The latter inference is in better agreement with the observation that the reactions of rhodium(III) have more SN₂ character than those of cobalt(III).

Crystal field theory can also be used in another comparison of rhodium and cobalt. Rearrangement of a

(26) For example, Cd(II) is more labile than Zn(II) (M. Eigen, private communication) and Sr(II) is more labile than Co(II), ref. 23.

square pyramid to a trigonal bipyramid involves a considerable loss in CFSE for a spin-paired d^1 -system, about $7.5Dq$ units by the usual approximate calculation. This indicates that only a comparable lowering of the energy, due to reduced ligand-ligand repulsion and to π -bonding, would allow rearrangement to occur. The larger size of rhodium, the greater value of Dq and the reduced importance of π -bonding all make rearrangement to a trigonal bipyramid unlikely for rhodium compared to the case of cobalt. This agrees with the stereochemical results of retention of configuration. It also predicts far less probability for complexes of rhodium(III) to react by a dissociation mechanism since stabilization of a five-coordinated intermediate by rearrangement to a trigonal bipyramid is of great importance in SN₁ reactions of octahedral complexes.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

Factors Controlling the Rate of Electron Transfer. II. Chelating Ability of Ligands such as Oxalate, Succinate, Maleate and Phthalate¹

By R. T. M. FRASER

RECEIVED NOVEMBER 5, 1962

Rate constants of the order 15–30 l. mole⁻¹ sec.⁻¹ for the acid-independent path are observed on reduction of tetraamminecobalt(III) complexes containing ligands such as acetate, succinate and phthalate by chromium(II) or vanadium(II). The tetraaminemaleate is an exception, with $k = 125$ l. mole⁻¹ sec.⁻¹, and a mechanism is proposed to account for this. In general, chelation in the transition state is not an effective path for electron transfer.

Much use has been made recently of Co(III) pentaamine complexes to study electron transfer through carboxylic acids as bridging groups.^{2,3} In particular, a study of the chromous ion reduction of the pentaaminemalonatocobalt(III) complex has been reported⁴ and the possibility of chelation of the Cr(II) by the malonate ligand discussed. The effect on the rate of reduction was concluded to be negligible. This paper reports the examination of some tetraamminecobalt(III)-chromous (or vanadous) ion oxidation-reductions, made in the light of the results of the corresponding pentaamminecobalt(III) reductions. It is found that chelation of the reductant by the ligand can take place if certain restricting steric conditions exist, but the effect is not common, nor is it as an efficient path for electron transfer as is a system of conjugated double bonds singly coordinated to the reductant.

Experimental

Materials.—The tetraamine $(\text{NH}_3)_4\text{Co}(\text{CO})_3(\text{ClO}_4)_5$ was used as the starting material in preparing the dicarboxylatocobalt(III) ions. Methods available in the literature were used for the preparation of *trans*-diacetato-,⁶ *cis*-succinato-,⁷ *cis*-phthalato-⁸ and *cis*-maleatetetraamminecobalt(III) perchlorates.⁷ In each case, the residue obtained from the reaction of the organic acid and the tetraaminocarbonatocobalt(III) perchlorate was dissolved in the least volume of hot water, the solution poured into an ether-alcohol mixture and the gummy precipitate collected on a spatula. This residue was triturated with more of the alcohol-ether solvent until a fine powder was obtained.

cis-Diacetatetetraamminecobalt(III) perchlorate was obtained by heating freshly prepared diaquotetraamminecobalt(III) perchlorate with potassium acetate.⁶

Tetraamineoxalatocobalt(III) perchlorate was obtained by the method of Palmer.⁹ Pentaamine complexes were obtained

by heating pentaammineaquocobalt(III) perchlorate with a mixture of the organic acid and sodium salt.²

Analyses.—The nitrogen, perchlorate and free acid ($-\text{CO}_2\text{H}$) content of each complex were determined as stated previously.¹ In all cases the values obtained were within 2% of those calculated on the basis of formula weights. The titrations with standard base showed that complexes of dibasic acids did in fact contain one chelated ligand, not two ligands each coordinated by one carboxyl group, and so were the *cis* isomers. *cis*- and *trans*-diacetatetetraamminecobalt(III) perchlorates were also compared with recorded optical spectra.¹⁰

Solutions of sodium perchlorate were prepared by neutralizing A.R. sodium hydroxide pellets dissolved in triply distilled water with A.R. perchloric acid. The preparation of the chromium(II) and vanadium(II) perchlorate solutions has been described previously.³

