

dium has been studied in 1 *N* sodium hydroxide solutions containing many different added anions, and information is presented on the ionic states of the vanadium in these solutions.

2. In solutions of sodium hydroxide less concentrated than about 0.25 *N*, +4 vanadium yields a double anodic wave which is ascribed to oxidation of the two ions  $V_2O_5^{--}$  and

$V_4O_9^{--}$  present in approximately equal quantities.

3. Anodic waves for the oxidation of +4 vanadium to the +5 state are obtained at all *pH* values greater than about 4.7, and the characteristics of the waves in acetate and bicarbonate buffers of varying *pH* have been studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

## The Oxygen-carrying Synthetic Chelate Compounds. VII. Preparation<sup>1</sup>

By R. H. BAILES<sup>2</sup> AND M. CALVIN

In previous papers of this series<sup>3</sup> a number of physical measurements on a selected group of chelate compounds in certain special states, were described. It is the purpose of the present paper not only to give the methods of preparation of these compounds in all of their forms, but to describe all of those which were prepared for the examination of their oxygen carrying properties, and sufficiently well characterized to be certain of their structure.<sup>4</sup>

### I. Cobalt Chelates Prepared from Salicylaldehyde and Its Derivatives and with Diamines of the Type of Ethylenediamine<sup>5</sup>

(1) Cobalt Di-(salicylal)-ethylenediimine.—Pfeiffer<sup>6</sup> reported the preparation of the red crystalline compound and stated that it slowly turned brown on standing exposed to air. He apparently did no further work with this compound. Tsumaki<sup>7</sup> took up the problem and announced that the darkening was due to a reversible oxidation. He recrystallized the red crystals (obtained from aqueous alcohol) from benzene and from chloroform. From benzene he obtained red brown needles which were slowly oxygenated in air and would, when heated to 100°, return to their original color and weight. From chloroform he obtained shining dark-red prisms which contained one solvated chloroform molecule. By heating the dark-red prisms to 100° they changed to a red-brown powder which would absorb oxygen much more rapidly than the needle-like crystals. They would become black after a day and reach a constant weight. The black powder would lose its oxygen easily when heated in a stream of

carbon dioxide and return to its original color and weight. This black compound contained one mole of oxygen to three moles of cobalt.

At this point we took up the problem. We very soon found that this chelate could be prepared readily in a well-defined crystal form which was inactive toward oxygen, of which the following method furnishes a yield of 86%.

Five hundred and seventy-six grams of salicylaldehyde and 203 g. of 68.6% ethylenediamine were dissolved in 6.5 liters of 95% ethanol placed in a 12-liter flask fitted with a stopcock. They react together to give the Schiff base which precipitates but will dissolve when warmed to about 60°; five hundred and seventy-six grams of cobaltous acetate tetrahydrate was dissolved in 3 liters of water and heated to 60°. The cobaltous acetate solution was then rapidly poured, with shaking, into the alcohol solution of the Schiff base. The flask was then closed with a stopper fitted with a stopcock and connected to the aspirator. When the boiling alcohol had swept all the air from the flask the stopcock was closed. At first a brown gelatinous product forms which rapidly changes to large red crystals provided the flask is kept warm. After cooling the crystals were filtered or centrifuged, washed with water and then dried in a vacuum desiccator. These large red crystals do not absorb oxygen. If the entire preparation is done at room temperature the product is a brown gelatinous material which is partially active to oxygen. If the brown gelatinous product is not filtered but is allowed to remain in the flask away from air it slowly changes to large dark red, almost black, crystals, the change being complete in about ten days depending upon the quantity and the room temperature.

*Analysis* of red-black crystals. Calcd.: C, 59.10; H, 4.30; N, 8.63; Co, 18.14. Found: C, 59.09, 59.23; H, 4.35, 4.06; N, 8.62; Co, 18.15, 17.91.

If methyl alcohol is substituted for ethyl in the above preparation, identical products are obtained.

The red crystals are insoluble in water, ether, carbon tetrachloride, triethylamine, slightly soluble in di-isopropylamine, ethanol, benzene, chloroform, acetone, *n*-propyl alcohol, isoamyl alcohol, methylene dichloride, soluble in piperidine, *n*-butylamine, aniline and pyridine.

It was found possible to crystallize the red inactive crystals from pyridine in absence of air. This was done by heating them to boiling under reflux in a good hood with 13 ml. of pyridine for each gram of chelate. When cooled an almost quantitative yield of fine bright red crystals is obtained which are monopyridinate. When heated for one and one-half hours at 170° at a pressure not greater than 2 mm. they lose 19.7% in weight while the calculated value for one pyridine is 19.55%. The color changes from bright red to brown.

*Analysis* of  $CoC_{16}H_{14}N_2O_2 \cdot 1C_5H_5N$ . Calcd.: C, 62.4; H, 4.74; N, 10.39; Co, 14.6. Found: C, 62.29, 62.18; H, 4.66, 4.62; N, 10.3, 10.1; Co, 15.0, 15.6.

This brown powder obtained by removal of the pyridine

(1) The work herein reported was done in part under contract OEM sr-276 between the National Defense Research Committee and the University of California during the period February 1941 to April 1944.

(2) Present address: Department of Chemistry, Boston University, Boston, Massachusetts.

(3) I through V, *THIS JOURNAL*, 68, Nov. (1946); VI, *ibid.*, 68, Dec. (1946).

(4) A further group of 119 compounds were also prepared but their characterization was incomplete. The list of these compounds together with the observations that were made of their behavior may be obtained upon request from the Library Photo Service, University of California, Berkeley (Photostat, \$1.50; Microfilm, \$1.00).

