

Fig. 1.

salts can be studied in the polarimeter. Nevertheless, a 0.01% solution of the levorotatory (less soluble) salt in 20% aqueous methanol shows the relatively enormous specific rotation (for the mercury green line 5461 Å.) of $-7,000^\circ$. From an aqueous methanolic solution of this salt the levorotatory iodide, l -[CoS]I, is precipitated by potassium iodide, its specific rotation after five recrystallizations being $-8,800^\circ$ (0.01% solution in 20% aqueous methanol), corresponding to a molecular rotation of $-50,160^\circ$.

It will be recalled that the highest molecular rotations previously observed ($-47,610^\circ$) were those observed by Werner⁴ for tri-[tetramminodiolcobaltic] cobaltic salts, whose optically active forms rapidly racemize. Solutions of l -IV in 20% aqueous methanol can be boiled (85°) for twenty minutes without appreciable racemization, but boiling aqueous solutions are racemized fairly rapidly.

The optically, somewhat impure, d -IV can be obtained from the more soluble α -bromocamphor- π -sulfonate fraction and, after nine recrystallizations, obtained pure with a molecular rotation of $+50,160^\circ$.

Condensation of the base II with 2-naphthol-1-aldehyde (2 moles) leads to ready formation of the Schiff base 1,8-bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane (VI), a substance relatively insoluble in alcohol. However, it dissolves readily in hot alcohol containing cobaltous acetate to a red-brown solution, passage of air through which leads to formation of the dark green complex cobaltic acetate in solution, from which dl -1,8-bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane cobaltic bromide can be readily precipitated as a crystalline dihydrate by potassium bromide. By conversion to the d - α -bromocamphor- π -sulfonates, followed by fractionation from a methanol-acetone mixture and

(4) A. Werner, *Ber.*, **47**, 3087 (1914).

then reconversion to the bromides, complete resolution of the complex into its optical antipodes can be effected. These show even greater molecular rotations than those of the optically active forms of IV, the observed molecular rotations (mercury green line 5461 Å.) being $-73,370^\circ$ and $+73,040^\circ$.

By constructing models it is easy to see that a molecule such as that of III can lose two protons and then wrap itself round a central cobalt ion practically strainlessly in such a way that the oxygen atoms and the sulfur atoms are in *cis*-positions to each other around an equatorial plane whilst the nitrogen atoms occupy *trans* positions to each other, and, at the same time, each of the two oxygen-nitrogen-sulfur atom sequences (commencing from the respective ends of the sexadentate moiety) lies in a plane (Fig. 2). Two enantiomorphous arrangements

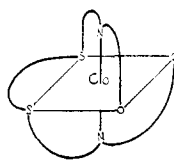


Fig. 2.

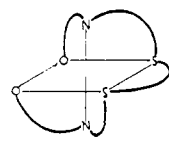


Fig. 3.

embodying these conditions are possible. Each of them is characterized by its possession of a dyad axis of symmetry. In such arrangements the sulfur atoms have their three covalences pyramidally disposed,⁵ whilst the three atoms attached to each nitrogen atom are coplanar, and each salicylidene-amine-metal ring is planar with the oxygen-metal-nitrogen sequence in the same plane as that of the benzene ring.

It is possible to write formulas, such as that in Fig. 3, but in these the three atoms covalently bound to each nitrogen atom would not be coplanar, and it is inconceivable that such configurations would be preferred to that shown in Fig. 2. At all events, the experimental evidence seems to show that the [CoS]· ion exists only in one or other of two enantiomorphous configurations, and the general nature of the complexes points very strongly to the fact that III and VI do very definitely function as sexadentate chelate compounds.

The results of further studies involving the use of sexadentate chelate compounds built up from (a) *o*-hydroxybenzaldehydes other than salicylaldehyde or 2-naphthol-1-aldehyde and (b) diamines similar to II but in which one or more of the ethylene bridges between the sulfur and nitrogen atoms have been replaced by trimethylene bridges will be reported shortly. It can, however, be stated here that compounds more suitable for studies of rotatory dispersion than the strongly light-absorbent compounds described in this paper have already been prepared and resolved.