Method.—Immediately before the kinetic measurements approximately 50 mg. of the cobalt complex was dissolved in 5 cc. of water. The solution was shaken with Dowex 1 ion-exchange resin in the perchlorate form (to remove any traces of other anions), filtered, then perchloric acid was added to give a solution 0.2 molar in $[\text{H}^+]$. This was shaken with Dowex 50 to remove any cationic species with external charges greater than one, filtered, and diluted to the required volume with the perchloric acid-sodium perchlorate solution. The initial Co(III) concentration was established spectrophotometrically at either 525 $m\mu$ (500 $m\mu$ for the pentaamine cobalt(III) complexes) or 355 $m\mu$. Nitrogen was passed through the solutions to remove any trapped oxygen.¹ All reaction mixtures used in the kinetic studies contained Co(III) in excess. The rate of reduction was followed in a Perkin-Elmer 350 or Beckman DKI spectrophotometer by observing the rate of disappearance of either the 525 $m\mu$ or the 365 $m\mu$ absorption maximum of the Co(III) complex. Acid-catalyzed aquation of the complexes does not occur to any significant extent during the reduction, at least under the conditions of $\mu = 1.0$ and $0.2 < [\text{H}^+] < 1.0 M$.¹¹

The method of Sebera and Taube² was used to determine the rate constants. Because the cobalt(III) complex was present in excess in all measurements, the reactions were followed spectrophotometrically to completion: in this way, the final optical density could be determined experimentally. In most cases, sets of duplicate runs (same cobalt(III) and chromium(II) or vanadium(II) concentrations) were made at both absorption maxima: these gave rate constants within $\pm 3\%$ of each other.

(1) Part I: *J. Am. Chem. Soc.*, **84**, 3436 (1962).

(2) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(3) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239, 2242 (1961).

(4) G. Svartos and H. Taube, *ibid.*, **83**, 4172 (1961).

(5) "Inorganic Syntheses," Vol. VI, E. G. Rochow, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 173.

(6) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

(7) J. C. Duff, *J. Chem. Soc.*, **119**, 385 (1921).

(8) J. C. Duff, *ibid.*, **119**, 1982 (1921).

(9) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p. 547.

(10) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

(11) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

TABLE I

RATES OF REACTIONS AS FUNCTIONS OF TEMPERATURE AND ACIDITY

$$[\text{Co(III)L}] = 4.0 \times 10^{-3} M, \mu = 1.0$$

Complex	Re-ductant [Cr(II)]	[V(II)]	Temp., °C.	$k, \text{l. mole}^{-1} \text{sec.}^{-1}$		
				[H ⁺] = 0.2	0.4	0.6 M
(i) Tetraammines						
<i>cis</i> -Diacetate	^a	13	11.5	14.6	17.7	
	^b	13	11.2	14.8	18.1	
Succinate	^a	25	15.4	19.7	24.0	
	^a	25	15.0 ^c	19.6 ^c	23.2	
	^a	24.5	12.8	14.4 ^c	16.0	
	^b	24.5	13.2	14.0	15.5 ^c	
	^a	43.0	36	41	47	
	^b	43.0	35	43	47 ^c	
Phthalate	^a	25.0	46	63	80	
	^b	25.0	46	62 ^c	80 ^c	
	^a	40.0	134	210 ^c	284	
	^b	40.0	138 ^c	215	277	
	^a	13.0	4.1	5.5	7.0	
	^b	13.0	4.0	5.3	7.0	
Oxalate	^a	25.0	6.6	8.8	11.0	
	^b	25.0	6.6 ^c	8.9	11.1	
	^a	10.0	10.3	12.5 ^c	14.5	
	^b	10.0	10.2	12.5	14.0	
	^a	25.0	21	30 ^c	36 ^c	
	^b	25.0	21	31	35	
Maleate	^a	13.0	23	25	27	
	^b	13.0	22	25	27	
	^a	23.0	47	51	55	
	^b	23.0	48 ^c	51 ^c	55	
	^a	13.0	10.5	11.3	12.0	
	^b	13.0	10.4	11.2	12.2 ^c	
Oxalate	^a	24.5	13.8	15.7	17.5	
	^b	24.5	13.8	16.0	17.9	
	^a	14.0	106	114	122	
	^b	14.0	109	114 ^c	120 ^c	
	^a	23.0	130	141	150	
	^b	23.0	125	146	150	
(ii) Pentaammines						
Oxalate	^a	24.5	21	25	28	
	^b	24.5	21	24 ^c	29 ^c	
	^a	44.0	128	147	169	
	^b	44.0	130 ^c	150	163	
Maleate	^a	25.0	645	860	1050	
	^b	25.0	630 ^c	860 ^c	1000 ^c	
	^a	26.0	15	18	20	
	^a	43.0	47	53	60	
Oxalate	^b	43.0	46	54	62	
	^a	14.0	220	242	260	
	^b	14.0	220	250	262	
	^a	23.0	460	488 ^c	522	
^b	23.0	450 ^c	490 ^c	530 ^c		

