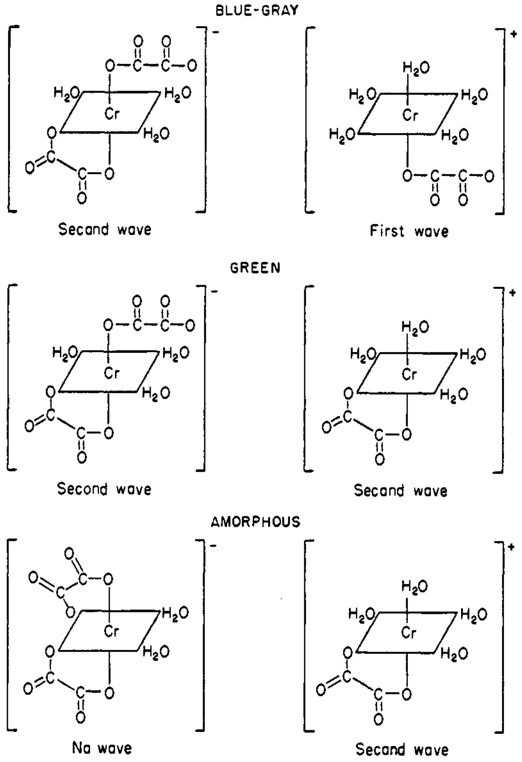
shown to be $Cr_2(C_2O_4)_3 \cdot xH_2O$. The silver-gray salt was the form of chromium oxalate which was first prepared by Wyrouboff[4] and later studied by Rosenheim and Cohn.[7] The blue-gray salt was the product formed by allowing the silver-gray salt to stand in air for several months. The green salt was formed by heating either the silver-gray or the blue-gray salt to 110° for one hour. The amorphous form was prepared by enclosing either the silver-gray or blue-gray forms in a container which contained small amounts of water or water vapor.



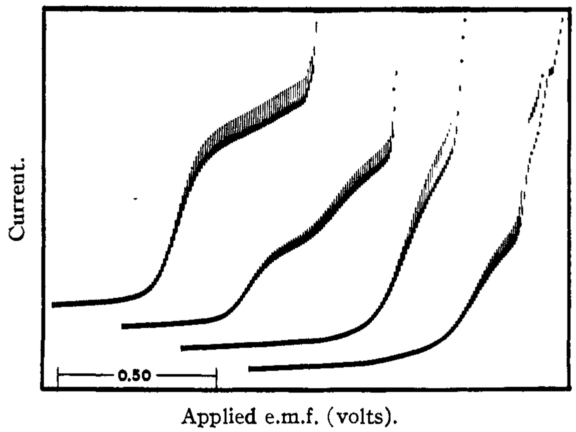


Fig. 4.—Polarograms of solutions of 0.050 g. of silver-gray, blue-gray, green and amorphous chromium(III) oxalate dissolved in 100 ml. of 0.30 *M* potassium nitrate and 0.005% gelatin. Each recording started at −0.500 volt *vs.* S.C.E.

The silver-gray salt was probably composed of hexaquochromium(III) and oxalate ions, but it went into solution as the green equilibrium mixture of species A and X which reacted with the excess oxalate until finally an equimolar mixture of monoxalatotetraquochromium(III) and dioxalatodiaquochromate(III) ions was formed.

The blue-gray salt contained some complexed oxalate as indicated by the presence of the second wave. The green salt contained only the second reducible species in which the oxalate is completely bound (no precipitate was obtained from a solution of the green salt when calcium chloride was added). The amorphous substance contained the second reducible species in about one-half the concentration of a comparable solution of the green salt. From the above observations, the above structures have been proposed for the positive and negative complex ions that exist in these compounds.

