

condition in which essentially all sulfate ions are combined in a complex such as  $\text{CeSO}_4^{++}$ . If, however, the cerium(IV) concentration is constant and the sulfate is increased, there is not any such constant value for  $\bar{D}$  since additional cerium-sulfate linkages may be formed as other sulfate ions become included in the complex. It may be noted that the experimental curve of  $\bar{D}$  versus sulfate does not level off at ordinary concentrations.

It may be concluded, therefore, that the complex ion made up of one cerium(IV) and one sulfate ion predominates in solutions less than 0.01  $M$  in concentration, with other complex ions being formed at higher concentrations.

Jones and Soper reported a "slight migration of color" toward the anode in transference experiments and concluded a complex anion must exist. This is also in accord with the results above, since these data indicate that in more concentrated solutions complex anions such as  $\text{Ce}(\text{SO}_4)_3^-$  may be present.

**Instability Constant.**—By assuming that the flat portion of the curve in Fig. 6 represented complete combination of sulfate to form complex ions, the extinction coefficient of this complex was calculated from the observed value of  $\bar{D}$  and the known concentration of sulfate. With this extinction coefficient and the values of  $\bar{D}$  observed for various points on the curves of Fig. 4, equilibrium concentrations of the complex ion, cerium(IV) ion, and sulfate ion were calculated. From these, the instability constant ( $K$ ) of the ion was calculated. The extent of ionization for the conditions of Fig. 6 was then calculated and corrections made in the extinction coefficient, the equilibrium concentrations and in the values of  $K$ . These corrections gave an average value of  $4.3 \times 10^{-4}$  for  $K$  in solutions having total cerium(IV) + sulfate concentrations equal to 0.00493  $M$ .

The extinction coefficient could also be used to calculate equilibrium concentrations for the points on curves such as those of Fig. 3. From these data, average values of  $K$  equal to  $4.7 \times 10^{-4}$  and  $5.3 \times 10^{-4}$  were obtained for solutions 0.0043  $M$  and 0.0020  $M$ , respectively, in total cerium(IV).

By further approximations in the extinction coefficient, somewhat better agreement in values for  $K$  might be obtained, but, because of the lack of temperature control, etc., the results would probably not be significant.

The methods used here did not supply any evidence as to the presence of  $\text{H}^+$  or  $\text{OH}^-$  ions in the complex. With such high acid concentrations, a complex ion containing  $\text{OH}^-$  is unlikely, but it is quite possible that hydrogen ion may be combined with the cerium(IV) and sulfate.

Experiments are now being carried out in these laboratories to determine whether these results will permit calculations of the influence of sulfate on the rates of reaction of cerium(IV) solutions and to determine the influence of ions such as chloride and nitrate upon the cerium(IV) sulfate complex.

### Summary

1. Spectrophotometric studies of cerium(IV) perchlorate solutions showed no evidence of any colored complex ion formation. Cerium(IV) perchlorate solutions obey Beer's law up to concentrations of 0.01  $M$ .

2. Spectrophotometric studies on cerium(IV) sulfate solutions indicated that in concentrations up to 0.01  $M$ , a complex ion containing one cerium(IV) and one sulfate ion predominates. Complex ions containing more than one sulfate ion may also be formed, but become appreciable only at higher concentrations.

3. An approximate value for the instability constant of the simplest complex ion was determined.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Preparation and Properties of Inorganic Coördination Compounds. I. The Action of Some Organic Amines upon Dichloro-diethylenediamine Cobaltic Chloride<sup>1</sup>

BY JOHN C. BAILAR, JR., AND LEALYN B. CLAPP<sup>1</sup>

The chlorine-cobalt bonds in dichloro-diethylenediamine cobaltic ion,  $[\text{Co en}_2\text{Cl}_2]^+$ , are very weak compared to the nitrogen-cobalt bonds, and the two chlorine atoms can be replaced in a variety of ways. Thus, they are readily displaced from the coördination sphere by carbonate, oxalate, thiocyanate, hydroxide and other anions having strong donor properties. On standing in water, the  $[\text{Co en}_2\text{Cl}_2]^+$  ion is aquated with the formation of  $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]^{++}$  and  $[\text{Co en}_2(\text{H}_2\text{O})_2]^{+++}$ .