^a [reductant] = $2.3 \times 10^{-3} M$. ^b [reductant] = $1.2 \times 10^{-3} M$. ^c [Co(III)L] = $2.0 \times 10^{-3} M$.

Second-order kinetics were established for each reaction by varying the initial concentrations of both the oxidant and reductant.

Ion exchange chromatography on Dowex 50 was used to determine the proportions of (Cr^{III}L)²⁺ and (Cr^{III}L₂)⁺ in the reaction mixtures.¹² The eluates were titrated with a standard sodium hydroxide solution using a Leeds and Northrup 7401 pH meter and Ingold 402 combination electrode. The titration curve was recorded on a Texas Instruments Inc. high speed 10 mv. recorder. Finally, the solutions were treated with alkaline hydrogen peroxide and the chromium concentration was determined spectrophotometrically as chromate.

(12) E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1954).

TABLE II
SUMMARY OF RATE CONSTANTS AT 25°
l. mole⁻¹ sec.⁻¹, μ = 1.0

Complex	Cr(II)		V(II)
	(i) Tetraammines	(ii) Pentaammines	
<i>cis</i> -Diacetate	11 + 22 (H ⁺)
<i>trans</i> -Diacetate	15 + 50 (H ⁺) ^a
Succinate	30 + 75 (H ⁺)	...	11 + 8 (H ⁺)
Phthalate	13 + 40 (H ⁺)	...	4.5 + 11 (H ⁺)
Oxalate	Too fast	...	43 + 22 (H ⁺)
Maleate	125 + 50 (H ⁺)	...	12 + 9.5 (H ⁺)
Malonate	30 + 20 (H ⁺) ^a
Acetate	0.18 ^b	...	0.43 ^c
Succinate	.27 ^b	...	0.89 ^c
Phthalate	.075 ^b	...	1.01 ^c
Oxalate	450 + 1000 (H ⁺)	...	17.5 + 18 (H ⁺)
Maleate	200 + 100 (H ⁺)	...	13 + 10 (H ⁺)
Malonate ^d	0.34 + 0.94 (H ⁺) + 1.08/(H ⁺)

^a Ref. 11. ^b Ref. 2. ^c R. T. M. Fraser, in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 287. ^d Ref. 4.

TABLE III
ENERGETIC DATA FOR ACID-INDEPENDENT PATH (TETRAAMMINE COMPLEXES)

Complex	Cr(II)		V(II)	
	ΔH‡, kcal. mole ⁻¹	ΔS‡, e.u.	ΔH‡, kcal. mole ⁻¹	ΔS‡, e.u.
<i>cis</i> -Diacetate	3.1	44
<i>trans</i> -Diacetate ^a	7.9	-26
Oxalate	11.4	-12.5
Malonate ^a	8.5	-24
Succinate	7.9	-25	9.0	-19
Phthalate	5.7	-35	6.6	-34
Maleate	3.3	-38	2.4	-43

^a Ref. 11.

Results

A summary of the kinetic data obtained with the tetraamminecobalt(III) complexes is given in Table I. The rate constant k is for the rate law

$$-d[\text{Co(III)L}_2^+]/dt = k[\text{reductant}][\text{Co(III)-L}_2^+] = (k_1 + k_2[\text{H}^+])[\text{reductant}][\text{Co(III)L}_2^+]$$

