further that a relatively stable double complex with both EDTA and pyrophosphate is formed. The shift of the ordinate between the Zr(IV) and ZrO(IV) curves corresponds to about one mole of base per gram-ion of metal, indicating that the former complexes probably contain fewer bridging hydroxo groups, very likely as a consequence of more extensive reaction with the two ligands present. Apparently the highly polymeric zirconyl(IV) system cannot combine as readily with these ligands as does the less hydrolyzed Zr(IV) solution.

The titration curves for the MoO_2(VI) system illustrated in Fig. 3 indicate that the 1:1 MoO_2(VI)–Tiron chelate compound previously described[9] does not react with pyrophosphate and that the latter anion is present in the same state as in the absence of the metal chelate.

The potentiometric data for the Zr(IV)–NTA–pyrophosphate systems illustrated in Fig. 3 clearly show that 1, the interaction of Zr(IV) with NTA is sufficient to keep the metal from precipitating below $-\log[H^+]$ of 7.5; and 2, in the presence of pyrophosphate, the normal pyrophosphate–Zr(IV) chelate only is formed, and the NTA behaves as if it is present in the free state in solution.

Correlation of Rates with Metal Chelates Formed.—A comparison of the kinetic data in Table I and Fig. 4, with the results of the potentiometric measurements in Figs. 1–3, indicates that the observed rates are probably the result of two opposing tendencies: 1, catalytic activity of the metal ion which increases as the number of uncoördinated positions on the metal increases, and 2, tendency of a polydentate chelating agent to lower the activity of the metal through coördination. Thus, high catalytic activity is seen in Table I for the Zr(IV) chelates with relatively few donor groups, such as PDS and NTA. In the case of EDTA, which forms a much more stable Zr(IV) chelate compound, the catalytic activity is greatly reduced.

The remarkably high catalytic activity of the ZrO(IV) chelate of EDTA is unique and, as suggested above, probably is due to a polymeric and highly olated or oxolated structure for this particular substance. In any case it is seen that the primary function of the chelating agent is to hold the metal in soluble form. Of the metal chelates with sufficient stability to maintain a homogeneous solution, those with the lowest stability seem to be the best catalysts.

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The Stereochemistry of Complex Inorganic Compounds. XXIV. Cobalt Stilbenediamine Complexes[1]

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A number of previously unreported cobalt(III) coördination complexes of active and *meso*-stilbenediamine have been prepared and their properties studied. Attempts to isomerize *trans*-dichloro-bis-*active*-stilbenediamine-cobalt(III) chloride to the *cis*-isomer failed. What is believed to be the *cis*-isomer was obtained by interaction of gaseous hydrogen chloride and solid carbonato-bis-*active*-stilbenediamine-cobalt(III) nitrate 1-hydrate. Efforts to obtain positive proof of the configuration by X-ray diffraction were unsuccessful due to the amorphous nature of the material. Reaction of *racemic*-stilbenediamine and carbonatotetrammine-cobalt(III) nitrate $^1/_2$-hydrate gave two carbonato bis-stilbenediamine complexes differing in composition only in that one was a monohydrate and the other a dihydrate. The two materials, however, differed greatly in their chemical and physical characteristics. Tartrato-bis-*active*-stilbene-cobalt(III) complexes prepared by reaction of *trans*-dichloro-bis-*active*-stilbenediamine-cobalt(III) nitrate with silver tartrate gave indication that the tartrate group was not behaving as a bidentate ligand. Unsuccessful attempts were made to resolve *racemic*-tartaric acid by reaction of its silver salt with *trans*-dichloro-bis-*levo*-stilbenediamine-cobalt(III) nitrate. Cobalt(III) complexes containing *meso*-stilbenediamine were found to be more difficult to prepare and to be considerably less stable than complexes containing the active amine.

The stereochemistry of coördination complexes containing the bidentate asymmetric propylenediamine has been studied extensively, and the propylenediamine-cobalt(III) complexes have been used to effect partial resolution of racemic organic compounds.[2,3] The possibility that a bidentate diamine containing two asymmetric centers might reenforce coördinative selectivity of optical antipodes and make possible complete resolution of organic racemates was considered an intriguing problem worthy of the present investigation.

Stilbenediamine was selected as the diamine to be used because it satisfies the stereochemical prerequisite of having vicinal amino groups attached to asymmetric carbon atoms; it exists in both *racemic*- and *meso*-forms.

The first extensive study of the metal complexes of stilbenediamine was conducted by Lifschitz and Bos.[4] In the present investigation their work on the cobalt complexes has been extended and a number of previously unreported complexes have been prepared and studied. Difficulties encountered in the synthetic work and the anomalous behavior of some of the complexes limited the extent of the stereochemical investigations. Further stereochemical studies of the complexes are under way.

The *trans*-dichloro-bis-stilbenediamine-cobalt(III) complexes containing *active*- and *meso*-amine were prepared by a modification of the procedure re-

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(1) Taken in part from the Doctoral Dissertation of O. F. Williams, University of Illinois, 1951.

(2) H. B. Jonassen, J. C. Bailar, Jr., and A. Gott, THIS JOURNAL, **74**, 3131 (1952).

(3) A. D. Gott and J. C. Bailar, Jr., *ibid.*, **74**, 4820 (1952).

(4) I. Lifschitz and J. G. Bos, *Rec. trav. chim.*, **59**, 173 (1940).

ported by Lifschitz. It was found that his procedure (air oxidation of a mixture of the diamine, cobalt(II) chloride and ethanol) was greatly improved by substituting 15% hydrogen peroxide for air. This allows better control of the concentration of the reactants, thereby producing the *trans*-dichloro complex in greater yield and in a higher state of purity.