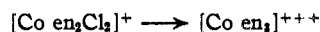
(1) Taken from a portion of the doctorate thesis of Lealyn Burr Clapp, 1941. Present address, Brown University, Providence, R. I.

Upon evaporation, the aquation reactions are reversed.

Anhydrous organic amines behave much as water does, but only one chlorine atom is replaced, and the compounds formed are stable enough that the amine is not readily expelled upon heating. For example, *s*-butylamine reacts with dichloro-diethylenediamine cobaltic chloride to give  $[\text{Co en}_2(\text{C}_4\text{H}_9\text{NH}_2)\text{Cl}]\text{Cl}_2$ . Secondary amines have little tendency to react in this way; tertiary amines (except heterocyclics), almost none.

In aqueous solution, several different types of

reaction with amines are possible: (1) amines with strong donor properties coordinate, as in the anhydrous condition; (2) strongly basic amines generate hydroxyl ion, which may displace the chlorine; (3) very weak bases often bring about "disproportionation" of the complex ion:



(4) Some other weak bases cause rearrangement of *trans*  $[\text{Co en}_2\text{Cl}_2]^+$  to the *cis* form.

The study of these effects is complicated by the fact that several different reactions may take place simultaneously, but in varying degree, and the two replaceable groups may react in different ways. Under slightly different experimental conditions, the same amine may give quite different products. The results reported in this paper are only roughly quantitative, but are thought to be sufficiently accurate to allow some general comparisons of the coordinating tendencies of different amines.

Meisenheimer and Kiderlen<sup>2</sup> came to the conclusion that the ease with which a primary amine displaces chlorine from *trans*- $[\text{Co en}_2\text{Cl}_2]^+$  increases with the basicity of the amine. The five amines which they used all yielded chloro-aminediethylenediamine-cobaltic ion,  $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]^{++}$ . The order of increasing activity was found to be aniline < *p*-toluidine < benzylamine < allylamine < ethylamine, which is also the order of increasing basicity. These amines are so different in structure, however, that other factors than basicity may well be important in determining the ease of formation and the strength of the cobalt-nitrogen link.

Meisenheimer and Kiderlen also studied the action of several secondary amines (diethylamine, benzylmethylamine, methylaniline, and *N,N'*-dimethylethylenediamine) upon *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ , but in no case did the amine enter the complex. The first two amines gave the  $[\text{Co en}_2(\text{OH})\text{Cl}]^+$  ion, and the last two,  $[\text{Co en}_3]^{+++}$ . Methyl-aniline also yielded some *cis*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ . Meisenheimer and Kiderlen measured the stability of the chloro-amino compounds which they obtained from primary amines by heating them with hydrochloric acid, with dilute sodium hydroxide, and with water. These experiments indicated that ethylamine forms the strongest cobalt-nitrogen link, and benzylamine the weakest, so it appears that the compound most readily formed is not necessarily the most stable. From this and his own work with a number of aromatic amines, Ablov<sup>3,4</sup> concluded that the basicity of the amine does not determine its action on the *trans*-dichloro salt. This hypothesis was strengthened by the present study, in which four aliphatic amines of about equal basicity

and pyridine, which is a much weaker base, were allowed to react with *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ . The amines used and their  $pK_H$  values are as follows: ( $pK_H = 14 - pK$ ) methylamine 10.64; ethylamine 10.67; isopropylamine 10.63; *s*-butylamine 10.56; and pyridine 5.21. The rates of reaction were not noticeably different in any of the five cases since the water solutions of the amines turned the dichloro salt to a deep red within five seconds. Pyridine, methylamine, and ethylamine formed  $[\text{Co en}_2 \text{ amine Cl}]\text{Cl}_2$  in good yield. Isopropylamine gave a mixture of products containing  $[\text{Co en}_2 \text{ amine Cl}]\text{Cl}_2$  (50%) and  $[\text{Co en}_2(\text{H}_2\text{O})\text{OH}]\text{Cl}_2$  (30%). Furthermore, the former of these compounds was much less stable to hydrochloric acid and to dilute sodium hydroxide than the methyl- and ethylamine complexes. *s*-Butylamine gave  $[\text{Co en}_2 \text{ amine OH}]\text{Cl}_2$  as the principal product. This establishes Ablov's contention and further shows that the nature and stability of the products do not depend entirely upon the basicity of the amine.