(5) Cf. *e. g.*, Mann, *J. Chem. Soc.*, 1745 (1930).

Finally, it should be pointed out that the tris-salicylidene derivative of the 2-aminomethyl-1,3-diaminopropane described by Geissmann, Schlatter and Webb⁶ should be capable of functioning as a sexadentate chelate compound, and that if it does so function, then, for example, its non-electrolyte cobaltic derivative should exist in enantiomorphous forms in which there is either a right- or left-handed partially spiral arrangement of the salicylideneamino groups (Fig. 4). Evi-

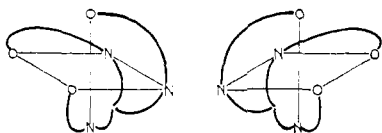


Fig. 4.

dence of such enantiomorphism would be a subtle proof of the relatively fixed octahedral disposition of coordination valences about a six-covalent metallic atom. We hope to complete the preparation and examination of such substances shortly.

Experimental

1,8-Diphthalimido-3,6-dithiaoctane (I).—Ethylene 1,2-dithiol (47 g.) was added to a solution of sodium ethoxide (from sodium (23 g.) and absolute ethanol (350 ml.)). Then, without delay, a solution of N-2-bromoethylphthalimide (254 g.) in hot absolute ethanol (500 ml.) was gradually added. The condensation product separated in a cream colored mass almost immediately, but the mixture was refluxed for two hours to complete the reaction. After removal of some of the alcohol the separated solid was filtered off and washed with water and alcohol. It could be readily recrystallized from boiling acetone or glacial acetic acid, being thus obtained in shining colorless prisms, m. p. 154°.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: N, 6.4. Found: N, 6.3.

1,8-Diamino-3,6-dithiaoctane (II).—The diphthalimido compound I (110 g.) was suspended in boiling ethanol (400 ml.), 50% hydrazine hydrate solution (50 g., excess) added and the boiling continued under reflux for two hours. The solid soon went into solution and the intermediate compound commenced to separate. Concentrated hydrochloric acid (100 ml.) was then added and the refluxing continued for forty minutes, after which most of the alcohol was distilled off, water (300 ml.) added and the precipitated phthalhydrazide filtered off. The filtrate was concentrated to half-bulk, cooled and made strongly alkaline with solid sodium hydroxide, the product eventually separating as a thick oil which was repeatedly extracted with ether (4-5 liters in all). The combined ethereal extracts were rapidly dried over solid potassium hydroxide and the solvent removed. The residual very pale yellow oil solidified to a colorless deliquescent solid on cooling, m. p. 41-43°; yield 39 g. (87%). Because of its deliquescent nature and its rapid absorption of carbon dioxide from the air this base was not analyzed as such but in the form of derivatives.

The dihydrochloride formed colorless needles. *Anal.* Calcd. for $C_8H_{18}Cl_2N_2S_2$: N, 11.1. Found: N, 10.8.

The diacetyl derivative formed colorless flat prisms m. p. 138°. *Anal.* Calcd. for $C_{16}H_{20}N_2O_2S_2$: N, 10.6. Found: N, 10.7.

The dipicrate formed long flat yellow needles m. p. 172-173° (dec.). *Anal.* Calcd. for $C_{18}H_{22}N_2O_{14}S_2$: N, 17.6. Found: N, 17.4.

(6) Geissmann, Schlatter and Webb, *J. Org. Chem.*, **11**, 736-740 (1946).