Although the *trans*-dichloro complex containing *active*-stilbenediamine can be prepared easily and in good yields, the corresponding complex containing the *meso*-amine is much more difficult to prepare and is obtained in very low yields. Furthermore, the complex containing *meso*-stilbenediamine is much less stable than the analogous complex containing the active-amine. These marked differences are undoubtedly due to steric effects, for in the *meso*-form of the base, one of the phenyl groups must occupy an axial position.[5] Measurements of stability constants of copper and nickel complexes containing *meso*- and active-stilbenediamine and butylenediamine[6] have shown that the complexes containing the *meso*-base are much less stable than those of the active base.

The *trans*-dichloro-bis-stilbenediamine complexes containing either active- or *meso*-diamine are quite soluble in polar organic solvents but insoluble in water. Unlike the analogous ethylenediamine and propylenediamine complexes, stilbenediamine complexes aquate only in boiling water and then to only a limited extent. This is probably a solubility effect, for in liquid ammonia, the two chlorines are displaced (to form the diamine-bis-stilbenediamine complex) much more readily than from the analogous ethylenediamine and propylenediamine complexes.

Since the very low solubility of the *trans*-dichloro chloride in water imposed serious limitations on the synthetic work as well as on the stereochemical investigations, attempts were made to find more soluble salts, which, of necessity, were those containing anions which would not displace the chloride ions from the coördination sphere. The fluoroborate, trifluoroacetate, nitrate, bromide and perchlorate were all found to be insoluble. This suggests that the highly organic character of the complex cation overshadows the influence of the anion on the solubility of the salt.

Attempts to isomerize *trans*-dichloro-bis-*active*-stilbenediamine-cobalt(III) chloride to the *cis*-complex by conventional methods failed. The *trans*-dichlorostilbenediamine complex showed no evidence of rearrangement to the *cis*-configuration nor did it decompose when heated to 210°. Evidence for the formation of the *cis*-isomer was obtained, however, when carbonato-bis-*active*-stilbenediamine-cobalt(III) nitrate suspended in ether was treated with gaseous hydrogen chloride. The lavender product had the composition calculated for $[Co(stien)_2Cl_2]Cl{\cdot}H_2O$. It is known that the cobalt(III) chloro-aquo-tetrammine complexes are violet, and it is possible that the complex obtained was actually of this type. However, this seems unlikely in view of the instability of the aquo and diaquo complexes which were obtained with difficulty when the *trans*-dichloro complex was heated in boiling water. Moreover, a dilute aqueous solution of diaquo complex chloride was observed to change immediately to the green dichloro complex when ethanol was added, whereas at least an hour was required for an absolute ethanol solution of the lavender product to assume the emerald green color characteristic of the *trans*-dichloro complex. The method of preparation of the lavender dichloro complex offers evidence for the *cis*-configuration since, when a bidentate ligand is replaced by two monodentate groups, the entering groups generally occupy *cis*-positions. An attempt was made to establish the structure by comparing the X-ray diffraction patterns of the *trans*-dichloro chloride and the lavender material. The latter, however, failed to give a diffraction pattern. Attempts to crystallize the material from solvents were frustrated by its isomerization to the *trans*-form. An attempt also was made to compare the X-ray diffraction patterns of the diammine derivatives of the *trans*-dichloro complex and the lavender material. It was found, however, that although the *trans*-dichloro complex reacted immediately with liquid ammonia to form the diammine, the *cis*-complex gave only the pink chloroammine. The second coördinated chloride ion was replaced only after addition of ethanol. The complex which was isolated failed to give an X-ray diffraction pattern.

Whereas the tris-stilbenediamine-cobalt(III) chlorides containing the active-amine were easily prepared and are quite stable, repeated attempts to prepare the corresponding complex containing the *meso*-amine were unsuccessful.

The method found most convenient for preparation of the carbonatostilbenediamine complexes involved displacement of ammonia from carbonatotetrammine-cobalt(III) nitrate by heating it with an alcohol solution of stilbenediamine. Reaction of racemic stilbenediamine with the carbonatotetrammine complex gave two carbonato complexes, one containing two molecules of water, $[Co(stien)_2CO_3]NO_3{\cdot}2H_2O$, and the other containing one molecule of water, $[Co(stien)_2CO_3]NO_3{\cdot}H_2O$. The two products differ markedly in physical and chemical characteristics. The dihydrate, hereafter referred to as "carbonato A," is insoluble in all common solvents and attempts to dehydrate it always resulted in complete decomposition. Its reaction with either alcoholic or gaseous hydrogen chloride gave the *trans*-dichloro chloride. The second carbonato complex, hereafter referred to as "carbonato B," is soluble in ethanol and other polar organic solvents. Its reaction with gaseous hydrogen chloride gave the lavender product believed to be the *cis*-dichloro chloride. Absorption peaks of "carbonato B" appear at about the same wave lengths as those reported for carbonato-bis-*levo*-propylenediamine-cobalt(III) chloride.[7] Differences in the two carbonato complexes suggest that in "carbonato A" the carbonate group is not behaving as a bidentate ligand but is coördinated *trans* to a molecule of water. A second possibility is that a bicarbonate ion may be coördinated *trans* to a hydroxy group.

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[5] E. J. Corey and J. C. Bailar, Jr., THIS JOURNAL, **81**, 2620 (1959).

[6] Fred Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954).

[7] M. Martinette, B.V.M. and J. C. Bailar, Jr., *ibid.*, **74**, 1054 (1952).