The investigations of Meisenheimer and Kiderlen and of Ablov on the stability of several of the chloro amino complexes were repeated in the present work and verified in every case. The great difference in stability between the aliphatic and aromatic amine complexes is noteworthy. In general, the compounds containing aliphatic amines withstood heating on the steam cone with dilute hydrochloric acid for thirty minutes or more, while those containing aromatic amines were mainly converted to *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  within five or ten minutes. All the compounds containing aliphatic amines except benzylamine gave water solutions stable to heating on the steam cone while solutions of complexes containing aromatic amines gave off a definite odor of the amine in three to ten minutes. The action of hot, dilute sodium hydroxide required five to ten minutes to precipitate cobaltic hydroxide from the aliphatic amine complexes  $[\text{Co en}_2 \text{ amine Cl}]\text{Cl}_2$ , but less than three minutes to decompose the corresponding aromatic amine compounds. The order of decreasing stability of the chloro amine compounds indicated by these qualitative tests is shown by the following list. The  $pK_H$  values of the amines<sup>5,6</sup> are shown in parentheses: methylamine (10.64) and ethylamine (10.67) > isopropylamine (10.63) > allylamine (9.75) and *s*-butylamine (10.56) > pyridine (5.21) > benzylamine (9.38) > *m*-toluidine (4.69) > *p*-toluidine (5.12) > aniline (4.62) > *o*-anisidine (4.49) > *p*-anisidine (5.29) > *o*-toluidine (4.39), *o*-phenetidine (4.47), and *p*-phenetidine (5.25).

The reactions of amines with *cis*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  do not always follow the same course as with the *trans* isomer. However, when compounds of the type  $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]\text{Cl}_2$  are formed, they have approximately the same properties as when pre-

(2) Meisenheimer and Kiderlen, *Ann.*, **438**, 238 (1924).

(3) Ablov, *Bull. soc. chim.*, [5] **3**, 2270 (1936).

(4) Ablov also has studied the reaction of amines with 1,6-dibromodiethylenediamine cobaltic bromide, *Bull. soc. chim.*, [5] **4**, 1783 (1937).

(5) Bredig, *J. physik Chem.*, **13**, 305 (1894).

(6) Hall and Sprinkle, *This Journal*, **54**, 3469 (1932).

TABLE I  
REACTIONS OF SOME AMINES WITH *cis*- AND *trans*-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl

The investigators reporting the results are indicated as follows: MK, Meisenheimer and Kiderlen; A, Ablov; BC, Bailar and Clapp.