The rate of reduction of all the tetraammines increases linearly with [H⁺] and the effect is not limited to the chelate complexes. Furthermore the rate of reduction is usually faster by a factor of approximately 100 than the rate of reduction of the corresponding pentaammine complexes, and this is not due to the lower charge of the tetraammines, since a similar effect is found in the reaction of the *cis*-tetraammineaquoacetatocobalt(III) ion¹¹ [(NH₃)₄Co(H₂O)O₂CCH₃]²⁺ (compared to the rate of reduction of [(NH₃)₅CoO₂-CCH₃]²⁺ or the rate of reduction of [(NH₃)₅CoH₂O]³⁺ by the acid-independent path). Possibly the increase in ease of reduction is related to the differences in thermodynamic stability of the tetraammines compared to the pentaammines.¹³ The rate constants for both reaction paths are summarized in Table II. Values for the chromium(II) reduction of the *cis*-diacetato complex are not listed, since close agreement between duplicate runs could not be obtained. The reaction is first order in both complex and reductant and is acid-catalyzed; measurements at 10° indicate $18 < k < 40 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, and this may be compared with the chromium(II)-*trans*-diacetato reaction, where k_{10° may be calculated from recorded data¹¹ as $17 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. In all other cases, the uncertainty in the second-order rate constants is $\pm 3\%$.

(13) The author wishes to thank one of the referees for emphasizing this point.

Table III lists the enthalpies and entropies of activation for the chromium(II) and vanadium(II) reductions by the acid-independent path.

There is a linear relation between ΔH^\ddagger and ΔS^\ddagger obtained from k_1 similar to that found in the reductions of Co(III) halogenocarboxylate complexes.¹ For the tetraammines the values of α and β in $\Delta S^\ddagger = \alpha\Delta H^\ddagger + \beta$ are 3.85×10^{-3} degree⁻¹ and -55.8 cal. mole⁻¹ degree⁻¹, respectively, for either V(II) or Cr(II) reduction. The limits of accuracy in the evaluation of ΔH^\ddagger and ΔS^\ddagger are ± 0.3 kcal. mole⁻¹ and ± 2 cal. mole⁻¹ degree⁻¹, and the only sets of values which do not obey the relation within experimental error are those for the tetraamminemaleatocobalt(III) complex.

A number of the reaction mixtures ($[H^+] = 0.2 M$) immediately after electron transfer were poured through columns of Dowex 50, eluted with $0.15 M HClO_4$ and then $1.0 M HClO_4$ to separate the $[Cr(III)]^{+1}$ and $[Cr(III)]^{+2}$ species: the percentages of $[Cr(III)]^{+1}$ are shown in Table IV. Titration of the eluates³ indicated

TABLE IV
PERCENTAGES OF Cr(III) RECOVERED IN THE +1 (CHELATED)
FORM AFTER ELECTRON TRANSFER
 $[H^+]_{initial} = 0.2 M$

Complex	$[Cr(III)]^{+1}, \%$
$(NH_3)_6Co$ maleate ^a	86
$(NH_3)_4Co$ maleate	<25
$(NH_3)_6Co$ acetate	< 2
$(NH_3)_4Co$ diacetate (<i>cis</i>)	>69
$(NH_3)_4Co$ diacetate (<i>trans</i>)	< 3
$(NH_3)_4Co$ oxalate	99
$(NH_3)_4Co$ 4,5-dicarboxybenzene-1,2-dicarboxylate	<10

^a Reference 3.

that at least 95% of the chromium(III) complex with charge of +1 was in the chelated form.

Discussion

The rates of reduction of all the tetraammine complexes studied are acid-catalyzed. It has been suggested¹¹ that this catalysis is due to stabilization of the acceptor antibonding orbital of the cobalt brought about by protonation of the second carboxylate group, with its attendant decrease in electron density at the coordinating oxygen. Because of the uncertainty of the pK_A values for the protonated complexes, this discussion will be limited to consideration of the acid-independent path. The ratios of the specific rate constants (k_1 tetraammine/ k_1 pentaammine) are shown in Table V.

TABLE V
RATIOS (k_1 tetraammine/ k_1 pentaammine) AT 25°

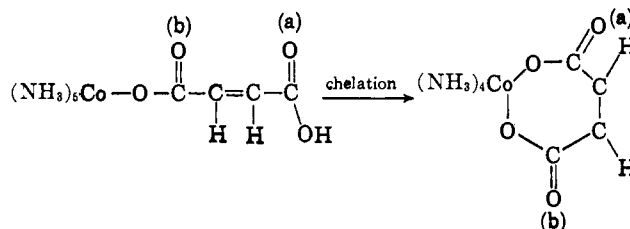
Complex	Cr ⁺⁺	V ⁺⁺
<i>trans</i> -Diacetate	88	...
<i>cis</i> -Diacetate	176	26
Succinate	110	12.4
Phthalate	73	4.4
Malonate	90	...
Oxalate	...	2.5
Maleate	0.60	0.92