(5) Nitrogen analyses were performed by the micro-Dumas technique. Carbon and hydrogen analyses were obtained by the micro-Liebig method. Cobalt values were calculated from the residues of the Liebig combustions and are frequently in error due to sublimation of the compound being burned. Occasionally a sample would explode so that no cobalt residue would be obtained.

(6) P. Pfeiffer, *Ann.*, 503, 84 (1933).

(7) Tsumaki, *Bull. Chem. Soc. Japan*, 13, 247 (1938).

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would absorb 4.94% of its weight of oxygen from the air or in an oxygen atmosphere within about two hours and change color from brown to jet black. This value corresponds exactly to two moles of chelate to one mole of oxygen. We were never able to increase this ratio of oxygen to chelate with this particular compound.

It was found impossible to remove the pyridine by heating the pyridinate at 100° at a pressure of 2 mm. A temperature of 160° seems necessary. Vacuum activation can be supplanted by other techniques. For example, if the dry pyridinate is spread in trays to a depth of not over one to two centimeters and placed in an oven heated to 160–220° with a stream of air or nitrogen blowing over the powder, satisfactory activation is obtained. We found it desirable to press the pyridinate into pellets under high pressure and then activate the pellets. This pressing increased the speed of oxygenation without decreasing the capacity and even seemed to increase that somewhat.

If the recrystallization of the inactive crystals from pyridine had taken place in the presence of air, or if one wets the red crystals with pyridine in the presence of air a black crystalline material is obtained. After drying in a desiccator these black crystals lose 21.7% in weight when heated at 170° for two hours *in vacuo*. These black crystals apparently are a pyridine peroxide.

*Analysis of*  $\text{CoC}_{16}\text{H}_{14}\text{N}_2\text{O}_2 \cdot \text{C}_6\text{H}_5\text{N} \cdot 0.5\text{O}_2$ . Calcd.: C, 59.9; H, 4.57; N, 10.0; Co, 14.1. Found: C, 59.84, 59.68; H, 4.88, 4.91; N, 9.74, 9.60; Co, 12.4, 11.9.

Recrystallization of the inactive compound from pyridine was an expensive as well as an unsatisfactory method for preparing the pyridinate. It was considered desirable to develop a method whereby it could be made directly. The following method was developed.

One-tenth mole of cobaltous acetate was dissolved in 250 ml. of boiling water. Four-tenths mole of pyridine was then added to the cobalt acetate solution, followed by 0.1 mole of ethylenediamine. This mixture was shaken thoroughly and then 0.2 mole of salicylaldehyde was added to it. Red crystals formed immediately and were allowed to grow for two hours out of contact with air. They were then cooled, filtered, washed with a small amount of water and then dried in a vacuum desiccator. This direct method for preparation of the pyridinate involves only a slight excess of pyridine and always furnishes a good product and a high yield (88%). These crystals prepared by the direct method seem to be completely identical with those prepared by recrystallization from pyridine.

The above direct method furnished us with a good method for preparing an active rapid form of this compound possessing the maximum capacity of 4.94%. Nevertheless it involved the use of pyridine which is expensive and has a most obnoxious odor. We considered it desirable to develop a method for its preparation using only water or water and some simple alcohol. The gelatinous material formed in aqueous alcohol at room temperature had been found to possess some activity. Accordingly, a large number of preparations were made varying the amounts and proportion of ethanol and water, the temperature, the order of mixing, etc. No method was ever developed that would give consistently a product of full capacity or as high a rate, as the material obtained via the direct pyridine method. The nearest approach was a technique using about a 50/50 mixture by volume of water and *n*-propyl alcohol as a solvent. It was never determined to our complete satisfaction whether the chelate was monosolvated with *n*-propyl alcohol.

Active samples were tested to see if they would absorb carbon monoxide. They would not when exposed to an atmosphere of carbon monoxide for over an hour. Samples so tested retained their full oxygen carrying abilities.

(2) Cobalt Di-(3-ethoxysalicylal)-ethylenediamine.— This compound was prepared easily as a red crystalline monohydrate by the following procedure.

Ten grams of 3-ethoxysalicylaldehyde was dissolved in 250 ml. of 95% ethanol in a round-bottom flask fitted with a rubber stopper and stopcock. To this was added

3 g. of ethylenediamine and 30 g. of sodium acetate trihydrate. The Schiff base precipitated but was redissolved by heating the mixture on a steam-bath. To this hot solution of Schiff base was added a hot solution of 7.5 g. of cobaltous acetate tetrahydrate dissolved in 100 ml. of water. Some of the excess solvent was boiled off by pumping through the stopcock while the flask was heated on a steam-bath. A red crystalline precipitate soon formed, was filtered under a rubber dam, washed with water and dried in a vacuum desiccator; yield was 85%.

The red crystals change to brown and lose 4.32% in weight when heated for one hour at 120° at a pressure of 2 mm. Four and two-tenths per cent. corresponds to a loss of one solvated water.

*Analysis of red hydrate.* Calcd.: C, 55.70; H, 5.57; N, 6.50; Co, 13.69. Found: C, 55.82, 55.96; H, 5.67, 5.81; N, 6.44, 6.43; Co, 13.57, 13.78.

The dehydrated crystals rapidly absorb 3.87% of their weight of oxygen from the air forming a jet-black peroxide. Calculated absorption on base of 2 moles of chelate to 1 mole of oxygen 3.87%.

*Analysis of black peroxide.* Calcd.: C, 55.95; H, 5.13; N, 6.53; Co, 13.75. Found: C, 55.85, 55.71; H, 5.20, 5.24; N, 6.51, 6.49; Co, 13.6, 12.6.

The red crystalline hydrate is insoluble in dioxane, water, slightly soluble in acetone, benzene, acetonitrile, formamide, nitroethane and chloroform, and chlorobenzene, fairly soluble in hot *n*-amyl alcohol, and soluble in pyridine. It is more soluble in methanol and *n*-propyl alcohol, than in ethanol.