Amine	<i>trans</i>		<i>cis</i>	
Methyl	[Co en <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	BC	[Co en <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·½H <sub>2</sub> O	BC
Ethyl	[Co en <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	MK, <sup>a</sup> BC	[Co en <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	MK, BC
Isopropyl	[Co en <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> + [Co en <sub>2</sub> (H <sub>2</sub> O)OH]Cl <sub>2</sub>	BC	[Co en <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	BC
Allyl	[Co en <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·2H <sub>2</sub> O	MK, <sup>a</sup> BC	[Co en <sub>2</sub> (H <sub>2</sub> O)OH]Cl <sub>2</sub>	MK, BC
Allyl (25 days)			[Co en <sub>2</sub> ]Cl <sub>3</sub>	BC
<i>s</i> -Butyl (anh.)	[Co en <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	BC	[Co en <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	BC
<i>s</i> -Butyl (aq.)	[Co en <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> )(OH)]Cl <sub>2</sub>	BC	[Co en <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> )(OH)]Cl <sub>2</sub> ·2H <sub>2</sub> O	BC
Pyridine	[Co en <sub>2</sub> (py)Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	BC	[Co en <sub>2</sub> (py)Cl]Cl <sub>2</sub>	BC
Benzyl	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	MK	[Co en <sub>2</sub> (H <sub>2</sub> O)OH]Cl <sub>2</sub>	MK, BC
Aniline	[Co en <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	MK, BC	[Co en <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	MK, BC
<i>p</i> -Toluidine	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	MK, BC	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	MK, BC
<i>o</i> -Toluidine <sup>c</sup>	<i>cis</i> [Co en <sub>2</sub> Cl <sub>2</sub> ]Cl + [Co en <sub>2</sub> (H <sub>2</sub> O)OH]Cl <sub>2</sub> ·3/2H <sub>2</sub> O	A <sup>d</sup>	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	BC
<i>m</i> -Toluidine	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> )Cl]Cl <sub>2</sub>	A		
<i>o</i> -Anisidine	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> ONH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	A, <sup>b</sup> BC	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> ONH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	BC
<i>p</i> -Anisidine	[Co en <sub>2</sub> (C <sub>7</sub> H <sub>7</sub> ONH <sub>2</sub> )Cl]Cl <sub>2</sub>	A		
<i>o</i> -Phenetidine	[Co en <sub>2</sub> (C <sub>8</sub> H <sub>9</sub> ONH <sub>2</sub> )Cl]Cl <sub>2</sub> ·2H <sub>2</sub> O	A		
<i>p</i> -Phenetidine	[Co en <sub>2</sub> (C <sub>8</sub> H <sub>9</sub> ONH <sub>2</sub> )Cl]Cl <sub>2</sub> + [Co en <sub>2</sub> ]Cl <sub>3</sub>	A, <sup>c</sup> BC	[Co en <sub>2</sub> ]Cl <sub>3</sub>	BC
<i>p</i> -Fluoroaniline	[Co en <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> FNH <sub>2</sub> )Cl]Cl <sub>2</sub> ·H <sub>2</sub> O	A		
<i>p</i> -Chloroaniline	<i>cis</i> [Co en <sub>2</sub> Cl <sub>2</sub> ]Cl	A		
<i>o</i> -Chloroaniline	<i>cis</i> [Co en <sub>2</sub> Cl <sub>2</sub> ]Cl	A		
<i>o</i> -Phenylenediamine	[Co en <sub>2</sub> ]Cl <sub>3</sub>	A		
<i>p</i> -Phenylenediamine	[Co en <sub>2</sub> ]Cl <sub>3</sub>	A		
<i>o</i> -Aminophenol	[Co en <sub>2</sub> ]Cl <sub>3</sub>	A		

<sup>a</sup> Meisenheimer and Kiderlen found the chloride to have one molecule of water of hydration. <sup>b</sup> Ablov reported that this salt crystallizes with two molecules of water. <sup>c</sup> Ablov reported a molecule of water of hydration. <sup>d</sup> Ablov reported the product of this reaction to be *cis*-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl with some admixed [Co en<sub>2</sub>]Cl<sub>3</sub>.

pared from the *trans* salt (see Table I). The configurations of the products are not known in most cases, and it cannot be stated with certainty that the compounds from the two series are identical. However, there are no gross differences in color, solubility, or stability in any of the pairs studied, and it seems probable that they have the same configuration. It is known that aqueous ammonia, reacting with either the *cis* or *trans* dichloro salt, always yields the *cis*-chloroamine, [Co en<sub>2</sub>(NH<sub>3</sub>)Cl]Cl<sub>2</sub>.