It was not possible to determine the rate of reduction of tetraammineoxalatocobalt(III) by chromous ion, but it was faster than the reduction of the pentaammine complex by a factor of at least 2. The only case found where the ratio was less than 1 was for the maleate complexes and there it is meaningless, since it is probable that the acid-independent k_1 for the pentaammine is composed of k_1 adj. and k_1' remote—that is, of two terms, only one of which refers to adjacent attack. The

(14) R. P. Bell, *Trans. Faraday Soc.*, **33**, 495 (1937)

second rate constant refers to remote attack on the unprotonated ligand.¹⁵

The actual value of k_1 for the chromous reduction of the tetraamminemaleate (Table II) is 125 l. mole⁻¹ sec.⁻¹, considerably larger than that of any of the other complexes (15–30 l. mole⁻¹ sec.⁻¹). At first sight this is unexpected, because formation of the tetraammine has resulted in the loss of a conjugated system capable of transmitting the electron



Both the carboxyl oxygens a and b are now adjacent to the cobalt; therefore remote attack is impossible. The shortest path from either of them to the cobalt possesses no conductivity above that of a succinate complex. Although one end of the maleate ligand can be freed by acid hydrolysis for remote attack, under the conditions of the experiment it was found to be negligible. Further, the values of ΔH^\ddagger and ΔS^\ddagger for both the vanadous and chromous ion reduction do not obey the relationship

$$\Delta S^\ddagger = 3.8 \times 10^{-3} \Delta H^\ddagger - 55.8$$

as do those of all the other tetraammines, suggesting a different mechanism.

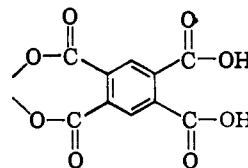
A possible explanation may be that electrons can be introduced directly into the $-C=C-$ bond: unpub-

lished observations¹⁶ have suggested this can occur with trisdipyridyl complexes of Cr(II) or V(II) and complexes containing a ligand such as $-O_2C-C\equiv C-CH_3$. Such a mechanism would involve approach of the chromous ion above the plane containing the $-C=C-$

system to give sufficient overlap of an e_g orbital (say d_{z^2}) with the π -system of the carbons. This would place the Cr^{++} group very close to the carbonyl oxygen ($-C=O$) of one carboxyl group, and the carboxyl oxygen ($-C-O-$) of the other. Therefore *chromium chelation* might be expected in the activated complex. Ion exchange resin separations do show that about one-fourth of the chromium after reaction is chelated by the maleate ligand.

The reaction of the tetraammine oxalate complex is interesting, first because the ring formed on chelation is very rigid, second because the two carbonyl oxygens are in just the correct positions to form a chelate with the incoming reductant. In contrast to the maleate, the acid-independent reduction is faster than that of the pentaammine even though remote attack is also possible (Table V). Ion-exchange resin separations show that essentially all the chromium oxidized is in the chelated form.

The last system studied was that of the 4,5-dicarboxybenzene-1,2-dicarboxylatocobalt(III) complex, where the ligand is



(15) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 564 (1961).

(16) R. T. M. Fraser and H. Taube.

Remote attack by the reductant should be favored here, just as with the pentaammineterephthalate complex, and further there exists the possibility of chelation by the two remote carboxyl groups to yield the symmetric activated complex

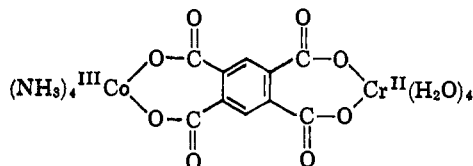


Table IV shows that only a minor fraction of reaction takes place by such a path. The rate of reduction appears to be at least as fast as that of the *p*-aldehydobenzoate complex,³ and it is not possible at the moment to establish whether chelation is an important factor in acceleration of the rate of reaction.