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[7] A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **28**, 337 (1901).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. III. Kinetics of Aquation of Some Cobalt(III) Complex Ions[1,2]

BY RALPH G. PEARSON, CHARLES R. BOSTON AND FRED BASOLO

RECEIVED FEBRUARY 2, 1953

Rates of aquation have been measured for a series of compounds of the type, *trans*-$[Co(AA)_2Cl_2]^{+1}$, in which the steric properties of the bidentate (AA) group were varied. It was found that in almost every case an increase in size or steric crowding of the bidentate was accompanied by an increase in the rate of aquation. This has been interpreted as evidence for the five coördinated intermediate of the SN1 or dissociation mechanism, and against the seven coördinated activated complex of the SN2 or displacement mechanism.

In the previous papers of this series the problem of determining the mechanism of substitution reactions in complex ions has been approached in two different ways. In the first paper,[3] the group being replaced was varied (with respect to both its size and base strength) and the resulting changes in rates of aquation and hydrolysis were studied. In the second paper,[4] a stereochemical approach to the problem was made by measuring the relative amounts of *cis* and *trans* isomers obtained during substitution reactions involving geometric isomers. The present paper concerns itself with still a third

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[1] Some of this material was presented as a communication, THIS JOURNAL, **74**, 2943 (1952).

[2] This investigation was supported by a grant from the United States Atomic Energy Commission under contract AT(11-1)-89-Project No. 2.

[3] F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

[4] F. Basolo, B. D. Stone and R. G. Pearson, THIS JOURNAL, **75**, 819 (1953).

approach which is to vary the unreactive portion of the complex, keeping the replaceable group the same, and observe how the rate of reaction is affected. The complexes used in this study were all of the type *trans*-$[\mathrm{Co(AA)_2Cl_2}]^{+1}$ and aquation of the first chlorine was the reaction studied.

Experimental

Preparation of Compounds.—The synthesis of most of these compounds has been described previously.[5] The *l*- and *meso*-1,2-diphenylethylenediamine (or stilbenediamine) complexes together with the complex containing both ethylenediamine and trimethylenediamine were obtained through the courtesy of Prof. John C. Bailar, Jr. The complex containing trimethylenediamine was prepared according to the directions of Bailar and Work.[6] The complex containing 1,3-diamino-2,2-dimethylpropane was prepared essentially according to the directions given in "Inorganic Syntheses"[7] for the corresponding ethylenediamine complex. The 1,3-diamino-2,2-dimethylpropane used was obtained by hydrogenation of the corresponding dinitro compound according to the directions of Lambert and Lowe.[8] The dinitro compound was also prepared according to their directions. Trimethylenediamine was obtained through the courtesy of the American Cyanamid Company

Procedure for Determining the Rates of Aquation.—The aquation of dichloro compounds of this type has been shown[9] to occur in steps

$$[\mathrm{Co(AA)_2Cl_2}]^{+1} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Co(AA)_2H_2OCl}]^{+2} + \mathrm{Cl^-} \quad (1)$$

$$\begin{array}{ccccccc} [\mathrm{Co(AA)_2H_2OCl}]^{+2} & + & \mathrm{H_2O} & \rightleftharpoons & [\mathrm{Co(AA)_2(H_2O)_2}]^{+3} & + & \mathrm{Cl^-} \\ -\mathrm{H^+}\downarrow\uparrow\mathrm{H^+} & & & & -\mathrm{H^+}\downarrow\uparrow\mathrm{H^+} & & \quad (2) \\ [\mathrm{Co(AA)_2OHCl}]^{+1} & + & \mathrm{H_2O} & \rightleftharpoons & [\mathrm{Co(AA)_2(H_2O)OH}]^{+2} & + & \mathrm{Cl^-} \\ & & & & & & \quad (3) \end{array}$$

The rate of aquation of the second chlorine from the aquo complex as in (2) is very slow. However, the hydroxo complex (3) aquates fairly rapidly. Therefore, to determine the kinetics of step (1) without interference from step (3), it is necessary to run the aquations in highly acidic solutions ($p\mathrm{H} < 3.0$) which serves to repress reactions (2) and (3) but does not affect reaction (1).