**Reactions of the *trans*-Dichloro Salt.**—In the reactions of the aliphatic amines of about the same basicity with *trans*-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl, it may be said that with increasing molecular weight, there is a greater percentage of hydroxo aquo diethylenediamine cobaltic chloride [Co en<sub>2</sub>(H<sub>2</sub>O)(OH)]Cl<sub>2</sub> formed. With ethyl- and methylamines, less than 10% of this compound is formed, with isopropylamine about 35%, and with *s*-butylamine about 45%. Closely related to this is the decreasing stability of the chloro amine compounds with increasing molecular weight of the amine. The chloro isopropylamine compound becomes an oil on warming whereas the chloro methyl- and ethylamine compounds are very stable to heat. The allyl- and isopropylamine complexes have about the same stability to hydrochloric acid, to

dilute sodium hydroxide, and in water solution. In the reaction with the *trans* salt, however, a greater percentage of [Co en<sub>2</sub>(H<sub>2</sub>O)OH]Cl<sub>2</sub> is formed with isopropylamine than with allylamine. The reaction of *s*-butylamine and *trans*-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl takes a course different from the others, giving hydroxo *s*-butylamine diethylenediamine cobaltic chloride as the main product.

**Reactions of the *cis*-Dichloro Salt.**—Nor does there seem to be any general rule which will predict the product of the reaction between *cis* [Co en<sub>2</sub>Cl<sub>2</sub>]Cl and an aliphatic amine at room temperature. Aqueous methyl-, ethyl- and isopropylamines yield chloro amines; aqueous allyl- and benzylamines yield [Co en<sub>2</sub>(H<sub>2</sub>O)OH]Cl<sub>2</sub>; and aqueous *s*-butylamine yields [Co en<sub>2</sub> amine OH]Cl<sub>2</sub>·2H<sub>2</sub>O. Pure allylamine decomposes the *cis* salt after twenty-five days to give [Co en<sub>3</sub>]Cl<sub>3</sub> as the main product; anhydrous *s*-butylamine gives no reaction at room temperature after twenty-one days but after keeping the mixture at a temperature of 50 ± 5° for five days, the chloro amine complex is formed in small yield. It will be observed that even with amines of approximately the same basicity, very different products are obtained.

The products obtained from the reactions of the substituted anilines with *cis* and *trans* [Co en<sub>2</sub>-

TABLE II

Dichloro-salt	Reactants		Formula of product	Description of product	Analyses of product, %			
	Amine	Time of reaction			Calcd.	Found	Calcd.	Found
<i>trans</i>	Aniline	0.5 hr.	$[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2$	Red-violet			28.14	28.52
<i>cis</i>	Aniline	0.5 hr.	$[\text{Co en}_2(\text{C}_6\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2$	Red-violet	18.49	18.08	28.14	28.63
<i>trans</i>	<i>p</i> -Toluidine	1.5 hr.	$[\text{Co en}_2(\text{p-C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red-brown	17.05	16.82	25.94	26.27
<i>cis</i>	<i>p</i> -Toluidine	6.5 hr.	$[\text{Co en}_2(\text{p-C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red-brown	17.05	16.96	25.94	25.89
<i>cis</i>	<i>o</i> -Toluidine	5 days	$[\text{Co en}_2(\text{o-C}_7\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2$	Red hygroscopic			27.13	27.23
								26.98
<i>trans</i>	<i>o</i> -Anisidine	0.25 hr.	$[\text{Co en}_2(\text{o-C}_7\text{H}_7\text{ONH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red	16.41	15.94	24.97	25.01
<i>cis</i>	<i>o</i> -Anisidine	0.25 hr.	$[\text{Co en}_2(\text{o-C}_7\text{H}_7\text{ONH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red	16.41	16.21	24.97	24.84
<i>trans</i>	<i>p</i> -Phenetidine	0.5 hr.	$[\text{Co en}_2(\text{p-C}_8\text{H}_9\text{ONH}_2)\text{Cl}]\text{Cl}_2$	Pale red	16.57	16.53	25.21	25.82
<i>cis</i>	Pyridine	6 hrs. (0°)	$[\text{Co en}_2(\text{C}_5\text{H}_5\text{N})\text{Cl}]\text{Cl}_2$	Light red	19.20	19.32	29.22	28.93
<i>trans</i>	Pyridine	0.25 hr.	$[\text{Co en}_2(\text{C}_5\text{H}_5\text{N})\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Bright red			27.84	27.96
<i>cis</i>	Methylamine	At once	$[\text{Co en}_2(\text{CH}_3\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	Bright red	21.51	21.61	32.72	32.78
<i>trans</i>	Ethylamine	5 min.	$[\text{Co en}_2(\text{C}_2\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2$	Bright red	21.18	20.91	32.23	32.27
<i>cis</i>	Ethylamine	10 min. (0°)	$[\text{Co en}_2(\text{C}_2\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2$	Bright red	21.18	20.85	32.23	32.27
<i>trans</i>	Isopropylamine	10 min.	$[\text{Co en}_2(\text{C}_3\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2$	Red-purple	20.32	20.18	29.46	29.40
<i>cis</i>	Isopropylamine	0.25 hr.	$[\text{Co en}_2(\text{C}_3\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red			27.99	27.79
<i>trans</i>	Allylamine	10 min.	$[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Red	18.50	18.43	28.14	27.70
<i>cis</i>	<i>s</i> -Butylamine	5 days (50°)	$[\text{Co en}_2(\text{C}_4\text{H}_9\text{NH}_2)\text{Cl}]\text{Cl}_2$	Bright red	19.53	19.76	29.71	29.53
<i>trans</i>	<i>s</i> -Butylamine	5 days	$[\text{Co en}_2(\text{C}_4\text{H}_9\text{NH}_2)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red			28.29	28.54