The hydrate can be prepared in an all aqueous solution without the use of the ethanol by dissolving the Schiff base in hot water with the calculated amount of sodium hydroxide. The hot aqueous solution of cobaltous acetate is then added. The use of ethanol has an advantage in that a more nicely crystalline product is obtained with its use. It was found possible to substitute dioxane for ethanol.

A sample of the hydrate was allowed to stand in 95% ethanol overnight. Apparently it was unharmed as it analyzed perfectly, lost the correct amount of water and absorbed the calculated quantity of oxygen.

Occasionally, instead of getting the red hydrate, one obtains long-needled yellow crystals when preparing the compound according to the above directions. Also occasionally one gets these same yellow needles when soxhletting the red crystalline hydrate with 95% ethanol. When heated at 120° for one hour *in vacuo*, these yellow needles change to red-brown and lose 4.37% in weight which corresponds to a monohydrate. This form is active and will absorb the theoretical amount of oxygen forming a brown peroxide rather than the jet-black peroxide. However, it is very slow as compared with the active form from the red hydrate.

*Analysis of yellow monohydrated needles.* Calcd.: C, 55.70; H, 5.57; N, 6.50; Co, 13.69. Found: C, 55.53, 55.51; H, 5.61, 5.66; N, 6.44, 6.36; Co, 13.3, 13.3.

The red crystalline monohydrate can be converted to a red crystalline monopyridinate by heating in the absence of air with an excess of 1-1 mixture of water and pyridine. An obvious crystalline transformation occurs from prisms to needles. When heated for one hour at 170° *in vacuo* a sample of the monopyridinate lost 15.7% in weight. Calculated loss is 16.1%. The depyridinated form is extremely rapid in its uptake of oxygen, being more rapid than the form obtained from the hydrate. It forms a jet-black peroxide and takes up the theoretical amount of oxygen.

The monopyridinate can be made directly with a yield of 90% according to the following directions: 0.2 mole of 3-ethoxysalicylaldehyde is added to a hot solution of 0.1 mole of ethylenediamine, 0.2 mole of sodium hydroxide and 0.6 mole of pyridine dissolved in 200 ml. of water. To this is then added a hot solution of 0.1 mole of cobaltous acetate and 0.2 mole of acetic acid dissolved in 50 ml. of

water. The red needles precipitate immediately, are cooled, filtered, washed with water and dried in a vacuum desiccator.

This compound cannot be stored for long periods of time as the monopiperidinate seems to recrystallize or change into an inactive form on standing.

(3) Cobalt Di-(3-fluorosalicylal)-ethylenediimine.—As in the case of the 3-ethoxy compound this one forms two different hydrates, of which the active form from one absorbs oxygen with extreme rapidity, the other being considerably slower in rate of uptake. However, in contrast to the 3-ethoxy compound whose slow form could only be obtained by chance and infrequently, the exact reverse applies to the 3-fluoro compound. The slow form is easily prepared in 88% yield by adding a hot aqueous solution of cobaltous acetate to a hot alcohol solution of the Schiff base in the absence of air. A reddish hydrate precipitates which is handled in the usual way. When heated it loses about 5.2% in weight and turns brown. One water would cause a loss of 4.75%. When exposed to oxygen it forms a brownish peroxide after absorbing the calculated 4.44% of oxygen.

Analysis of hydrate. Calcd.: C, 50.7; N, 7.39; H, 3.70; Co, 15.6. Found: C, 50.7, 50.9; N, 7.36, 7.46; H, 3.68, 3.75; Co, 16.1, 16.3, 15.0, 14.7.

At least 250 preparations were made in an attempt to find a reliable method of preparing the fast hydrate which forms a jet-black peroxide. In this we have to report failure.

When either red hydrate is mixed with ether and then exposed to air, the color changes to jet-black with the formation of a hydrate-peroxide. A sample when heated lost 8.56% in weight. The calculated loss of one water and 0.5 O<sub>2</sub> per cobalt is 8.55%. The resultant product is very speedy in its oxygen absorption but usually has a lowered capacity.

The 3-fluoro compound is easily solvated by a molecule of piperidine. The piperidinate is readily prepared by mixing the hydrate with aqueous piperidine or it can be prepared directly. When prepared directly one adds a hot aqueous solution of cobaltous acetate to a hot aqueous or hot aqueous-alcohol solution of the Schiff base and excess piperidine. A 90-100% yield of a red crystalline precipitate forms, which, after drying loses 20.0% in weight when heated for one hour at 160° *in vacuo*. The activated material thus obtained picks up the theoretical quantity of oxygen and is the fastest compound that we have prepared.

Analysis of piperidinate. Calcd.: C, 56.5; H, 5.16; N, 9.42; Co, 13.22. Found: C, lost; H, 5.32, 5.39; N, 9.39, 9.22; Co, 13.2, 13.1.

A sample of the monopiperidinate was treated with 100 psi. of oxygen for ten minutes. No color change or oxygen absorption was observed.

It was noticed that occasionally samples of the piperidinate when heated at 170° at a pressure of 2 mm. would remain red when exposed to oxygen. A series of samples from one preparation were heated at various temperatures to determine the optimum temperature for activation. The results are shown in the table.

TABLE I

Temp., °C.	Time, hours	Pressure, mm.	Loss in weight, %	Oxygen absorption, %
200	1	2	22.1	3.9 <sup>a</sup>
170	1	2	21.8	0
161	1	2	21.8	4.10
151	1	2	21.7	4.30
140	1.1	2	21.7	4.39
130	1	2	21.0	4.26
130	1.33	2	21.3	4.36
120	1	2	9.4	"

<sup>a</sup> These two tests were performed at different times and on a different preparation.