It appears possible that the two carbonato complexes possess different configurations and that steric forces exerted by the stilbenediamine molecules around the cobalt atom open the carbonato chelate ring in "carbonato A." In many respects the two carbonato complexes resemble the two carbonato-bis-*levo*-propylenediamine-cobalt(III) complexes,[7] these differ in composition in that one is a dihydrate and the other is a monohydrate. It was observed that the monohydrate slowly changed to the dihydrate on standing in solution. The evidence indicated that this transformation was not a simple matter of hydration but rather, an isomerization of the *levo*-form of the complex, L-[Co *l*-pn_2CO_3]$^+$, to the *dextro* form, D-[Co *l*-pn_2CO_3]$^+$. No such conversion of one carbonato compound to the other was observed with the complexes derived from stilbenediamine, but it is possible that such a conversion does not occur as readily as with the propylenediamine complexes because the complex is insoluble.

Tartrato complexes of *active*- and *levo*-stilbenediamine were prepared by the reaction of silver tartrate with *trans*-dichloro-bis-stilbenediamine cobalt(III) chloride. All of the tartrato complexes prepared and dried at room temperature had the composition of the dihydrate. Drying at elevated temperatures *in vacuo* failed to remove all of the water. Attempts to obtain a resolution of *racemic*-tartaric acid by preferential coördination with the complex containing the active diamine were unsuccessful. In solution in boiling ethanol, the tartrato complexes reacted very slowly with barium chloride to precipitate barium tartrate; this suggests that the tartrato ligand was held by strong coordinate bonds. Unlike the other complexes of *active*- and *meso*-stilbenediamine, but like other tartrato complexes, these substances showed no tendency to crystallize. Concentration of their alcoholic solutions produced sirups which defied all efforts to induce crystallization. The complexes were isolated as amorphous precipitates by addition of water to the alcohol concentrates.

The behavior of the tartrato complexes suggests that the tartrate group may behave as a monodentate group with a water molecule in the position *trans* to it. In view of the already observed instability of the *cis* configuration, it appears that if the tartrate group is bidentate, the chelate ring is unstable, If such is the case, rearrangement and aquation of the complex with a molecule of water occupying the position *trans* to the tartrato group might be expected. If the tartrate behaves as a monodentate group, the degree of preferential coördination would be expected to be much less than that observed for the corresponding tartrato complexes containing *levo*-propylenediamine. Although the experimental evidence favors the supposition that the carbonato group in "carbonato B" behaves as a bidentate ligand, the situation is not necessarily the same with the tartrato group, which, because of its larger size, would be more susceptible to steric effects.

Experimental

Hydrobenzamide.—Hydrobenzamide was prepared by a modification of Laurent's[8] procedure. A mixture of freshly distilled benzaldehyde and liquid ammonia was allowed to stand with occasional stirring until all of the ammonia had evaporated. The crude product obtained in 99.5% yield was recrystallized from cyclohexane. The pure material melted at 101–102° cor.

Amarine.—The preparation of amarine (2,4,5-triphenyl-3-imidazoline) involves thermal isomerization of hydrobenzamide.[8,9] It was found during the present investigation that amarine is obtained in much better yields and in higher purity when hydrobenzamide is heated in an inert solvent. A mixture of hydrobenzamide (1422 g., 4.77 moles) and benzene (316 ml.) was refluxed for 5 hr. The temperature of the solution was never allowed to exceed 130°. More benzene was added when necessary to maintain that temperature. At the end of the heating period, 1184 ml. of benzene was added and the solution was cooled to room temperature. The pale yellow crystalline product was twice filtered and slurried with high boiling petroleum ether (1 l.). The crude amarine (1015 g., 71% of theory), was obtained as a white crystalline solid (m.p. 128–131° cor.). An additional quantity of amarine was obtained by evaporating the combined filtrates to a volume of 1.5 l., adding enough benzene (about 150 ml.) to make the solution homogeneous and allowing it to cool. This crop of crystals was purified as before. The total yield was 1161 g. (81.5% of theory).

Isoamarine.—The procedure used for the preparation of isoamarine (2,4,5-triphenyl-2-imidazoline) is a modification of the method of Lifschitz and Bos.[4] A stirred mixture of sodium hydroxide (250 g., 6.25 moles), water (150 ml.), amarine (1161 g., 3.9 moles) and diethylene glycol (790 ml.) was boiled in an open beaker until the temperature reached 155°. This temperature was maintained for 45 minutes, during which time the sodium salt of isoamarine precipitated and the solution became a thick slurry. After cooling, the slurry was treated with glacial acetic acid (570 g., 9.5 moles). When most of the product had dissolved, 95% ethanol (2.5 l.) was added and the solution was heated to boiling. After cooling, the solution was neutralized with excess concentrated aqueous ammonia. Isoamarine precipitated slowly as a mass of light tan crystals. This was filtered and washed with cold 95% ethanol; m.p., 198–201° cor., yield, 780 g. (66% of theory). The product was used without further purification.

racemic- **and** *meso*-**N-Benzoyl-N′-acetyl-stilbenediamine.**[4]—Preparation of the *racemic*-form involved acetylation of isoamarine and hydrolytic cleavage of the imidazoline nucleus. The *meso*-form was obtained by a similar procedure starting with amarine.

racemic-**Stilbenediamine.**—The low aqueous solubility of *racemic*- and *meso*-N-benzoyl-N′-acetylstilbenediamine renders their conversion to the free amine difficult. The ethanol-hydrochloric acid procedure[4] was improved by using a glacial acetic acid–hydrobromic acid mixture.