$\text{Cl}_2$ ] $\text{Cl}$  were the same as those previously obtained by Meisenheimer and Kiderlen and by Ablov. However, some new reactions were carried out with the *cis* salt. The chloro amine compounds of *o*-toluidine and *o*-anisidine were prepared but with *p*-phenetidine, the *cis* salt was decomposed to yield  $[\text{Co en}_2]\text{Cl}_3$  as the principal product. The stability of these compounds has already been discussed.

All attempts to prepare compounds of the type  $[\text{Co en}_2(\text{RNH}_2)_2]\text{Cl}_3$  were fruitless. Attempts to force the reactions of *cis*  $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  with allylamine beyond the formation of  $[\text{Co en}_2(\text{C}_3\text{H}_5\text{NH}_2)\text{Cl}]\text{Cl}_2$  gave none of the desired product, but a small amount of triethylenediamine cobaltic chloride.

**Reactions of Optically Active *cis*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ .**—Reactions of several of the amines with optically active (levo) *cis*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  were carried out, to determine whether optically active (and hence, *cis*) products are formed. At room temperature, aniline, *o*-anisidine, and allylamine gave inactive products of various sorts. At 0°, as at room temperature, isopropylamine gave only inactive products. *p*-Toluidine yielded dextro- $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]\text{Cl}_2$  and methyl- and ethylamines (at 0°) gave mixtures of optically inactive  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Cl} \cdot 1.5\text{H}_2\text{O}$  and dextro- $[\text{Co en}_2(\text{RNH}_2)\text{OH}]\text{Cl}_2$ . The formation of the latter compound evidently takes place through the formation of the intermediate  $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]^{++}$  rather than  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Cl}$ , for the chlorohydroxo compound will not react with ethylamine to give  $[\text{Co en}_2(\text{C}_2\text{H}_5\text{NH}_2)\text{OH}]\text{Cl}_2$ .

### Experimental

*cis*- and *trans*-dichloro-diethylenediamine-cobaltic chloride were prepared and the *cis* salt was resolved as described by Bailar and Auten.<sup>7</sup> The amines used were all commercial products of high purity.

Meisenheimer and Kiderlen effected their reactions by occasional shaking of a suspension of the finely powdered *trans* salt in water with a water or alcohol solution of the

amine. Using aromatic amines, Ablov hastened the reactions by warming the mixtures of the reactants but most of the reactions still required two to three hours with the *trans* salt and a week with the *cis* salt. In the present work, the time of reaction with both *cis* and *trans* salts was greatly decreased by grinding the reactants together.

The aliphatic amines reacted in a few seconds with the *trans* salt and in a few minutes with the *cis* salt while the aromatic amines were submitted to grinding for one-half hour and then allowed to stand until the reaction was completed. With aniline, for example, the reaction time was shortened from two or three hours to thirty minutes for the *trans* salt and from one week to one day for the *cis* salt.