The rates of aquation were followed by chloride analysis and also by spectrophotometric analysis.

A satisfactory method[10] was found for the determination of chloride ion in colored solutions of low *p*H. Titrating with mercuric nitrate and using sodium nitroprusside as indicator, the end-point is marked by the appearance of a turbidity due to precipitated mercuric nitroprusside. Stock solutions (250 ml.) were made up approximately 0.005 *M* in complex and 0.1 *M* in nitric acid and kept in a constant temperature bath at the desired temperature ±0.05°. From this stock solution samples (25 ml.) were pipetted into cracked ice to quench the reaction. These samples were then titrated with 0.0295 *N* $\mathrm{Hg(NO_3)_2}$ from a 10-ml. buret.

The spectrophotometric method was found to be particularly suitable for following these aquations since at wave lengths of 520 to 560 mμ the starting material, *trans*-$[\mathrm{Co(AA)_2Cl_2}]^{+1}$, has a minimum ($\epsilon \simeq 10$) in its absorption curve whereas the final product, *trans*-$[\mathrm{Co(AA)_2H_2OCl}]^{+2}$, has a maximum ($\epsilon \simeq 60$). Thus, at these wave lengths a large change in optical density is observed as the reaction proceeds. Stock solutions (50 ml.) were again made up approximately 0.005 *M* in complex and 0.1 *M* in nitric acid. These were kept in a constant temperature bath and water from this bath was pumped continuously through jackets surrounding the cell compartment of a Beckman Model DU spectrophotometer. In this way the temperature was controlled during a run to within ±0.1°. The spectrophotometric method was employed exclusively when the amount of complex available was limited or when the reaction was very rapid.

Results

Almost every compound in this series was found to have an excess of ionic chloride initially, presumably due to contamination with varying amounts of HCl from which the compounds were isolated. Therefore, in the titration method it was necessary to correct for this factor.

Rate constants were calculated for the spectrophotometric method by plotting log $(D_\infty - D_0)/(D_\infty - D)$ against time, where D represents optical density. The initial optical density, D_0, was determined by extrapolation to zero time. Since aquation of the second chlorine is extremely slow at low *p*H's as compared with aquation of the first, it was possible to determine D_∞ by following the reaction until a "leveling off" occurred and taking the optical density at this point to be D_∞. Agreement between the titration and spectrophotometric methods was obtained when this procedure was used (see Table I).

The complex ion, $[\mathrm{Cotn_2Cl_2}]^+$, aquated much too rapidly to measure by either of the above methods. However, these reactions are characterized by a color change from green to red as the reaction proceeds and it was observed during some of the slower reactions of the series that the half-life is marked by a colorless or grayish solution. Thus, it was possible to determine the half-life (and hence an approximate rate constant) for the trimethylenediamine complex by simply measuring with a stopwatch the time required for the solution to reach the colorless point.

The results are listed in Table I. The compounds studied are listed according to their bidentate group since the rest of the complex remains the same throughout the series. Rate constants were measured at three different temperatures in most cases. Activation energies were then calculated and are shown in Table I. The differences in rate are seen to be due to differences in activation energies rather than probability factors.

Discussion

From compounds 1 to 6 of Table I it appears that the progressive substitution of methyl groups on the carbon atoms of ethylenediamine produces a continuous increase in the rates of aquation of the corresponding complexes and when substitution is complete as for the tetramethylethylenediamine complex, the aquation is too rapid to measure even at low temperatures. This would seem to rule out a displacement, or SN2, mechanism since a decrease in rate is usually observed for reactions of this type as the reaction center becomes less accessible. However, the increasing rate would be expected if the activated complex were pentacoördinated as in a dissociation, or SN1, mechanism. In fact, a steric acceleration of reaction velocity as has been observed in the solvolysis of highly branched tertiary halides[11] seems to be operating here.