From these data it is seen that at temperatures over 161° the material changes to an inactive crystal modification. The optimum temperature is 140° for removal of the piperidine, and at temperatures below 130° the piperidine is incompletely removed.

A sample of the piperidinate was activated at 151° for one hour at a pressure of 2 mm. Its capacity at that time was 4.30%. It was then placed in a vacuum heater and heated for the following lengths of time at 160° and its slow conversion to an inactive form observed.

After 0 hours	4.30% Capacity
2	4.03
4	3.80
10	3.64
15	3.54
20	3.32
30	3.30

The previous test had shown that only one hour at 170° *in vacuo* was necessary to completely deactivate the compound. At 160° the activity drops from 4.30 to 3.30% after thirty hours.

A sample of the slow hydrate was exposed to 175 p.s.i. oxygen pressure for ten minutes. No color change nor oxygen absorption was observed.

Another sample of the slow hydrate was stirred and washed with methanol in the presence of air. It changed from brown to black, and lost 5.44% in weight when heated at 120° following vacuum drying. Its oxygen uptake decreased from 4.0 to 2.1%. A preparation in methanol when exposed to air, blackened, and had an activity of 2.2%.

When the chelate is prepared in aqueous dioxane, hydrates having low capacities are found.

If prepared in the presence of ammonia a monoammoniate is obtained. The sample loses 4.85% in weight and absorbs oxygen quite slowly.

Anal. Calcd.: C, 50.8; H, 3.97; N, 11.1. Found: C, 50.69, 50.45; H, 4.12, 4.14; N, 10.96, 10.84.

A monopiperidinate can be obtained directly by preparing the chelate in the presence of an excess of pyridine. A sample lost 17.02% in weight. Calcd. loss was 17.95%. The activated sample takes up the full amount of oxygen, though more slowly than the active material obtained *via* the fast hydrate or piperidinate.

When a sample of peroxide was refluxed with toluene, oxygen was released and red crystals were formed. These red crystals are unsolvated and will not absorb oxygen. They are paramagnetic and have the same X-ray powder pattern as the red form obtained by heating the piperidinate at high temperatures.

Analysis of red inactive di-(3-fluorosalicylal)-ethylenediimine. Calcd.: C, 53.2; H, 3.32; N, 7.76. Found: C, 52.96, 52.85; H, 3.47, 3.48; N, 7.77, 7.89.

When prepared in the presence of propionitrile, acetone, di-isopropylamine, diethanolamine or triethanolamine, the slow hydrate was always obtained.

If the chelate is prepared in the presence of an excess of ethylenediamine, the compound is solvated with one ethylenediimine. Just as in the case of cobalt di-(salicylal)-ethylenediimine it was impossible to drive off the solvated ethylenediamine, by vacuum heating.

(4) Cobalt Di-(3-nitrosalicylal)-ethylenediimine.—This brown compound would absorb oxygen very rapidly but not as fast as the 3-fluoro compound. It could be prepared in all aqueous medium as a monohydrate.

Analysis of hydrate. Calcd.: C, 44.4; H, 3.24; N, 12.98. Found: C, 45.7; H, 3.36; N, 12.32.

The hydrate was dissolved in pyridine and when water was added a red crystalline product precipitated which appeared to be a dipiperidinate. One sample lost 28.8% in weight and another 29.4% when heated for 1 hour at 170° *in vacuo*: Calcd. 2 pyridines = 27.6%. These activated samples would absorb oxygen (2-1) at a very rapid rate.

Analysis of dipiperidinate. Calcd.: C, 54.5; H, 3.84; N, 14.7. Found: C, 52.0; H, 3.98; N, 16.1.

(5) The chelate of cobalt with water weighed 2.89; N, 13.83.

The orange cobalt solution.

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The orange cobalt solution.

## (5) Cobalt Di-(5-nitrosalicyl)-ethylenediimine.—

The chelate was prepared by heating the calculated quantities of aldehyde, cobaltous acetate and ethylenediimine in an aqueous pyridine mixture in the absence of air. The red precipitate was filtered under a rubber dam, washed with water and ether and dried in a vacuum desiccator. A weighed sample lost 13.4% in weight when heated in a vacuum at 170° for one and one-half hours. One solvated pyridine would mean a loss of 16%. It was insoluble in most reagents such as ethanol, dioxane, benzene, chloroform and glacial acetic acid thus making it difficult to purify. However, it was soluble in pyridine.

*Analysis* of desolvated product. Calcd.: C, 46.2; H, 2.89; N, 13.5. Found: C, 48.1, 48.4; H, 3.07, 3.11; N, 13.83, 14.05.

The orange-yellow Schiff base was prepared and treated with cobaltous acetate in an aqueous *n*-propyl alcohol solution. The red product was washed with ether and dried in a vacuum desiccator, though it seemed quite stable in air. A weighed sample lost 21% when heated for one and one-half hours at 140° *in vacuo*. Two solvated *n*-propyl alcohols would be 22.4%. All samples of this compound when tested would absorb reversibly about 1.5% of their weight of oxygen.

## (6) Cobalt Di-(5-methylsalicyl)-ethylenediimine.—

The Schiff base was dissolved in hot *n*-propyl alcohol and was treated with the calculated amount of cobaltous acetate dissolved in water. The mixture was heated on a steam-bath *in vacuo*. The red brown crystals were washed with water, then ether, and dried in a vacuum desiccator. When heated *in vacuo* a sample lost 8% in weight, which is slightly high for one solvated water molecule.

*Anal.* Calcd.: C, 61.3; H, 5.1; N, 7.93; Co, 16.72. Found: C, 61.40; H, 5.35, 5.36; N, 8.13, 8.17; Co, 16.66.