In every case, the following standard procedure was used: One or two grams of the acid-free *trans* dichloro chloride (or the *cis* salt), suspended in two or three cubic centimeters of water, is ground in a mortar with slightly more than the calculated amount of the amine, which is dissolved in alcohol if it is insoluble in water. If the reaction is not complete at the end of half an hour, the mixture is set aside until no further change is apparent (in some cases this takes several days). If the product is in solution, it is precipitated by the addition of 50 cc. of alcohol (precipitation may not take place at once), and after filtration, is dissolved in a minimum quantity (3–4 cc.) of water heated to 70°. Upon the addition of a few drops of concentrated hydrochloric acid and cooling to 0°, crystallization takes place. The salt may then be washed with alcohol and dried over potassium hydroxide. The results of these experiments are summarized in Table II.

The mother liquor from the original alcohol precipitation was treated with 50 cc. of ether, which caused the precipitation of a deep red oil. This was dried over potassium hydroxide and analyzed without further purification. It proved to be  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ .

Using *s*-butylamine, the standard procedure gave a crude product which was obviously different from that obtained with the lower homologs. It was a very voluminous, light pink precipitate. It was purified by dissolving it in 3–4 cc. of water, reprecipitating by the addition of 5 cc. of alcohol, and washing with alcohol and then ether. Analysis showed it to be  $[\text{Co en}_2(\text{C}_4\text{H}_9\text{NH}_2)\text{OH}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ . Calcd.: N, 18.62; Cl, 18.88. Found: N, 18.46; Cl, 18.86, 18.91. The chloro-amino type of compound was obtained with this butylamine when the anhydrous base was heated to 50° for five days with the *dry* dichloro compound. The product was recrystallized in the usual way.

The crude product from the reaction of the *trans* dichloro salt and isopropylamine did not completely dissolve in a small amount of water. Analysis showed the residue to be  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ . The part that had gone into solution was reprecipitated by addition of alcohol.

(7) Bailar and Auten, THIS JOURNAL, 66, 774 (1934).

dried over potassium hydroxide, and shown by analysis to be  $[\text{Co en}_2(\text{C}_6\text{H}_7\text{NH}_2)\text{Cl}]\text{Cl}_2$ .

**Reactions of Bases which Do not Enter the Coördination Sphere.**—In several other cases, the standard procedure outlined above did not yield the chloro-amino type of complex cation. 2,4,6-Trichloroaniline did not enter the coördination sphere, but converted the green *trans* dichloro salt to the violet *cis* modification in five days. The very weak base *m*-nitroaniline only partially converted the green salt to the violet in eight months. Quinoline also converted the *trans* isomer to the *cis*, and formed a small amount of  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ . As Table II shows, methyl-, ethyl- and isopropylamines gave  $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]\text{Cl}_2$  as the main product; in each case, however, a little of the hydroxo-aquo chloride was formed.

Allylamine reacted readily with *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  to give the chloro-amine, but with the *cis* isomer it gave only  $[\text{Co en}_3]\text{Cl}_3$  and  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ . The former of these was precipitated from the solution by addition of alcohol and was identified by its characteristic yellow color and by chloride analysis. Calcd.: Cl, 30.83. Found: Cl, 30.97.

The latter was precipitated as a red oil from the alcoholic filtrate by addition of ether. This oil crystallized on standing in a vacuum desiccator and was identified by chloride analysis. Calcd.: Cl, 24.91. Found: Cl, 24.71. (The compound  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$  which might be formed in this reaction is ruled out as it is blue-gray in color.)

The secondary amine, N-methylaniline, was allowed to react with both *cis* and *trans*  $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ . The main product in each case was  $[\text{Co en}_3]\text{Cl}_3$ , and no compound of the type  $[\text{Co en}_2\text{RR}'\text{NHCl}]\text{Cl}_2$  could be detected.