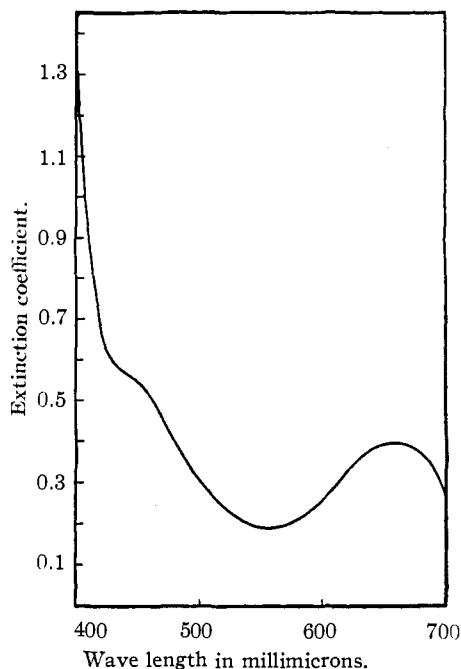


Fig. 5.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane (III).—A solution of the base II (18 g.) in hot ethanol (100 ml.) was added to a solution of freshly redistilled salicylaldehyde (24.4 g., 2 mols.) in hot ethanol (100 ml.) and the solution allowed to boil for a few minutes. The Schiff base separated almost at once. After cooling, the solid was collected and washed with a little alcohol. Further small amounts could be obtained by concentrating the filtrate, the yield being practically quantitative. For analysis it was recrystallized from hot alcohol and thus obtained in lemon-yellow shining leaflets m. p. 108°. It could also be made conveniently by treatment of a hot aqueous alcoholic solution of the hydrochloride of II with the calculated quantity of sodium acetate and then a hot alcoholic solution of salicylaldehyde.

Anal. Calcd. for $C_{20}H_{24}N_2O_2S_2$: C, 61.9; H, 6.2; N, 7.5. Found: C, 61.7; H, 6.3; N, 7.7.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Zinc.—Zinc acetate (1.2 g.) and the Schiff base III (1.9 g.) were added to hot methanol (80 ml.) and the solution refluxed for twenty minutes. After cooling and addition of water a yellow precipitate of microcrystalline platelets m. p. 224° was formed. The substance was soluble in pyridine, sparingly soluble in chloroform, very slightly soluble in acetone or alcohol and insoluble in benzene or petroleum ether. Also, after precipitation from methanol it appeared to be insoluble in that solvent.

Anal. Calcd. for $Zn(C_{20}H_{22}N_2O_2S_2)$: Zn, 14.5; C, 53.1; H, 4.9; N, 6.2. Found: Zn, 14.5; C, 52.7; H, 5.0; N, 6.2.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Iron (II).—Solutions of ferrous chloride hexahydrate (1.2 g.) and anhydrous sodium acetate (0.5 g.) in hot methanol (30 ml.) were mixed and then a methanol solution of III (2 g.) added. The red ferrous complex formed immediately and precipitated. It was practically insoluble in alcohol but readily soluble in chloroform to a red solution, or less readily in hot benzene. For analysis it was recrystallized from hot benzene and obtained in red scales m. p. 230-233° with previous sintering at 150°.

Anal. Calcd. for $Fe(C_{20}H_{22}N_2O_2S_2)$: Fe, 12.6; C, 54.2; H, 5.0; N, 6.3. Found: Fe, 12.5; C, 54.1; H, 5.0; N, 6.3.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Nickel.—The base III (3.9 g.) was added to a boiling solution of nickel acetate hexahydrate (2.85 g.) in boiling methanol (100 ml.). The yellow crystals soon went into solution and a yellowish-green precipitate formed. This was increased by dilution with water. The precipitate was collected and dried and then dissolved in hot chloroform. Addition of petroleum ether to this solution caused the complex to separate in pale green crystals m. p. 266°, which were quite soluble in hot alcohol or acetone, but only moderately so in hot benzene.

Anal. Calcd. for $\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)$: Ni, 13.1; C, 53.9; H, 5.0; N, 6.3. Found: Ni, 12.9; C, 52.0; H, 4.9; N, 5.9.

In this reaction a small amount of a second product was also isolated which appeared to be an acetate of the above complex. It was readily soluble in alcohol but insoluble in benzene. However, as it was not obtained pure it was not further investigated.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Copper.—Admixture of hot methanolic solutions of equimolecular amounts of III and copper acetate led to formation of a greenish-yellow precipitate which dissolved easily in benzene or chloroform, and when recrystallized from a mixture of benzene and petroleum ether melted at 190°.

Anal. Calcd. for $\text{Cu}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)$: Cu, 14.2; C, 53.4; H, 4.9; N, 6.2. Found: Cu, 14.1; C, 53.4; H, 5.0; N, 6.2.