A mixture of *racemic*-N-benzoyl-N′-acetylstilbenediamine (690 g., 1.77 moles), glacial acetic acid (1 l.) and 42% hydrobromic acid (2 l.) was refluxed for 24 hr. The solution then was concentrated to a volume of 250 ml. and cooled to −10°. The precipitate was filtered, washed with cold ether and dissolved in 1 l. of water. When the solution was neutralized with 40% aqueous sodium hydroxide (500 g., 12.5 moles) and cooled to 15°, the amine precipitated. The temperature was never allowed to exceed 20° during neutralization. The mixture was extracted with three 200-ml. portions of ether and the combined extracts were dried over sodium hydroxide. After removal of 500 ml. of ether by distillation, high boiling petroleum ether (100 ml.) was added. On cooling, *racemic*-stilbenediamine separated as colorless needles (m.p. 80–82° cor.). The yield was 300 g. (77% of theory).

levo-**Stilbenediamine.**—Resolution of the *racemic*-base was accomplished by recrystallization of its *d*-tartrate.[4] For a 0.1% ether solution of the *levo*-stilbenediamine, $[\alpha]^{24}\text{D}$ −85°.

meso-Stilbenediamine was prepared by hydrolysis of *meso*-N-benzoyl-N′-acetylstilbenediamine.[10]

racemic-Tartaric acid was prepared according to the procedure of Campbell, Slotin and Johnston[11] and was resolved by Marckwald's[12] procedure.

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(8) M. A. Laurent, *Ann.*, **21**, 130 (1837).

(9) C. Bertagnini, *ibid.*, **88**, 127 (1853); G. Fownes, *ibid.*, **54**, 364 (1845).

(10) W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.*, 843 (1935).

(11) A. N. Campbell, Louis Slotin and S. A. Johnston, THIS JOURNAL, **55**, 2604 (1933).

(12) W. Marckwald, *Ber.*, **29**, 43 (1896).

***trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl.**—A solution of 10 g. of *rac*-stilbenediamine (0.047 mole) in 50 ml. of 95% ethanol was added with stirring to a solution of 6 g. of $CoCl_2 \cdot 6H_2O$ (0.025 mole) in 50 ml. of 95% ethanol. Hydrochloric acid (4 *N*, 4 ml.) was added and after cooling to 15°, 15% hydrogen peroxide (10 ml.) was added slowly with stirring. During the oxidation, the color of the solution changed from blue-green to emerald green and small crystals of the latter color formed slowly. After standing at room temperature for 6 hr., the mixture was acidified with hydrochloric acid (12 *N*, 5 ml.) and was concentrated to 1/3 of its original volume on the steam-bath. After cooling to −5°, the product was filtered, washed with water, then with 95% ethanol and finally with ether. During the ether wash, the crystals crumbled to a light green powder. After drying, the crude product weighed 9.1 g. (62% of theory based on stilbenediamine).

For purification, the crude material was dissolved in 100 ml. of 95% ethanol. Water (100 ml.) was added and the resulting solution was evaporated to 50 ml. During concentration, the color of the solution changed from its original dark green to deep red. On further concentration, the complex separated as light green crystals. The product was collected on a filter, washed with 50% ethanol and dried. The yield was 8 g. (54% of theory). *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl·H$_2$O: C, 55.32; H, 5.64; N, 9.22. Found: C, 55.40; H, 5.60; N, 9.07.

An identical procedure was used for preparation of [Co(*l*-stien)$_2$Cl$_2$]Cl.

***trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H$_2$O.**—The procedure employed was the same as for the chloride except that 1:1 nitric acid was added (instead of hydrochloric acid) to the reaction mixture before oxidation. *Anal.* Calcd. for *trans*-[Co(*active*- stien)$_2$,Cl$_2$]NO$_3$·0.25H$_2$O: C, 54.16; H, 5.28; N, 11.25. Found: C, 54.12; H, 5.45; N, 11.45.

***trans*-[Co(*active*-stien)$_2$Cl$_2$]Br·2H$_2$O.**—The procedure for the chloride was used except that a stoichiometric quantity of 42% hydrobromic acid was added to the reaction mixture before oxidation. *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$ Cl$_2$]Br·2H$_2$O: C, 50.16; H, 5.41; N, 8.36. Found: C, 49.99; H, 5.50; N, 8.20.

The solubility of the bromide in absolute ethanol was considerably less than that of the corresponding chloride and nitrate. The complex described here has been designated as having two chloride ions coördinated to the cobalt, but it is possible that the complex is the isomeric *trans*-[Co(*active*-stien)$_2$BrCl]Cl·2H$_2$O.

Attempted Preparation of *trans*-[Co(*active*-stien)$_2$Cl$_2$]BF$_4$ and *trans*-[Co(*active*-stien)$_2$Cl$_2$]CF$_3$CO$_2$.—Attempts were made to prepare the fluoroborate and trifluoroacetate of the *trans*-dichloro complex in the hope that these anions would give water-soluble salts; the synthetic work as well as the resolution studies would thus be facilitated. The procedure employed in the attempted preparations was identical with that described for the chloride of the complex except that stoichiometric quantities of the acids corresponding to the respective anions were substituted for hydrochloric. The expected salts were not obtained. The trifluoroacetate underwent decomposition when attempts were made to purify it by recrystallization. Analysis of the salt obtained from fluoroboric acid corresponded more closely to the theoretical values for a hydroxyfluoroborate. *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$Cl$_2$]BF$_2$(OH)$_2$·2H$_2$O: C, 49.94; H, 5.56; N, 8.32. Found: C, 49.99; H, 5.50; N, 8.20.

***trans*-[Co(*meso*-stien)$_2$Cl$_2$]Cl·1.75H$_2$O.**—The synthesis of this complex was identical to that employed for the compound containing the active-amine except that *meso*-stilbenediamine was used. Yields of the complex were always extremely low (about 1%). Upon recrystallization from absolute ethanol, partial decomposition occurred and a white precipitate of *meso*-stilbenediamine dihydrochloride formed. The *trans*-dichloro-*meso*-stilbenediamine complex has considerably less thermal stability than the complex containing the active-amine and is more soluble in polar organic solvents. *Anal.* Calcd. for *trans*-[Co(*meso*-stien)$_2$Cl$_2$]Cl·1.75 H$_2$O: C, 54.11; H, 5.64; N, 9.02. Found: C, 54.14; H, 5.50; N, 9.02.