At 15 p.s.i. oxygen pressure the chelate would absorb no oxygen. However, at 300 p.s.i. it would take 3.0% by weight and turn dark.

A sample of the above hydrate was recrystallized from a pyridine-water mixture. A brown-red monohydrate was obtained which turned bright orange when desolvated.

*Analysis* of hydrate. Calcd.: C, 53.6; H, 4.96; N, 6.95; Co, 14.64. Found: C, 53.8, 53.9; H, 4.97, 5.00; N, 6.87, 6.85; Co, 14.8, 14.9.

## (7) Cobalt Di-(3-methoxysalicyl)-ethylenediimine.—

A beautiful yellow crystalline product was obtained from an aqueous *n*-propyl alcohol solution. The crystals were monohydrated as they lost 5.05% in weight when heated for one and one-half hours at 170° *in vacuo*; calcd. 1 H<sub>2</sub>O, 4.47%. They rapidly took up 4.22% oxygen from the air to form a black peroxide; calculated for two moles of chelate to one mole of oxygen 4.16%.

Many repeat preparations duplicated all of the above results.

## (8) Cobalt Di-(4-ethoxysalicyl)-ethylenediimine.—

One equivalent of Schiff base and two equivalents of sodium hydroxide were dissolved in hot *n*-propyl alcohol. To this was added a hot aqueous solution of cobaltous acetate and the air was pumped out of the reaction flask. A reddish crystalline precipitate formed at first which then rapidly changed to yellow in color. After drying in a vacuum desiccator a sample lost 8.03% in weight when heated to 170° *in vacuo* for one hour. This corresponds exactly to a dihydrate. The desolvated sample took up about 1% of its weight of oxygen on standing in an atmosphere of oxygen.

*Analysis* of desolvated product. Calcd.: C, 56.1; H, 4.68; N, 7.28; Co, 15.3. Found: C, 56.1, 55.9; H, 4.58, 4.54; N, 7.16, 7.08; Co, 15.57, 15.56.

(9) Cobalt Di-[5-( $\beta$ -carboxyethyl)-salicyl]-ethylenediimine.—A red crystalline unsolvated material obtained from aqueous *n*-propyl alcohol solution; washed with water, alcohol and ether, and then dried in a vacuum desiccator.

*Anal.* Calcd.: C, 56.3; H, 4.69; N, 5.97; Co, 12.59.

Found: C, 53.6, 53.5; H, 4.65, 4.64; N, 5.73, 5.69; Co, 13.93, 14.32.

The crystals were insoluble in 95% ethanol, chloroform, dioxane, benzene, pyridine and water. They were slightly soluble in sodium acetate solution and very soluble in sodium carbonate and dilute ammonia. Acetic acid will reprecipitate it from the dilute ammonia solution.

The solid crystals will absorb about 1% of their weight of oxygen when subjected to 175 p.s.i. of oxygen.

A sample was dissolved in dilute ammonia, reprecipitated by adding dilute acetic acid, filtered, washed with water and dried in vacuum desiccator. A diammoniate was formed.

*Anal.* Calcd.: C, 52.3; H, 5.58; N, 11.10; Co, 11.6. Found: C, 51.7, 51.7; H, 5.20, 5.18; N, 10.65, 10.69; Co, 11.5, 11.4.

## (10) Cobalt Di-(3-carboxysalicyl)-ethylenediimine.—

From aqueous propyl alcohol a crystalline dihydrate was obtained. A sample lost 8.5% in weight when heated for one and one-quarter hours at 120° *in vacuo*; calcd. for 2 H<sub>2</sub>O is 8.02%. The crystals are insoluble in water, pyridine, ethanol, acetone, chloroform and dioxane. They are soluble in ammonium hydroxide and will take up about 1% oxygen.

*Analysis* of dihydrate. Calcd.: C, 48.1; H, 4.01; N, 6.24; Co, 13.1. Found: C, 47.9, 47.7; H, 4.08, 4.12; N, 5.94, 5.81; Co, 13.5.

When recrystallized from ammonium hydroxide a red crystalline dihydrate was obtained since it lost the correct amount of weight on heating and gave the correct analysis. Found: C, 48.14, 48.97; H, 4.09, 4.14; N, 6.30, 6.31; Co, 13.45, 13.44.

## (11) Cobalt Di-(6-methylsalicyl)-ethylenediimine.—

Red brown crystalline material obtained from aqueous propyl alcohol. The crystals were not solvated. Calcd.: C, 61.2; H, 5.09; N, 7.94; Co, 16.72. Found: C, 61.24, 61.14; H, 5.01, 4.94; N, 7.51, 7.44; Co, 16.80, 16.85.

These crystals would absorb 1.36% of their weight of oxygen when exposed at 150 p.s.i. oxygen pressure.

A sample was recrystallized from a pyridine-water mixture and a monopyrindinate was obtained as it lost 21.8% in weight when heated one and one-quarter hours at 170° *in vacuo*. This product was no more active than the above sample.

## (12) Cobalt Di-(4-methoxysalicyl)-ethylenediimine.—

Two preparations in an aqueous *n*-propyl alcohol solution yielded beautiful light brown crystals which were monohydrated as a sample lost 5.17% in weight on vacuum heating following drying in a vacuum desiccator. When desolvated the crystals are red. During exposure to 15 lb. oxygen slow uptake of about 0.9% was noted. When exposed to high pressure oxygen the crystals turned black with the absorption of 4.34% oxygen. This corresponds to two moles of chelate to one mole of oxygen. The black crystals release their oxygen when pumped, turning red again. Calcd.: C, 56.1; H, 4.67; N, 7.28; Co, 15.32. Found: C, 52.94, 52.94; H, 4.88, 4.92; N, 7.55, 7.68; Co, 14.57, 14.55.