As the alkyl chain length of N-alkyl substituted ethylenediamines is increased the rate of aquation increases. This is indicated by compounds 7, 8 and 9 of Table I. Here again increased crowding

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[5] F. Basolo, THIS JOURNAL, **75**, 227 (1953).

[6] J. C. Bailar and J. B. Work, *ibid.*, **68**, 232 (1946).

[7] "Inorganic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 222.

[8] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

[9] J. P. Mathieu, *Bull. soc. chim.*, [5] **2**, 2121 (1936).

[10] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, New York, N. Y., 1942, p. 332.

[11] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

TABLE I

RATES OF AQUATION OF SOME *trans*-$[Co(AA)_2Cl_2]^{+1}$ IONS AT *p*H 1

$[Co(AA)_2Cl_2]^+ + H_2O = [Co(AA)_2H_2OCl]^{+2} + Cl^-$

	Diamine (AA)	Symbol	$k \times 10^3$ (min.$^{-1}$) 10°	15°	25°	35°	Method[a]	*Ea*, kcal.
1	$NH_2-CH_2-CH_2-NH_2$	en		0.46	1.9	9.5	T	28
					1.8[b]		S	
2	$NH_2-CH_2-CH(CH_3)-NH_2$	pn		0.84	3.7	18.0	T	28
					3.6[b]		S	
3	*dl*-$NH_2-CH(CH_3)-CH(CH_3)-NH_2$	*dl*-bn		2.1	8.8	37.0	T	26
					8.7		S	
4	*meso*-$NH_2-CH(CH_3)-CH(CH_3)-NH_2$	*m*-bn	32.0	82.0	~250[b]		S	24
5	$NH_2-CH_2-C(CH_3)_2-NH_2$	iso-bn	12.5	30.0	~130		S	26
6	$NH_2-C(CH_3)_2-C(CH_3)_2-NH_2$	tet-me	Inst.					..
7	$NH_2-CH_2-CH_2-NH(CH_3)$	Me-en		0.24	1.0	4.4	T	27
					0.90[b]		S	
8	$NH_2-CH_2-CH_2-NH(C_2H_5)$	Et-en		1.2	5.9	28.3	T	28
					3.6[b]		S	
9	$NH_2-CH_2-CH_2-NH(n\text{-}C_3H_7)$	*n*-Pr-en		1.6	7.1	31.7	T	27
10	$NH_2-CH_2-CH_2-CH_2-NH_2$	tn	600				H	..
	$NH_2-CH_2CH_2-NH_2$	(en)(tn)		5.9	26.0	90.0	S	26
11	$NH_2-CH_2-CH_2-CH_2-NH_2$							
12	$NH_2-CH_2-C(CH_3)_2-CH_2-NH_2$	dan	23.0	68.0	~180		S	24

[a] T = titration method; S = spectrophotometric method; H = half-life determination. [b] *p*H 2.6.

around the central ion increases the rate of aquation.

In going from the ethylenediamine complex to the N-methylethylenediamine complex, we find a decrease in rate with increased crowding. However the inductive effect of the methyl group which should be negligible in the case of C-substitution can no longer be neglected in the case of N-substitution. In addition to increased crowding we now have a modification of the Co–N link by virtue of N-substitution. We have not been able to satisfactorily explain why the observed effect is a decrease in rate. Other factors, such as solvation energies, must be considerably changed also. Since the inductive and solvation effects change very little as the chain length of the alkyl group is increased, the crowding effect again becomes dominant and the rate of aquation increases.

The importance of steric factors is shown perhaps most clearly by the thirty-fold difference in aquation rates between the *dl*- and *meso*-2,3-diaminobutane complexes (compd. 3 and 4 of Table I). From the molecular models of these two compounds it can be seen that there is considerable crowding of the two methyl groups when they are on the same side of the five-membered ring as in the *meso*-2,3-diaminobutane complex. Clearly a seven-coördinated activated complex such as in the displacement mechanism would not relieve this crowding but a coördination number of five could reduce it considerably.