[Co(*active*-stien)$_2$CO$_3$]$_2$CO$_3$·4H$_2$O.—*trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl·H$_2$O (0.5 g., 0.824 mmole) and 95% ethanol (50 ml.) were refluxed until all of the solid had dissolved, and a solution of anhydrous sodium carbonate (2 g., 0.021 mole) in 50 ml. of water was added. The color of the solution slowly changed from green to red and most of the product precipitated during 2 hr. of refluxing. The amorphous red precipitate was collected, washed several times with water and then with absolute ethanol. The yield was 0.4 g. (80% of theory). For purification, a mixture of 0.2 g. of the crude product and one liter of methanol was refluxed until most of the solid had dissolved. The hot solution was filtered and 800 ml. of methanol was removed by distillation. The product which precipitated was washed with methanol and dried *in vacuo* at 100° over phosphorus(V) oxide. *Anal.* Calcd. for [Co(*active*-stien)$_2$ CO$_3$]$_2$CO$_3$·4H$_2$O; C, 58.12; H, 5.95; N, 9.19. Found: C, 58.23; H. 5.91; N, 9.17.

This carbonato complex differs from the analogous ethylenediamine and propylenediamine complexes in being only slightly soluble in water whereas the latter are extremely soluble. A suspension of the complex in water reacts slowly with concentrated hydrochloric acid to form the *trans*-dichloro complex. Treatment of the solid with gaseous hydrogen chloride gave a mixture of the *cis*- and *trans*-dichloro complexes.

[Co(*active*-stien)$_2$CO$_3$]NO$_3$·H$_2$O and [Co(*active*-stien)$_2$ CO$_3$] NO$_3$·2H$_2$O.—A mixture of *rac*-stilbenediamine (5 g., 0.024 mole), [Co(NH$_3$)$_4$CO$_3$]NO$_2$·0.5H$_2$O, (3.1 g., 0.012 mole), 400 ml. of 95% ethanol and 65 ml. of water was refluxed for 6 hr. Ammonia escaped during the reaction and after 1 hr. of heating, most of the carbonatotetrammine complex had dissolved. The hot solution was filtered and concentrated on the steam-bath. When the volume of the solution had been reduced to about one-half, a lavender solid slowly separated. When the volume was 50 ml., the precipitate ("carbonato A") was filtered, washed several times with 5-ml. portions of hot absolute ethanol and dried *in vacuo* over phosphorus(V) oxide. The yield was 3.2 g. The filtrate was further concentrated to 15 ml., whereupon a microcrystalline pink solid ("carbonato B") precipitated. After cooling, the product was filtered, washed with ethanol and dried over P_2O_5. The yield was 2.8 g.

"Carbonato A" is extremely insoluble in water and in organic solvents. The sample submitted for elemental analysis was not purified because of the lack of a suitable recrystallizing solvent. Attempts to remove the water of hydration always resulted in decomposition of the complex. Attempts to dehydrate the sample involved heating in an oven at 80°, drying *in vacuo* over P_2O_5 at 100°, and Soxhlet extraction with absolute ethanol. "Carbonato A" reacted slowly with concentrated hydrochloric acid and with gaseous hydrogen chloride to give *trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl. Reaction with concentrated nitric acid caused complete decomposition of the complex.

"Carbonato B" is quite soluble in pyridine but only moderately soluble in absolute ethanol. Its solubility in 50% ethanol is considerably enhanced by the presence of a small quantity of sodium carbonate. As in the case of "carbonato A," attempts to dehydrate "carbonato B" resulted in extensive decomposition of the complex. Unlike "carbonato A," it reacted with *dextro*-tartaric acid to yield [Co(*active*-stien)$_2$*d*-tart.]NO$_3$·2H$_2$O. In absolute ethanol saturated with anhydrous hydrogen chloride, it reacted slowly to give a violet solution which changed to green within a few minutes. Reaction of the solid material with gaseous hydrogen chloride gave a purple solid believed to be the *cis*-dichloro complex.

Anal. Calcd. for [Co(*active*-stien)$_2$CO$_3$]NO$_3$·2H$_2$O ("carbonato A"): C, 54.29; H, 5.66; N, 10.92. Found: C, 54.50; H, 5.68; N, 11.23.

Anal. Calcd. for [Co(*active*-stien)$_2$CO$_3$]NO$_3$·H$_2$O ("carbonato B"): C, 55.86; H, 5.50; N, 11.23. Found: C, 55.96; H, 5.26; N, 11.21.

The procedure described above, using *levo*-stilbenediamine instead of the *racemic*-mixture, gave only the carbonato nitrate 2-hydrate with chemical and physical characteristics similar to those of "carbonato A." Its extreme insolubility in all solvents made measurement of its optical rotation impossible.

[Co(*meso*-stien)$_2$CO$_3$]NO$_3$.—The procedure described for the preparation of "carbonato A" and "carbonato B," but employing *meso*-stilbenediamine, gave two products which corresponded in solubility and in color to the compounds obtained before but differing greatly in stability. Attempts to obtain good samples for analysis were frustrated by difficulties associated with their lack of stability and the extreme insolubility of the one isomer. Attempts to obtain the carbonato complex by reaction of the *trans*-dichloro nitrate with aqueous sodium carbonate were unsuccessful, as extensive decomposition took place.