1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobalt (II) Trihydrate.—Solid III (1.5 g.) was added to a boiling solution of cobaltous acetate hexahydrate (1.1 g.) in methanol (20 ml.) in a carbon dioxide atmosphere under reflux, and the boiling continued for ten minutes. The orange-brown solution was then rapidly filtered out of contact with air from a yellowish-brown precipitate of indefinite composition. The filtrate was then allowed to cool in a carbon dioxide atmosphere, when the cobaltous complex separated in orange-red needles m. p. 168°, which rapidly became brown and finally black on keeping.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)$: Co, 11.8; C, 48.0; H, 5.6; N, 5.6. Found: Co, 11.7; C, 48.1; H, 5.4; N, 5.8.

The black substance formed on keeping this cobaltous complex does not regain its color on heating. Analysis indicates that extensive decomposition has occurred. The black material is partially soluble in water giving a solution alkaline to litmus—suggesting that the oxide or hydroxide of the cobaltic complex has been formed. In acids it dissolves partially giving the green solution characteristic of the complex cobaltic ion, but some black tar remains undissolved.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Iodide (IV).**—A solution of cobaltous acetate hexahydrate (2.88 g.) in hot methanol (40 ml.) was added to a solution of III (3.97 g.) in hot methanol (150 ml.) and the solution was refluxed. The color changed to orange, then darkened to brown. Air was drawn through the solution for thirty minutes after which an equal volume of water was added and the air aspiration continued for a further two and one-half hours. The solution was then freed from a small amount of dark brown decomposition product by filtration, and then to this green solution of the acetate at 80° a solution of potassium iodide (15 g.) in water (50 ml.) was gradually added. On cooling and scratching very dark brown crystals separated. They were collected and recrystallized from hot water to which a little potassium iodide was added. The crystalline precipitate varied a little in color—from black needles to dark brown plates or needles—according to the particle size, and melted at 264° (dec.).⁷ It was sparingly soluble in cold water to a bright green solution and moderately soluble in boiling water to a very dark brownish-green solution. On heating, dilute aqueous solutions become brownish-

green in color, but the original green is restored on cooling. The substance is apparently stable in acid solution but alkalis decompose it, especially on warming, with formation of an orange-brown substance of unknown constitution.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)\text{I}$: Co, 10.3; C, 42.0; H, 3.8; N, 4.9; I, 22.2. Found: Co, 10.3; C, 41.4; H, 3.8; N, 4.9; I, 22.2.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Perchlorate.**—A solution of *dl*-1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobaltic acetate was prepared as described above and then 2% sodium perchlorate solution was gradually added, a very dark brown microcrystalline precipitate being formed. It was very sparingly soluble in all solvents and could not be recrystallized. It exploded violently when heated, so that carbon-hydrogen analyses could not be made.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)\text{ClO}_4$: Co, 10.8; N, 5.1. Found: Co, 10.7; N, 5.1.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Nitrate Monohydrate.**—A solution of the salt IV in hot water was treated with the theoretical amount of silver nitrate solution. The precipitated silver iodide was filtered off and the deep green solution concentrated on the water-bath. A small amount of a dark brown precipitate formed but was removed by filtration. Finally, violet-black prisms very soluble in water, alcohol or acetone were obtained.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)\text{NO}_3 \cdot \text{H}_2\text{O}$: Co, 11.2; C, 45.7; H, 4.6; N, 8.0. Found: Co, 11.1; C, 45.9; H, 4.5; N, 8.1.

The equivalent conductivities of 0.001 and 0.0001 *M* solutions of this salt at 25° were 101 mhos and 122 mhos, respectively, indicating the salt to be a binary electrolyte.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Chloride Monohydrate (V).**—A solution of the salt IV in hot water was shaken for some time with a large excess of freshly precipitated pure silver chloride. After filtration the solution was evaporated to small bulk and again filtered free from traces of silver salts. On evaporation to dryness a green gum was obtained. This was taken up in methanol and precipitated by the addition of ether several times, black glistening needles of the monohydrated salt being obtained. On heating, the substance apparently lost its water of hydration and then melted at 210° (dec.).