The compounds listed in Table II were prepared by the same general methods as those described in detail in the first few compounds listed. None of those in Table II were found to absorb oxygen reversibly in the solid state.

II. Cobalt Chelates Prepared from Salicylaldehyde and its Derivatives, with  $\gamma,\gamma'$ -Diaminodipropylamine as the Amine Component

1. Cobalt Di-(salicyl)-3,3'-diimino-di-*n*-propylamine.—The following technique was developed which allows one to prepare this compound with an 85% yield.

Twenty-six and two-tenths grams of 3,3'-diamino-di-*n*-propylamine was dissolved in 400 ml. of 95% ethanol. To this was added 49 g. of salicylaldehyde. The Schiff base formed as considerable heat was evolved and the color changed to yellow. Fifteen grams of sodium hydroxide

TABLE II

Preparation	Color	Solvent of crystal	C	Analyses, %			Co
				H	N		
(13) Cobalt di-(salicylaldehyde) CoAc, aq. + salic. in alc.	Co(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> ) <sub>2</sub> Orange	2H <sub>2</sub> O	49.8	4.16		17.5	
			49.3	4.17		17.7	
			49.4	4.10		17.8	
(14) Cobalt di-(3-methylsalicylal)-ethylenediimine CoAc, aq. and Schiff base of aldehyde and amine in aqueous propyl alcohol	Co(C <sub>9</sub> H <sub>9</sub> ON) <sub>2</sub> Brown, changes to red on vacuum heating at 170°	None	61.2	5.09	7.93		
			61.24	5.05	8.06		
			61.32	4.99	8.18		
(15) Cobalt di-(salicylal)-propylenediimine CoAc, aq. + Schiff's base of aldehyde and amine in aq. <i>n</i> -propyl alcohol	Co(C <sub>17</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> ) Red needles from bz.	None	60.2	4.72	8.26	17.40	
			60.17	4.83	8.70	17.20	
			60.45	4.90	8.73	17.3	
			60.44	4.91		17.3	
(16) Cobalt di-(3-chlorosalicylal)-ethylenediimine CoAc, aq. + 3-Cl-Sal + en in aq. <i>n</i> -propanol or pyridine  pyridine peroxide Compound 4 recrystallized from pyridine in the presence of oxygen	Co(C <sub>8</sub> H <sub>6</sub> ONCl) <sub>2</sub> Brown oil or gelatinous ppt. Changing to red crystals upon prolonged heating  Black	None	Loses 23% by wt. upon vacuum heating at 170°				
			C <sub>6</sub> H <sub>5</sub> N <sup>1/2</sup> O <sub>2</sub>				
(17) Cobalt di-(5-methoxysalicylal)-ethylenediimine CoAc, aq. + Schiff base in aq. <i>n</i> -propyl alcohol	Co(C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> N) <sub>2</sub> Red crystals	H <sub>2</sub> O	56.1	4.67	7.28	15.3	
			53.9	4.55	7.44	17.3	
			53.6	4.55	7.56	17.4	
(18) Cobalt di-(3-allylsalicylal)-ethylenediimine CoAc, aq. + alde. and amine in aq. pyridine  recrystallized from CHCl <sub>3</sub> (also direct prep. in aq. <i>n</i> -propanol)  sodium salt of Schiff base + CoAc <sup>o</sup> aq.	Co(C <sub>11</sub> H <sub>11</sub> ON) <sub>2</sub> Red oil which crystallizes upon prolonged heating  Red crystals	C <sub>6</sub> H <sub>5</sub> N					
(19) Cobalt di-(3- <i>i</i> -propyl-6-methyl salicylal) ethylenediimine CoAc, aq. alde. and amine in aq. <i>n</i> -propanol	Co(C <sub>11</sub> H <sub>13</sub> ON) <sub>2</sub> Red-orange	None	65.95	6.87	6.41		
			66.3	6.49	6.81		
			66.5	6.50	6.86		
(20) Cobalt di-(salicylal)- <i>trans</i> -1,2-diiminocyclohexane CoAc, aq. + alde. and amine in aqueous <i>n</i> -propanol	Co(C <sub>10</sub> H <sub>11</sub> ON) <sub>2</sub> Yellow	None	63.3	5.28	7.40	15.56	
			63.45	5.13	7.32	15.0	
			63.49	5.08	7.18	14.9	
(21) Cobalt di-(salicylal)- <i>cis</i> -1,2-diiminocyclohexane CoAc, aq. + alde. and amine in aq. <i>n</i> -propanol	Co(C <sub>10</sub> H <sub>11</sub> ON) <sub>2</sub> Red crystals	None	63.3	5.28	7.40	15.56	
			63.1	5.01	7.71	15.60	
			63.0	4.99	7.85	15.87	
(22) Cobalt di-(3-phenylsalicylal)-ethylenediimine CoAc, aq. + sodium salt of Schiff base in water	Co(C <sub>14</sub> H <sub>11</sub> ON) <sub>2</sub> Brown	None	70.4	4.61	5.87	12.37	
				4.74	5.90	11.2	
				4.76	5.95	11.3	
(23) Cobalt di-(salicylal)- <i>trans</i> -1,2-diiminocyclopentane CoAc, aq. + alde. and amine in aq. <i>n</i> -propanol	Co(C <sub>19</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub> ) Yellow crystals	None	62.5	4.93	7.67	16.17	
			62.05	4.96	7.69	16.35	
			62.01	4.97	7.72	16.38	
(24) Cobalt di-(salicylal)-trimethylenediimine CoAc, aq. + sodium salt of Schiff's base in <i>n</i> -propanol recrystallized from chloroform	Co(C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> ) Yellow crystals  Yellow crystals	None	60.2	4.72	8.26	17.4	
			56.5	5.10	8.36	17.5	
			56.4	5.12	8.36	17.1	
			58.3	4.59	8.26	18.03	
(25) Cobalt di-(6-methoxyglalicylal)-ethylenediimine	Co(C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> N) <sub>2</sub>	None	58.2	4.64	8.28	18.09	
			56.15	4.67	7.27	15.3	