***cis*-[Co(*active*-stien)$_2$Cl$_2$]Cl·H$_2$O.**—Several procedures were employed in attempts to isomerize *trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl to the *cis*-dichloro complex. None of these procedures effected the desired isomerization, but what appears to be the *cis*-dichloro complex was obtained when "carbonato B" was treated with anhydrous hydrogen chloride. A saturated solution of hydrogen chloride in absolute ether (100 ml.) was added to [Co(*active*-stien)$_2$CO$_3$]NO$_3$·H$_2$O (0.5 g.). The complex reacted immediately as indicated by the change of the suspended solid from red to lavender. After standing at room temperature for 4 hr., the solid was collected, washed with absolute ether and dried *in vacuo* at 100° over P$_2$O$_5$. After drying, the solid was dark purple. *Anal.* Calcd. for *cis*-[Co(*active*-stien)$_2$Cl$_2$]Cl·H$_2$O: C, 55.32; H, 5.64; N, 9.22; Cl, 17.50. Found: C, 55.33; H, 5.66; N, 9.43; Cl, 17.26.

The *cis*-dichloro complex appeared to be stable in air but isomerized to the *trans*-dichloro complex within 1 hr. when heated at 90° or when dissolved in absolute ethanol. The *cis*-isomer is insoluble in water.

An attempt was made to establish the *cis*-configuration of the complex by comparing its X-ray diffraction pattern with that of *trans*-[Co(*active*-stien)$_2$Cl$_2$]Cl·H$_2$O. However, the *cis*-dichloro complex prepared by the above procedure failed to give a diffraction pattern. Attempts to crystallize it from organic solvents were unsuccessful because polar organic solvents which dissolved it also caused isomerization to the *trans*-isomer.

Alternate evidence for the *cis*-structure was sought by converting the compound to [Co(*active*-stien)$_2$(NH$_3$)$_2$]Cl$_3$. It is possible that rearrangement might take place during the reaction, but rearrangement from a *trans*-form to a *cis*-form is improbable. Demonstration of the *cis*-configuration for the diammine complex would therefore furnish evidence that the dichloro compound is also *cis*. When the supposed *cis*-dichloro compound was dissolved in liquid ammonia, the solution gradually assumed a pink color, which indicated that only one of the chloride ions had been displaced by ammonia. When the ammonia was allowed to evaporate and absolute ethanol was added to the pink residue, a yellow solid possessing the characteristic color of the cobalt (III) hexammines formed immediately. The complex gave no X-ray diffraction pattern.

[Co(*active*-stien)$_3$]Cl$_3$·2H$_2$O.—The procedure of Lifschitz and Bos[4] was used except that hydrogen peroxide was used for the oxidation instead of air, since it gives consistently better yields.

A solution of 10 g. of *rac*-stilbenediamine (0.0472 mole) in 50 ml. of 95% ethanol was added with stirring to a solution of cobalt(II) chloride 6-hydrate (2.86 g., 0.012 mole) in 25 ml. of 95% ethanol. Hydrochloric acid (6 *N*, 2 ml.) was then added and after cooling to 15°, 10 ml. of 15% hydrogen peroxide was added slowly with stirring. Yellow crystals of the tris-stilbenediamine complex precipitated during the addition. The mixture was allowed to stand at room temperature for 6 hr. Hydrochloric acid (12 *N*, 5 ml.) was then added and the mixture was heated on a steam-bath for 1 hr. After cooling to room temperature, the yellow-orange crystals were collected, washed with water, then with ethanol and finally with ether. After drying, the crude product weighed 8.3 g. (81% based on cobalt (II) chloride). *Anal.* Calcd. for [Co(*active*-stien)$_3$]Cl$_3$·2H$_2$O: C, 60.18; H, 6.25; N, 10.03. Found: C, 60.17; H, 6.44; N, 10.07.

The tris-*active*-stilbenediamine salts are considerably less soluble in polar organic solvents than the *trans*-dichloro salts. Unlike the analogous propylenediamine and ethylenediamine complexes, the stilbenediamine complex is only slightly soluble in water.

Attempted Preparation of [Co(*meso*-stien)$_3$]Cl$_3$.—Unsuccessful attempts were made to prepare the tris-*meso*-stilbenediamine complex by the method used for the preparation of the active-amine complex. Two products were always isolated from the reaction mixture. One product was a green crystalline material which was evidently the *trans*-dichloro complex. *Anal.* Calcd. for [Co(*meso*-stien)$_2$Cl$_2$]Cl: C, 57.00; H, 5.47; N, 9.50. Found: C, 57.10; H, 5.51; N, 8.79. Analysis of the second product showed that it contained three chlorine atoms, and a molecule of water, but its buff color indicated that it was not a hydrate of the dichloro chloride. It was, perhaps, one of the isomeric forms of the aquo-chloro chloride. *Anal.* Calcd. for [Co(*meso*-stien)$_2$H$_2$O Cl]Cl$_2$: C, 55.32; H, 5.64. Found: C, 55.33; H, 5.99.

[Co(*levo*-stien)$_2$*d*-tart]NO$_3$·O·5H$_2$O.—A mixture of *trans*-[Co(*levo*-stien)$_2$Cl$_2$]NO$_3$ (2 g., 0.0032 mole) and *d*-tartaric acid (0.525 g., 0.0035 mole) was dissolved in 300 ml. of boiling absolute ethanol. A solution of silver nitrate (1.19 g., 0.007 mole) in 300 ml. of hot absolute ethanol then was added. As heating was continued, silver chloride precipitated and the color of the solution changed from green to ruby red. After heating for 3 hr., the solution was allowed to cool, filtered repeatedly to remove all of the silver chloride and concentrated to a volume of 5 ml. Distilled water (50 ml.) then was added slowly with stirring. The pink precipitate which formed was filtered, washed with water and reprecipitated by dissolving in 5 ml. of 95% ethanol and diluting with 50 ml. of water.