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)\text{Cl} \cdot \text{H}_2\text{O}$: Co, 11.7; C, 48.1; H, 4.8; N, 5.6; Cl, 7.2. Found: Co, 11.7; C, 47.6; H, 4.8; N, 5.6; Cl, 7.1.

The values for the molecular weight (cryoscopically) in water solutions of 0.0154, 0.037 and 0.0513 *M* were, respectively, 251, 269 and 287; calcd. 498.9. The light transmittance curve for V was determined with a General Electric Recording Spectrophotometer and is shown in Fig. 1.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane-cobaltic *d*- α -Bromocamphor- π -sulfonate Monohydrate.**—A solution of silver *d*- α -bromocamphor- π -sulfonate (4.75 g.) in hot water (50 ml.) was added to a solution of the salt IV (6.5 g.) in hot water (500 ml.). The solution was then evaporated on the water-bath until the volume had diminished to 250 ml., when it was filtered free of silver iodide and then evaporated to dryness. The residual dark green gum was taken up in hot methanol and, after filtration and some concentration of the solution, was induced to deposit greenish-brown micro crystals melting at 233°. These were soluble in water, alcohol or acetone, forming brown solutions in the latter solvents.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)(\text{C}_{10}\text{H}_{14}\text{BrO}_2\text{S})\text{H}_2\text{O}$: Co, 7.5; C, 46.6; H, 4.7; N, 3.6. Found: Co, 7.6; C, 46.4; H, 4.9; N, 3.6.

***l*,1,8-Bis-(salicylideneamino)-3,6-dithiaoctane-cobaltic *d*- α -Bromocamphor- π -sulfonate Monohydrate.**—The above described mixture of *d*- and *l*-1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobaltic *d*- α -bromocamphor- π -sulfonates (10 g.) was dissolved in methanol (150 ml.) and fractionally precipitated with dry ether. The brown tar

(7) This melting point was previously reported (THIS JOURNAL, 69, 2917 (1947)) as 245° (dec.) owing to the unsuspected substitution of a faulty thermometer in the melting-point apparatus.

precipitated as the first fraction gradually crystallized on standing and washing with dry ether. By careful checking of very dilute solutions in the polarimeter it soon became apparent that the least soluble fractions were levorotatory (for the mercury green line 5461 Å.) whilst the more soluble fractions were dextrorotatory. By systematic refractionation from methanol with ether and then repeated recrystallization of the least soluble fraction from a methanol-ether mixture there was finally obtained a salt crystallized in square brown plates. A 0.01% solution of it in 20% methanol-water at 20° in a 2-dcm. tube had a rotation of -1.40° ; whence $[\alpha]_{5461}^{20} -7,000^\circ$. It was not found possible to use solutions stronger than 0.01% owing to their intense green color.

Anal. Calcd. for $\text{Co}(\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2)(\text{C}_{10}\text{H}_{14}\text{BrO}_4\text{S})\text{H}_2\text{O}$: Co, 7.6; C, 46.6; H, 4.9; N, 3.6. Found: Co, 7.5; C, 46.5; H, 4.8; N, 3.6.

***l*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Iodide.**—A solution of the above described levorotatory salt (0.4 g.) in methanol (20 ml.) was poured into ice-water (60 ml.) and then 5% potassium iodide solution slowly stirred in. The *l*-CoS I precipitated in brown plates or leaflets. The precipitate was washed with ice-cold dilute potassium iodide solution, dried on a porous tile and then taken up in warm methanol (20 ml.), water (40 ml.) at 60° added and then a little potassium iodide to incipient crystallization. The salt then crystallized out on cooling. After five such recrystallizations glistening brown plates m. p. 270° (dec.) were obtained.

Anal. Calcd. for $\text{CoC}_{22}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2\text{I}$: C, 42.0; H, 3.8; N, 4.9; I, 22.2. Found: C, 41.5; H, 3.8; N, 4.9; I, 22.0.