CoAc, aq. +  
or *n*-propyl  
Cobalt di-(3-  
CoAc, aq. +  
Easily recrystallized  
acetone  
Cobalt di-(3-  
ylenediimine  
Cobaltic tri  
CoSO<sub>4</sub> + sa  
aqueous (

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15.0; N, 10.22,

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Anal. Calc  
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3. Cobal  
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0° and a pre  
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irreversible o

TABLE II (Concluded)

Analyses, %				Preparation	Color	Solvent of crystal	Analyses, %			
C	H	N	Co				C	H	N	Co
49.8	4.16		17.5	CoAc, aq. + alde. and amine in aq. ethanol or <i>n</i> -propanol	Red-brown	None	56.13	4.48	7.32	15.1
49.3	4.17		17.7				56.00	4.45	7.37	
49.4	4.10		17.8	(26) Cobalt di-(3-ethylsalicylal)-ethylenediimine	Co(C <sub>10</sub> H <sub>11</sub> ON) <sub>2</sub>					
61.2	5.09	7.93		CoAc, aq. + alde. and amine in aq. ethanol	Red crystals	None	63.0	5.78	7.35	
61.24	5.05	8.06		Easily recrystallized from CHCl <sub>3</sub> , Et <sub>2</sub> O, or acetone			62.97	5.67	7.35	
61.32	4.99	8.18					62.88	5.68	7.40	
60.2	4.72	8.26	17.40	(27) Cobalt di-(4-hydroxy-6-ethylsalicylal)-ethylenediimine	Co(C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> N) <sub>2</sub>		55.70	5.57	6.49	13.69
60.17	4.83	8.70	17.23		Red crystals	H <sub>2</sub> O	55.0	5.90	6.65	13.2
60.45	4.90	8.73	17.3	(28) Cobaltic trisalicylal-diimine	Co(C <sub>7</sub> H <sub>6</sub> ON) <sub>3</sub>		54.7	5.88	6.70	13.3
60.44	4.91		17.3	CoSO <sub>4</sub> + salicylaldehyde and excess NH <sub>3</sub> in aqueous ethanol in the presence of air	Green-yellow	None	60.2	4.30	10.02	14.10
							59.7	4.29	9.99	14.1
							59.6	4.26	9.82	14.1

was dissolved in 25 ml. of water and added to the alcohol solution of the Schiff base. To this solution was added a hot solution of 50 g. of cobaltous acetate tetrahydrate in 75 ml. of water. This mixture was evaporated and pumped while being heated on the steam-bath. After a short while a yellow-brown crystalline material precipitated. The mixture was cooled, filtered under a rubber dam, washed with water and dried in a vacuum desiccator. When heated for one and one-half hours at 100° *in vacuo* it lost 4.40% in weight; calculated for one water, 4.37%.

*Analysis of hydrate.* Calcd.: C, 58.00; H, 6.09; N, 10.14; Co, 14.23. Found: C, 58.16, 57.88; H, 5.97, 5.70; N, 10.22, 10.35; Co, 14.16, 14.35.

The hydrate is insoluble in 6 *N* sodium hydroxide, slightly soluble in ether, acetone and water, quite soluble in 95% ethanol and pyridine and very soluble in chloroform and benzene. It will absorb oxygen reversibly in benzene solution. The oxygenated solution is deep red while the deoxygenated is brown.

Samples of this compound would pick up varying amounts of oxygen depending upon the preparation and the oxygen pressure. In one atmosphere of oxygen the samples would usually absorb about 1%. As the oxygen pressure was increased to 300 p.s.i., the samples would take up from 8 to 11.5%. The disadvantage of this compound with respect to its use for oxygen production, was that as it was cycled, considerable irreversible oxygenation would occur, and then, too, a high pressure is required to oxygenate it. A 1-1 oxygen uptake would correspond to an 8.4% increase in weight.

2. Cobalt di-(3-chlorosalicylal)-3,3'-diimino-di-*n*-propylamine was a brown crystalline compound which does not appear to be hydrated. After drying in a vacuum desiccator, of several samples tested, none would lose more than 1 to 2% in weight when heated *in vacuo*.

*Anal.* Calcd.: C, 51.6; H, 4.52; Co, 12.7; N, 9.03; Cl, 15.26. Found: C, 51.3, 51.2; H, 4.58, 4.59; Co, 12.8, 12.4; N, 9.78, 9.75; Cl, 15.48, 15.67.

Samples would absorb very little oxygen at one atmosphere. However, at high pressures (175-1300 p.s.i.) they would absorb up to 4.68% at room temperature and 5.18% at 0°. A 1-1 absorption would correspond to a 6.89% uptake.

3. Cobalt di-(3-methylsalicylal)-3,3'-diimino-di-*n*-propylamine was a brown-yellow crystalline product which does not appear to be hydrated as weight losses on vacuum heating were too low. The crystals are slightly soluble in hexane, soluble in ethanol, propanol and acetonitrile, and extremely soluble in benzene, ether, chloroform, methanol, acetone, dioxane and carbon tetrachloride. Calcd.: N, 9.90. Found: N, 9.3, 9.2.

This compound would absorb 6.84% oxygen when exposed to 180 p.s.i. for one hour at room temperature. At 0° and a pressure of 100 p.s.i. a sample absorbed 7.6%; calculated for a 1-1 ratio 7.55%. After several cycles irreversible oxygenation was observed.