The tartrato complexes, [Co(*levo*-stien)$_2$*levo*-tart.]NO$_3$, [Co(*levo*-stien)$_2$*active*-tart.]NO$_3$, [Co(*active*-stien)$_2$*d*-tart.]NO$_3$ and [Co(*active*-stien)$_2$*active*-tart.]NO$_3$ were prepared by the above procedure. All of them contained one or more molecules of water per molecule of complex. Removal of all of the water of hydration would indicate with a resonable degree of certainty that the tartrato group was behaving as a bidentate ligand. However, attempts to dehydrate by heating in an oven at 90° for one week and by evaporation of absolute ethanol solutions of the complexes were unsuccessful. Drying in an oven at 110° caused complete decomposition. The following are analytical data obtained on samples dried *in vacuo* over P$_2$O$_5$ at 100° for four days:

Anal. Calcd. for [Co(*levo*-stien)$_2$-*d*-tart.]NO$_3$·0.5H$_2$O: C, 54.70; H, 5.31; N, 9.97. Found: C, 54.67; H, 5.55; N, 9.85. Found for [Co(*levo*-stien)$_2$*levo*-tart.]NO$_3$·0.5H$_2$O: C, 54.67; H, 5.59; N, 9.99. Found for [Co(*levo*-stien)$_2$*active*-tart.]NO$_3$·0.5H$_2$O: C, 54.58: H, 5.45; N, 9.87.

[Co(*active*-stien)$_2$-*d*-tart]$_2$*d*-tart.·4H$_2$O was prepared by treating the *trans*-dichloro chloride with excess silver *d*-tartrate. Attempts to obtain the anhydrous complex were unsuccessful. *Anal.* Calcd. for [Co(*active*-stien)$_2$-*d*-tart.]$_2$*d*-tart.·4H$_2$O: C, 55.06; H, 5.44; N, 9.44. Found: C, 55.15; H, 5.53; N, 9.42.

[Co(stien)$_2$tart]$^+$ salts are extremely soluble in polar organic solvents (glacial acetic acid, acetone, nitrobenzene, ethylene glycol, etc.) and insoluble in non-polar solvents. Attempts to find suitable recrystallizing solvents were unsuccessful, so fractional precipitation from ethanol was employed in attempts to isolate isomeric forms of the complexes. Optical rotation measurements of the fractions indicated, however, that no separation had been accomplished. That the tartrato groups were firmly coördinated was indicated by the fact that barium chloride dissolved in alcohol solutions of the complexes precipitates barium tartrate very slowly, even upon boiling. Concentrated solutions of the complexes reacted with excess *rac*-stilbene-diamine to yield [Co(*active*-stien)$_3$]$^{+++}$ salts. In more dilute solutions, however, the reaction took place much less readily and appeared to be reversible.

***trans*-[Co(*active*-stien)$_2$(NO$_2$)$_2$]NO$_2$·1.5H$_2$O.**—A mixture of *trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H$_2$O (0.7 g., 0.0011 mole), sodium nitrite (0.197 g., 0.0023 mole) and absolute ethanol (50 ml.) was heated on a steam-bath for 1 hr. The solution then was cooled in an ice-bath, filtered to remove sodium chloride and concentrated on the steam-bath to 10 ml. The solution was filtered hot and cooled with ice. After washing the yellow needles with water and then with 50% ethanol, the product was dried *in vacuo* over P$_2$O$_5$. The yield was 6.2 g. (84% of theory based on starting *trans*-dichloro nitrate). Purification was effected by recrystallization from absolute ethanol. *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$(NO$_2$)$_2$]NO$_2$·1.5H$_2$O: C, 51.85; H, 5.44; N, 15.12. Found: C, 51.76; H, 5.40; N, 15.17. The dinitro complex is soluble in polar organic solvents but insoluble in water. It reacts readily with concentrated hydrochloric acid to yield the *trans*-dichloro chloride.

***trans*-[Co(*active*-stien)$_2$(CNS)$_2$]CNS·1.5H$_2$O.**—A mixture of *trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H$_2$O (1 g., 0.00162 mole), sodium thiocyanate (0.5 g., 0.00618 mole) and 95% ethanol (100 ml.) was refluxed for 1 hr. While heating, sodium chloride precipitated and the color of the solution changed from dark green to deep red. The dark red crystals which formed when the solution was cooled to 0° were isolated and washed with 5 ml. of cold absolute ethanol and then with water. The product was dried *in vacuo* over calcium chloride for 24 hr. The yield was 0.9 g. (81% of theory). Purification was accomplished by recrystallization from absolute ethanol. *Anal.* Calcd. for *trans*-[Co(*active*-stien)$_2$(CNS)$_2$]CNS·1.5H_2O: C, 54.37; H, 5.15; N, 14.32. Found: C, 54.66; H, 5.41; N, 14.49.

***trans*-[Co(*active*-stien)$_2$(SO$_3$)$_2$]Na·C_2H_5OH.**—*trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H_2O (1 g., 0.00162 mole) was dissolved in 50 ml. of boiling 95% ethanol. A hot solution of 0.8 g. of sodium sulfite (0.00635 mole) in 50 ml. of water was added and the mixture was refluxed for 30 minutes. The yellow, crystalline sulfite complex was washed with water, then with 95% ethanol and dried at 100° *in vacuo* over P_2O_5. *Anal.* Calcd. for [Co(*active*-stien)$_2$(SO$_3$)$_2$]Na·C_2H_5OH: C, 50.55; H, 5.37; N, 7.86. Found: C, 50.61; H, 5.25; N, 7.74.