**Reactions of Optically Active  $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ .**—The reaction of *p*-toluidine with optically active (levo)- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  was carried out in the usual way. The product was  $[\text{Co en}_2\text{C}_6\text{H}_7\text{NH}_2\text{Cl}]\text{Cl}_2$  and showed rotations at 25° in a 0.1% solution:  $[\alpha]_C = 0^\circ$ ,  $[\alpha]_D = +100^\circ$ ,  $[\alpha]_E = +110^\circ$ . The product must, therefore, have the *cis* configuration. The same procedure, carried out at room temperature with aniline, *o*-anisidine, methyl-, ethyl- and allylamines gave optically inactive products. If these have the *cis* configuration, racemization has taken place during the reaction. They may, of course, have the *trans* configuration. In an attempt to obtain more of these compounds in optically active form, reactions of several amines with levo- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  were carried out at 0°. At this temperature, the reactions were entirely different than at room temperature. With isopropylamine, two inactive products were isolated— $[\text{Co en}_3]\text{Cl}_3$  and  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ . The former was identified by its characteristic color. Chloride analysis for the latter: Calcd.: Cl, 24.91. Found: Cl, 24.91.

With methyl- and ethylamines, two products were formed. In each case, the addition of alcohol after the reaction had proceeded for twenty-five minutes precipitated a blue-gray, optically inactive product within half an hour. Analysis showed this to be  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Cl}\cdot\frac{3}{2}\text{H}_2\text{O}$ . Calcd.: Cl, 24.15; N, 19.05. Found (from

the reaction with methylamine): Cl, 24.59; N, 19.29. (From the reaction with ethylamine): Cl, 24.26; N, 18.86. On standing overnight, the alcoholic solutions precipitated more of this material, mixed with a red, optically active product. The red product from the reaction with ethylamine was obtained in pure form, and proved to be *dextro*- $[\text{Co en}_2\text{C}_2\text{H}_5\text{NH}_2(\text{OH})]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ . Calcd.: Cl, 20.40; N, 20.69. Found: Cl, 20.32; N, 20.74. Using a 0.1% solution at 25°,  $[\alpha]_C +97^\circ$ ,  $[\alpha]_D +180^\circ$ ,  $[\alpha]_E +275^\circ$ . The methylamine analog was not obtained in pure form, but it seemed to be entirely analogous. It also showed a *dextro* rotation. For both the methyl- and ethylamine compounds, the optical activity fell to about half in two hours, and completely disappeared in a day.

### Summary

The reactions of several organic amines with *cis*- and *trans*-dichloro-diethylenediamine cobaltic chloride have been studied. The amines used were aniline, *p*-toluidine, *o*-toluidine, *o*-anisidine, *p*-phenetidine, pyridine, methylamine, ethylamine, isopropylamine, allylamine, *s*-butylamine, 2,4,6-trichloroaniline, *m*-nitroaniline, quinoline and N-methylaniline.

The last four amines mentioned do not enter the coördination sphere, but cause rearrangement (from *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  to the *cis* form) and disproportionation to  $[\text{Co en}_3]\text{Cl}_3$ .

The other amines form compounds of the type  $[\text{Co en}_2(\text{RNH}_2)\text{Cl}]\text{Cl}_2$ . The products seem to be the same whether they are prepared from the *cis* or from the *trans* dichloro salt. That containing *p*-toluidine was obtained in optically active form from levo- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ , and so must have the *cis*-configuration.

In addition to the chloro-amino salts described above, several other types of products form in some cases. These include  $[\text{Co en}_2(\text{RNH}_2)\text{OH}]\text{Cl}_2$ ,  $[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ ,  $[\text{Co en}_2(\text{OH})(\text{Cl})]\text{Cl}$ , and products of rearrangement and disproportionation. Compounds of the type  $[\text{Co en}_2(\text{RNH}_2)\text{OH}]\text{Cl}_2$ , containing methyl and ethyl amines, were obtained in optically active form.

It was not found possible to prepare compounds of the type  $[\text{Co en}_2(\text{RNH}_2)_2]\text{Cl}_3$ .

The type of complex ion which is formed from any amine does not depend primarily upon the basicity of the amine.

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