In summary then, it may be stated that while reductant chelation is potentially an efficient way for increasing the rate of reaction, the steric requirements are so stringent as to make reduction following attack at a single point the usual mode of reaction. The rate measured is the over-all rate of reaction, and involves the rate of combination of the reductant with the ligand, the rate for the actual electron transfer process and finally the rate of decomposition of the Co(II)-Cr(III) (or Co(II)-V(III)) intermediate. Although electron transfer is rapid, the probability for the transfer may be small, due to the requirement of energy matching at the two metal sites¹⁷; that is, the transmission coefficient for the transfer step may be very much less than one. If small enough, this probability would control the over-all rate of reaction. Chelation of the reductant should result in a more symmetric transition state for the tetraammines, resulting in easier energy matching. Seven complexes where chelation of the chromium can take place without destroying or reducing conjugated systems are the tetraammines *cis*-diacetate, 4,5-dicarboxybenzene-1,2-dicarboxylate,

(17) B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Rev.*, **55**, 157 (1955).

oxalate and *cis*-aquoacetate and the pentaammines oxalate, maleate and malonate. Some degree of chelation has been shown in the case of the first three, the fifth and sixth; inferred for the fourth, and not found for the malonate. Only in the cases of the tetraammine oxalate and the pentaammine oxalate and maleate is there any evidence for the rate law for an accelerating effect: none of the other tetraammines react more rapidly, and none of them show complete chelation to the chromium. Apparently the probability of electron transfer through a carboxylate system is not too small: reduction usually occurs after one bond has been formed with the reductant, before the second is formed. Oxalate is a special case since no rearrangement of the ligand is necessary to bring the oxygen into the chelating configuration.

If the tetraammine complex contains a chelate ring formed from a dibasic ligand, reduction at the remote carboxyl is no longer possible, but this is unimportant unless the ligand contains a system of conjugated double bonds. A more important loss is that of intensive rearrangement of the ligand: examination of molecular models shows this may be complete, giving an inflexible ring as in oxalate. The order of flexibility remaining is oxalate < malonate < succinate < phthalate < maleate, and it is found (Table II) that this is just the order of decreasing ΔS^\ddagger for both Cr⁺⁺ (-24 e.u. for malonate to -38 for maleate) and V⁺⁺ (-12.5 e.u. for oxalate to -43 for maleate) reductions. Aside from the values of ΔH^\ddagger and ΔS^\ddagger for the maleate, there is good agreement with the relation

$$\Delta S^\ddagger = 3.8 \times 10^{-3} \Delta H^\ddagger - 55.8$$

showing the mechanism of reduction in all cases is the same, attack at an adjacent carboxyl.

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[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITA' DI FIRENZE, FIRENZE, ITALY]

The Occurrence of Paramagnetic Tetrahedral Forms of N-Arylsalicylaldiminonickel(II) Complexes in Solution at Elevated Temperatures

BY L. SACCONI AND M. CIAMPOLINI

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Magnetic and spectrophotometric measurements on a series of N-arylsalicylaldiminonickel(II) complexes in solution in inert solvents have been carried out up to a temperature of 200°. These have shown that 2-substituted phenyl complexes, which are diamagnetic both in the solid state and in solution, retain a square-planar structure at all temperatures. For the 3- and 4-substituted phenyl complexes, the decrease in the amount of association which is observed with an increase in temperature is accompanied by the appearance of a tetrahedral species whose concentration increases with temperature. Dilution too causes a decrease in the amount of association and favors the formation of tetrahedral species. Thus in the solutions in inert solvents of these complexes there exists an equilibrium between paramagnetic polymer, diamagnetic planar and paramagnetic tetrahedral forms. Following the discovery of a tetrahedral structure for the N-*sec*-alkyl- and N-*n*-alkylsalicylaldiminonickel(II) complexes in the solid state and/or in solution, the present study confirms that a tetrahedral coordination for nickel(II) chelates is not a rare occurrence, especially at high temperatures. A comparison of the reflectance spectra of the paramagnetic solid N-aryl complexes with the spectra of the paramagnetic solid form of bis-(N-methylsalicylaldimino)-nickel(II) complex and also with the spectra of some adducts with pyridine and methanol of salicylaldiminonickel(II) complexes suggests that the paramagnetic N-aryl complexes are in some way associated even in the solid state.

Introduction

In a recent study of bis-(N-arylsalicylaldimino)-nickel(II) complexes, Holm¹ has reported that in solution in toluene and in chloroform near room tempera-

ture all of these complexes, except the 2-substituted ones, are paramagnetic and extensively associated. From a study of the temperature dependence up to 70° of the magnetic susceptibility as well as of the absorption spectra of some representative complexes it was concluded that there exists a paramagnetic polymer-

(1) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).