[Co(*active*-stien)$_2$C$_2$O$_4$]NO$_3$·1.5H_2O.—A mixture of *trans*-[Co(*active*-stien)$_2$Cl$_2$]NO$_3$·0.25H_2O (0.7 g., 0.00114 mole), sodium oxalate (0.7 g., 0.00217 mole), water (30 ml.) and 95% ethanol (50 ml.) was refluxed for 30 minutes. During the heating, the color of the solution changed from dark green to red, and a pink precipitate formed. The hot solution was filtered and concentrated to 15 ml. on the steam-bath. After cooling to 10°, the red crystals were filtered and washed with water and then with cold absolute ethanol. After drying over calcium chloride, the product weighed 0.65 g. (86.6% of theory). The crude material was purified by two recrystallizations from 50% ethanol. *Anal.* Calcd. for [Co(*active*-stien)$_2$C$_2$O$_4$]NO$_3$·1.5H_2O: C, 54.54; H, 5.34; N, 10.60. Found: C, 54.28; H, 5.14; N, 10.50.

Attempted Resolution of *racemic*-Propylenediamine.—A solution of *trans*-[Co(*levo*-stien)$_2$Cl$_2$]Cl·H_2O (2 g., 0.0033 mole) in 100 ml. of absolute ethanol was cooled to −60° in a Dry Ice–acetone bath, and 85% *racemic*-propylenediamine (0.6 g., 0.007 mole) was added. The color of the solution changed slowly from green to red and a yellow precipitate formed. After an hour, the precipitate was filtered and an excess of 12 *N* hydrochloric acid was added to the filtrate. The amine hydrochloride which precipitated was washed with several portions of absolute ethanol. After two recrystallizations from 50% ethanol the hydrochloride showed the specific rotation $[\alpha]^{17}\mathrm{D}$ −15°. This was approximately equal to the rotation ($[\alpha]^{17}\mathrm{D}$ −18.7°) for *levo*-stilbenediamine dihydrochloride, suggesting that propylenediamine had displaced the coördinated *levo*-stilbenediamine. This was confirmed by the melting point of the amine.

Attempted Resolution of *racemic*-Tartaric Acid. Experiment I.—A mixture of *trans*-[Co(*levo*-stien)$_2$Cl$_2$]NO$_3$·1.25H_2O (1.232 g., 0.002 mole) and *racemic*-tartaric acid (0.6 g., 0.004 mole) was dissolved in 300 ml. of absolute ethanol. A solution of silver nitrate (1.36 g., 0.008 mole) in absolute ethanol (100 ml.) then was added and refluxing was continued for 6 hr. The filtered solution was concentrated to 10 ml., diluted with 20 ml. of water and the precipitated tartrato complex was filtered. Barium chloride 2-hydrate (0.9 g., 0.004 mole) dissolved in water (10 ml.) was added to the filtrate and, after making it slightly alkaline with dilute aqueous ammonia, the precipitated barium tartrate was isolated. The dried sample was decomposed with dilute sulfuric acid and the precipitated barium sulfate was removed. The solution showed no rotation; resolution had not been effected.

Experiment II.—Hamilton[13] effected partial resolution of *racemic*-tartaric acid by reaction of the acid with [Co(*levo*-pn)$_2$ *active*-tart]Cl$_2$. The attempted resolution of *racemic*-tartaric acid using a similar procedure but employing [Co(*levo*-stien)$_2$ *active*-tart]NO$_3$ as the resolving agent was not successful.

A solution of [Co(*levo*-stien)$_2$*active*-tart]NO$_3$·2H_2O (0.3926 g., 0.000539 mole) in absolute ethanol (200 ml.) showed a rotation of −0.55°. This solution was diluted to 500 ml. and 0.134 g. of *racemic*-tartaric acid was added. The rotation of this solution was −0.24°. When the solution was refluxed for three days without change in rotation, the alcohol was removed by distillation and the residue was heated in an oven at 90° for two days. The residue, again dissolved in absolute ethanol, showed a rotation of −0.28°. The solution was then concentrated to 10 ml. and the precipitated tartaric acid was removed by filtration. An aqueous solution of this acid showed no rotation.

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[13] N. H. Hamilton, Thesis, University of Illinois, 1947.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCES, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Solvent Shifts of Absorption Bands of 8-Quinolinol and its Zinc Chelate[1]

BY OREST POPOVYCH[2] AND L. B. ROGERS

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Positions of the long wave length absorption maxima of 8-quinolinol and its zinc chelate were investigated as a function of solvent. Both ligand and chelate exhibited similar shifts and obeyed an equation, derived by McRae, which incorporates the polarizability and dipolar character of the solvent. The chelate reacted to some extent with dimethylformamide and was decomposed completely by N-methylformamide.

Introduction

During a study of the effects of structural changes on absorption and fluorescence spectra of 8-quinolinol (oxine) and its chelates, solubility problems often necessitated the use of different solvents. As a result, spectral shifts had to be corrected for changes in solvent before they could be assigned to structural changes.

Previous knowledge of solvent effects on the spectra of oxine was limited to the qualitative observation that oxine bands experienced a red shift in the series ethanol, chloroform and iso-octane.[3] Bands for oxine chelates occurred at lower frequencies in chloroform than in ethanol.

The present study shows that, in most cases, the shifts for oxine and its zinc chelate obey an equation proposed by McRae.[4]

Results

Oxine.—Ultraviolet absorption spectra of (neutral) oxine were recorded in the range between 400 mμ and the ultraviolet cut-off of the solvent in question. The study was extended over 13 solvents ranging in refractive indices from 1.329 (methanol) to 1.457 (carbon tetrachloride). In both the earlier[3] and the present study, the reported positions of the maxima and their shifts refer to the low-frequency band of oxine, because the high-frequency peak (∼250 mμ) was inaccessible in many of the solvents. In the case of oxine, the low-frequency band was found to be a composite of two pi-pi bands and the n-pi band; in the chelate,

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[1] From a thesis submitted by Orest Popovych in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, February, 1959.

[2] Allied Chemical and Dye Fellow, 1957–1958.

[3] W. E. Ohnesorge and L. B. Rogers, *Spectrochim. Acta.*, **14**, 27 (1959).

[4] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).