The observed rotation of a 0.01% solution in 20% methanol-water at 20° in a 2 dcm. tube for the mercury green line 5461 Å. was -1.76° ; whence $[\alpha]_{5461}^{20} -8,800^\circ$ and $[\text{M}]_{5461}^{20} -50,160^\circ$. The observed rotation of a 0.01% solution in 20% methanol-water had not decreased after heating to the boiling point (85°) for twenty minutes. However, in boiling aqueous solution the rotation declined. After twenty minutes boiling the rotation (at 20°) had declined to -0.30° (83% loss of activity); and after thirty minutes boiling to -0.08° (94% loss of activity). The activity had been completely lost after sixty minutes boiling. From this solution a salt could be recovered which melted at 264° after recrystallization. The loss of activity would thus appear to be due to racemization—an involved process in such a complicated molecule in which several of the coordinate links must be broken, presumably by the intervention of water molecules, and then reformed. It is worthy of note that the green color of the solution changes to brown on heating to 100° but that it becomes green again on cooling. The rotation of a 0.01% solution was unchanged after being kept for five weeks at room temperature (20–25°).

***d*-1,8-Bis-(salicylideneamino)-3,6-dithiaoctane Cobaltic Iodide.**—Repeated refractionation of the more soluble *d*- α -bromocamphor- π -sulfonate fractions described above failed to raise the specific rotation $[\alpha]_{5461}^{20}$ above $+2,400^\circ$ (*i. e.*, about two-thirds dextro-form and one-third levo-form). The salt (1.5 g.) was dissolved in methanol (20 ml.) and warm water (80 ml.) added. Solid potassium iodide (0.2 g.) was then rapidly dissolved in the solution. On cooling, brown glistening leaflets were deposited. For a 0.01% solution of these in 20% methanol-water at 20° $[\alpha]_{5461}^{20}$ was found to be $+3,750^\circ$, whilst that of the salt remaining in the filtrate was found to be only $+500^\circ$. The optically active iodide is thus apparently less soluble than the *dl*-iodide. Systematic recrystallization from hot aqueous methanol with the addition of potassium iodide eventually gave the pure dextro iodide, m. p. 268°, with a specific rotation $[\alpha]_{5461}^{20}$ of $+8,800^\circ$ (0.01% solution in 20% methanol-water). In all, nine recrystallizations were necessary.

Anal. Found: C, 41.4; H, 3.8; N, 4.8; I, 22.1.

1,8-Bis-(hydroxy- α -naphthylideneamino)-3,6-dithiaoctane (VI).—Ethanol (400 ml.) and then sodium acetate

(35 g.) were added to a solution of the dihydrochloride of the base II (10.12 g.) in water (20 ml.) and the solution warmed. The sodium chloride which separated on cooling was filtered off and then a solution of 2-hydroxy-1-naphthaldehyde (13.76 g.) in ethanol (200 ml.) added and the whole boiled for ten minutes. The yellow crystalline Schiff base (18 g.) soon crystallized. Recrystallized from much alcohol it formed yellow leaflets m. p. 155°.

Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$: C, 68.9; H, 5.7; N, 5.7. Found: C, 68.6; H, 5.8; N, 5.7.

***dl*-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane Cobaltic Bromide Dihydrate.**—A solution of cobaltous acetate hexahydrate (4.5 g.) in methanol (50 ml.) was added to a suspension of the Schiff base VI (7.4 g.) in boiling alcohol (400 ml.). The base soon dissolved to a brown solution, cooling of which led to deposition of reddish-brown crystals, presumably of the cobaltous derivative. The solution was kept hot whilst air was aspirated through it for one hour, after which it was allowed to cool and the passage of air continued for a further two hours. Water (600 ml.) was then added and the dark green solution allowed to stand in the air for two days, after which it was filtered free from a small amount of some dark brown decomposition product heated to 80° and treated with potassium bromide solution. The complex bromide was then soon induced to crystallize in dark brown needles, which were recrystallized by solution in hot alcohol, addition of two volumes of hot water, filtration, and then addition of strong potassium bromide solution. The final product formed dark brown (almost black) glistening needles m. p. 217–219° (dec.).