As another example of this effect it was found that the *meso*-1,2-diphenylethylenediamine complex aquated in 50% methanol[12] approximately sixty times as fast as the *l*-1,2-diphenylethylenediamine complex. For comparison, the ethylenediamine complex was also run in 50% methanol and was found to aquate about three times as fast as $[Co(l\text{-}stien)_2Cl_2]^+$. Since these reactions were only partially complete in 50% methanol, it was necessary to correct for the reverse reaction which is second order. These corrections, however, did not change the relative order of rates: *meso*-stien >> en > *l*-stien. No explanation is offered for the fact that the ethylenediamine complex aquates more rapidly than the more sterically crowded *l*-1,2-diphenylethylenediamine complex. The corrected rate constants for runs made in 50% methanol are shown in Table II.

TABLE II

RATES OF AQUATION OF SOME *trans*-$[Co(AA)_2Cl_2]^{+1}$ IONS IN 50% METHANOL AT 25°

$[Co(AA)_2Cl_2]^+ + H_2O = [Co(AA)_2H_2OCl]^{+2} + Cl^-$

Diamine (AA)	Symbol	$k \times 10^4$ (min.$^{-1}$)	Method
$NH_2-CH_2-CH_2-NH_2$	(en)	0.8	T
l-$NH_2-CH(C_6H_5)-CH(C_6H_5)-NH_2$	(*l*-stien)	0.3	T
meso-$NH_2-CH(C_6H_5)-CH(C_6H_5)-NH_2$	(*m*-stien)	17	S

Further evidence for the existence of steric strain in some of the substituted complexes comes from measurements of the formation constants of $[Ni(AA)_3]^{+2}$. In aqueous solution the following order of decreasing stabilities is obtained[13]: en > *dl*-bn > pn >> *m*-bn > Me-en iso-bn > Et-en > *n*-Pr-en. In 50% aqueous dioxane en > *l*-stien >> *m*-stien.

The last three complexes (10, 11 and 12) in Table I show the effect of expanding the chelate ring from five to six members. A comparison of the ethylenediamine and trimethylenediamine complexes shows that the aquation rate increases by more than a thousandfold when the chelate ring is expanded by one carbon atom. Again it can be shown by the use of molecular models that such a six-membered chelate ring involves considerable strain and that this strain would be lessened by a decrease in the coördination number. In addition, it has been shown[14] that five-membered chelate rings are usu-

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[12] The 1,2-diphenylethylenediamine complexes were run in 50% methanol since they are not water-soluble.

[13] F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5243 (1952); F. Basolo, Y. T. Chen and R. K. Murmann, forthcoming publication.

[14] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 137.

ally more stable than six-membered rings when the ring contains no double bonds.

An apparent exception to the foregoing examples of increased aquation rate with increased crowding is the case of the 1,3-diamino-2,2-dimethylpropane complex (no. 12 in Table I). A comparison with the trimethylenediamine complex shows that in this case the rate is actually lessened as a result of adding methyl groups to the bidentate chain. There seems to be no simple explanation as to why methyl substitution on a six-membered chelate ring decreases the rate of aquation while methyl substitution on a five-membered ring increases the rate of aquation.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

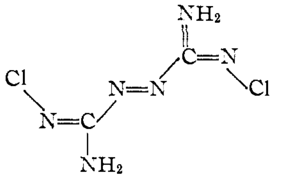
The Dipole Moments, Ultraviolet Spectra and Structure of Azo-bis-(chloroformamidine) and Azo-bis-(nitroformamidine)