Anal. Calcd. for $\text{CoC}_{28}\text{H}_{30}\text{BrN}_2\text{O}_3\text{S}_2$: Co, 8.9; C, 50.8; H, 4.2; N, 4.3; Br, 12.1; H_2O (of cryst.), 5.4. Found: Co, 8.9; C, 50.6; H, 4.4; N, 4.2; Br, 12.2; H_2O , 5.6.

The complex iodide and perchlorate could be readily obtained as very insoluble greenish-brown amorphous precipitates by addition of sodium iodide or sodium perchlorate to a solution of the acetate, but they were not further studied.

***dl*-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane Cobaltic *d*- α -Bromocamphor- π -sulfonate Monohydrate.**—A solution of silver *d*- α -bromocamphor- π -sulfonate (6.3 g.) in methanol (50 ml.) was added to a solution of the above described complex bromide (9.4 g.) in boiling alcohol (400 ml.). After boiling for two to three minutes, hot water (3000 ml.) was added and the boiling continued for a further five minutes. The hot solution was then at once filtered free of precipitated silver bromide, evaporated to dryness on the water-bath, the residue taken up in methanol (150 ml.) and filtered free from traces of silver bromide. The solvent was again evaporated and the residual black gum stirred with ether. It soon solidified to a brown microcrystalline powder, m. p. 263°, very soluble in methanol, soluble in ethanol, sparingly soluble in acetone and practically insoluble in water.

Anal. Calcd. for $\text{Co}(\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2)(\text{C}_{10}\text{H}_{14}\text{BrO}_4\text{S})\text{H}_2\text{O}$: Co, 6.8; C, 52.2; H, 4.8; N, 3.2. Found: Co, 6.7; C, 52.4; H, 4.9; N, 3.3.

***l*-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane Cobaltic *d*- α -Bromocamphor- π -sulfonate Monohydrate.**—The above described mixture of salts was dissolved in just sufficient boiling 15% methanol-85% acetone, the solution filtered and then allowed to stand in an ice-bath. A crop of greenish-brown needles separated, and proved to be almost pure *l*-base-*d*-acid salt. Fractional precipitation with ether was then carried out. By systematic recrystallization of the least soluble fractions from 15% methanol-85% acetone the pure *l*-base-*d*-acid salt was eventually obtained. *Anal.* Found: C, 52.6; H, 5.0; N, 3.2. The specific rotation $[\alpha]_{5461}^{20}$ was $-8,050^\circ$ (observed rotation of a 0.01% solution in 20% methanol-water at 20° (2-dcm. tube) was -1.61°).

***dl*-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane Cobaltic *d*- α -Bromocamphor- π -sulfonate Monohydrate.**—The most soluble fractions from the separation described above were systematically refractionated

from 15% methanol-85% acetone with ether. After several refractionations the most soluble fraction was recrystallized several times from the methanol-acetone mixture. Its observed rotation (0.01% solution in 20% methanol-water at 20° in a 2-dcm. tube) was +1.63°, whence $[\alpha]_{5461}^{20} = +8,150^\circ$. *Anal.* Found: C, 52.1; H, 4.9; N, 3.2.

d- and *l*-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane Cobaltic Bromide Dihydrates.—Because the above described α -bromocamphor- π -sulfonates are less soluble than the corresponding bromides the following method was adopted for transformation of the *l*-base-*d*-acid salt to the *l*-base bromide, and an exactly similar method was used to convert the *d*-base-*d*-acid salt to the *d*-base bromide: The *l*-base-*d*-acid salt (1.25 g.) was dissolved in methanol (50 ml.) and water (20 ml.) and the solution heated almost to boiling. Potassium iodide (0.25 g.) was then added, a greenish-brown precipitate of the complex *l*-base iodide separating. This was collected and dissolved in a boiling mixture of methanol (80 ml.) and water (20 ml.) and a concentrated solution of silver nitrate (1.2 mols) added. The precipitated silver iodide was filtered off and sufficient potassium bromide to precipitate the excess silver added to the hot solution. After removal of the precipitated silver bromide excess potassium bromide was added to the filtrate which was then cooled. Greenish-brown needles of the active bromide separated. These were recrystallized three times from hot 50% aqueous methanol to which some potassium bromide was added before cooling. The final product formed finely felted needles m. p. 220–222° (dec.). *Anal.* Found: C, 50.4; H, 4.3; N, 4.3; Br, 12.2. The observed rotation of a 0.01% solution in 20% methanol-water at 20° in a 2-dcm. tube for the mercury green line 5461 was -2.22° , whence $[\alpha]_{5461}^{20} = -11,100^\circ$ and $[M]_{5461}^{20} = -73,370^\circ$.

d-1,8-Bis-(β -hydroxy- α -naphthylideneamino)-3,6-dithiaoctane cobaltic bromide dihydrate was similarly obtained in greenish-brown needles m. p. 220–222° (dec.). *Anal.* Found: C, 50.5; H, 4.4; N, 4.2; Br, 12.1. The observed rotation of a 0.01% solution in 20% methanol-water at 20° in a 2-dcm. tube for the mercury green line 5461 was $+2.21^\circ$, whence $[\alpha]_{5461}^{20} = +11,050^\circ$ and $[M]_{5461}^{20} = +73,040^\circ$.

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Summary

1,8-Diamino-3,6-dithiaoctane has been prepared and treated with salicylaldehyde (2 mols) and with 2-hydroxy-1-naphthaldehyde (2 mols) to give the corresponding Schiff bases. These form coordination compounds with metals such as zinc, copper, nickel, iron and cobalt. The cobaltous complexes oxidize very easily in presence of acid to cobaltic salts in which the organic moiety is attached to the central cobalt atom at six points. The complex cobaltic cations so obtained are asymmetric. Resolution of these cobaltic salts has been effected. The optically active salts are distinguished by their optical stability and their tremendous molecular rotations which are higher than any previously recorded.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Low Temperature, Low Pressure, Hydrogen Atom Initiated Combustion of Hydrocarbons¹

BY ELMER J. BADIN

A study of hydrocarbon combustion initiated by atomic hydrogen has not previously been carried out, although Geib and Harteck² have reported that methane-oxygen and acetylene-oxygen mixtures reacted at low temperatures when mixed with hydrogen from a discharge tube. Some preliminary results on the oxidation of C₄-hydrocarbons have already been reported.³ This study has been continued, since the initial experiments indicated that, under the reaction conditions used [low temperatures (20°) and low pressures (0.20–0.55 mm.)], definite information about the manner of hydrocarbon combustion could be obtained. The results of this study are reported here.

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(2) K. H. Geib and P. Harteck, *Z. physik. Chem.*, **170**, 1 (1934).

(3) E. J. Badin, *This Journal*, **70**, 3965 (1948).

Experimental

Experiments were carried out in an apparatus similar to that previously described.⁴ Hydrocarbon and oxygen were admitted through two capillary-type flowmeters. Hydrogen was electrolyzed from a dilute sulfuric acid-water solution and passed directly into the phosphoric acid-coated discharge tube. The degree of dissociation of the hydrogen from experiments with hydrogen and oxygen alone was estimated to be of the order of 60–70%.

The two gas streams passed into a reaction trap (51 mm. o.d.) through two concentric tubes (17.5 mm. o.d. and 8.0 mm. o.d., respectively), the hydrocarbon-oxygen mixture entering through the inner tube. The inlet tubes for hydrogen and hydrocarbon-oxygen were coated with phosphoric acid. The reaction trap, condensing traps and connecting tubes were of untreated Pyrex glass.

In most experiments the gases mixed in the main reaction trap and the products were condensed in a trap (liquid nitrogen cooled) about 30 cm. removed from the point of mixing of the gases.

Analyses for liquid products (aldehydes, ketones, hydrogen peroxide, organic peroxides) were obtained by dissolving the total product at the end of an experiment in an ice-water mixture and analyzing aliquot portions.

Total aldehyde and ketone was determined by precipitation with 2,4-dinitrophenylhydrazine in 3 *M* hydrochloric

(4) E. J. Badin, *ibid.*, **70**, 365 (1948).