BY W. D. KUMLER

RECEIVED FEBRUARY 7, 1953

Azo-bis-(chloroformamidine) has a dipole moment of 1.95 *D* and azo-bis-(nitroformamidine) a moment of 3.63 *D*. The comparatively low moments considering the size of the individual group moments making up the molecules suggest the compounds have the *trans* configuration about the N=N double bond. The chloro compound with a λ_{max} 345, ϵ_{max} 14,700 absorbs at longer wave length and with higher extinction than the nitro compound λ_{max} 312, ϵ_{max} 5840. The imine structures are capable of accounting for the behavior. A consideration of the properties of the ion produced by the removal of a proton from either the chloroimine or chloroamine structure suggests the molecule has the chloroimine structure. The same reasoning applies to the nitro compound.

The problem of structure in these molecules is concerned mainly with whether they are *cis* or *trans* with respect to the azo linkage and whether the chlorine atoms and the nitro groups are attached to a singly or doubly bonded nitrogen atom. The two *trans* structures for the chlorine compound are represented by structures (1) and (2).



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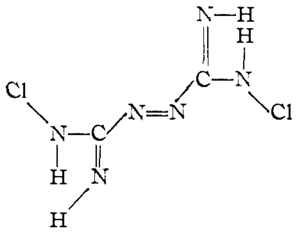

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The dipole moments of the compounds were measured in dioxane at 30°. The dioxane was purified as before.[1] The compounds were highly purified samples supplied to us by Professor George F. Wright. The dipole moments were calculated using the equation and method of Halverstadt and Kumler.[2]

$$p_{2_0} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + (\nu_1 + \beta)\,\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

$$P_{2_0} = p_{2_0}\, M_2$$

$$\mu = 0.01281\,\sqrt{(P_{2_0} - P_{E_2})T}$$

ϵ_1 and ν_1 were obtained by extrapolating the straight line ϵ_{12}-ω_2 and ν_{12}-ω_2 curves to zero concentration.

Azo-bis-(chloroformamidine)

ω_2	ϵ_{12}	ν_{12}
0.000400	2.2063	0.97375
.000577	2.2067	.97365
.000794	2.2072	.97357
.000975	2.2081	.97344
.001193	2.2087	.97335

ϵ_1	α	ν_1	β	P_{2_0}	P_{E_2}	μ
2.2050	3.00	0.97393	−0.48	116.6	40.4	1.95

Azo-bis-(nitroformamidine)

ω_2	ϵ_{12}	ν_{12}
0.000189	2.2076	0.97374
.000312	2.2089	.97366
.000429	2.2102	.97360
.000536	2.2107	.97353
.000805	2.2128	.97334

ϵ_1	α	ν_1	β	P_{2_0}	P_{E_0}	μ
2.2062	8.37	0.97385	−0.59	306.6	41.6	3.63

The comparatively low moments of both of these compounds considering the moments of the individual groups that make them up suggest that the compounds have the *trans* and not the *cis* configuration. A *cis* structure would enable the groups to augment one another so the expected moment would be considerably larger than the observed moment. On the other hand, the *trans* structure allows enough opposition so that the observed moments are reasonable for such a configuration.

The dipole moments do not enable a decision to be made with regard to whether the chlorine and nitro groups are attached to singly or doubly bonded nitrogen atoms. The ultraviolet spectra of the compounds, however, shed some light on this question. The chlorine compound with λ_{max} 345 and ϵ_{max} 14,700 absorbs at considerably longer wave length and with higher extinction than the nitro compound with λ_{max} 312 and ϵ_{max} 5,840. It is unusual for corresponding nitro and chlorine compounds to act in this manner, for the reverse is the usual behavior, namely, that the nitro compound absorbs at longer wave lengths and with higher extinction. For example nitrobenzene absorbs at longer wave lengths and with higher extinction than chlorobenzene. The behavior of these azo compounds can be accounted for in the following way. If the chlorine compound has structure (1), then resonat-

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[1] W. D. Kumler and I. F. Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

[2] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).