4. Cobalt di-(5-nitrosalicylal)-3,3'-diimino-*n*-propylamine.—When prepared in the usual manner, a reddish crystalline non-hydrated compound resulted. A 2% oxygen uptake was observed, at 180 p.s.i. Calcd.: C, 49.3; H, 4.32; N, 14.37. Found: C, 48.34, 48.30; H, 4.25, 4.24; N, 14.43, 14.51.

The compound exploded while being ignited for a carbon and hydrogen analysis, so that no cobalt analysis could be obtained.

5. Cobalt di-(5-chlorosalicylal)-3,3'-diimino-di-*n*-propylamine was a brown crystalline non-hydrated compound which would absorb less than 1% of its weight of oxygen, at 180 p.s.i. Calcd.: C, 51.6; H, 4.52; N, 9.03; Co, 12.7. Found: C, 51.5, 51.4; H, 4.52, 4.44; N, 9.51, 9.56; Co, 15.51, 15.42.

6. Cobalt di-(5-methylsalicylal)-3,3'-diimino-di-*n*-propylamine was a crystalline monohydrated compound which was prepared in the usual way. It was clearly monohydrated for with three different preparations after drying in a vacuum desiccator and then heating for one and one-half hours at 120° *in vacuo*, the following weight losses were recorded: 4.07, 3.92 and 3.73%.

*Analysis of hydrate.* Calcd.: C, 59.77; H, 6.0; N, 9.50; Co, 13.34. Found: C, 59.93, 59.98; H, 6.65; N, 9.76, 9.86; Co, 13.65, 13.65.

The compound would absorb up to 6.86% in weight of oxygen at high pressure. However, it would not undergo many cycles, as considerable irreversible oxygenation occurred.

7. Cobalt di-(3-nitrosalicylal)-3,3'-diimino-di-*n*-propylamine was an orange-red crystalline monohydrate. A sample lost 3.31% in weight when heated for one and one-half hours at 150° *in vacuo*; calculated for 1 H<sub>2</sub>O, 3.57%.

*Analysis of hydrate.* Calcd.: C, 47.6; H, 4.57; N, 13.90. Found: C, 47.60, 47.54; H, 4.22, 4.13; N, 13.88, 14.01.

Dehydrated samples would absorb up to 3.5% of their weight of oxygen, calculated for 1-2 absorption 3.3%. It seemed fairly stable as little irreversible oxygenation was noted.

8. Cobalt di-(3-methoxysalicylal)-3,3'-diimino-di-*n*-propylamine was a green crystalline monohydrated compound. A sample lost 3.74% in weight when heated for one hour at 170° *in vacuo*.

*Analysis of anhydrous product.* Calcd.: C, 57.9; H, 5.92; N, 9.21; Co, 12.94. Found: C, 57.6, 57.4; H, 5.88, 5.86; N, 9.51, 9.59; Co, 13.16, 13.32.

It would absorb up to 5.66% of its weight of oxygen; 7.05% calculated for 1-1 uptake. Considerable irreversible oxygenation occurs.

9. Cobalt di-(salicylal)-3,3'-diimino-di-*n*-propylamine, a beautiful brown-yellow crystalline material which was unsolvated, would not absorb oxygen. Calcd.: C, 61.4; H, 6.09; N, 10.24; Co, 14.4. Found: C, 61.4, 61.2; H, 6.06, 6.04; N, 10.39, 10.51; Co, 14.6, 14.6.

Loses 23% by wt. upon vacuum heating at 170°

56.1 4.67 7.28 15.3  
53.9 4.55 7.44 17.3  
53.6 4.55 7.56 17.4

65.2 5.44 6.92 14.56  
64.98 5.37 7.03 14.56  
64.96 5.35 7.17 14.60  
After dehydration picked up 1.7% O<sub>2</sub> at 185 psi.  
65.95 6.87 6.41  
66.3 6.49 6.81  
66.5 6.50 6.86

63.3 5.28 7.40 15.56  
33.45 5.13 7.32 15.0  
33.49 5.08 7.18 14.9  
33.3 5.28 7.40 15.56  
33.1 5.01 7.71 15.60  
33.0 4.99 7.85 15.87

70.4 4.61 5.87 12.37  
4.74 5.90 11.2  
4.76 5.95 11.3

32.5 4.93 7.67 16.17  
32.05 4.96 7.09 16.35  
32.01 4.97 7.72 16.38  
30.2 4.72 8.26 17.4  
36.5 5.10 8.36 17.5  
36.4 5.12 8.36 17.1  
38.3 4.59 8.26 18.03  
38.2 4.64 8.28 18.09  
36.15 4.67 7.27 15.3

This chelate differs from the preceding compounds only in having a methyl group instead of a hydrogen atom attached to the central nitrogen. Its inability to absorb oxygen is undoubtedly associated with a steric interference by this methyl group, which probably occupies the space in a neighboring molecule, normally free for a sixth coordination group.

10. Cobalt di-(3-ethyl-4-hydroxysalicylal)-3,3'-diimino-di-*n*-propylamine was a brown crystalline non-hydrated product which would absorb only 1.24% oxygen when exposed to 1300 p.s.i. oxygen pressure for two hours.

*Anal.* Calcd.: C, 59.5; H, 6.41; N, 8.68; Co, 12.18. Found: C, 59.44, 59.65; H, 6.35, 6.30; N, 8.67, 8.59; Co, 12.15, 12.06.

11. Cobalt di-(3-ethyl-4-methoxysalicylal)-3,3'-diimino-di-*n*-propylamine.—A crystalline non-hydrated product which would absorb up to 5.6% of its weight of oxygen when exposed at 175 p.s.i. for two hours. It was not cycled enough to determine whether there was irreversible oxygenation. It was still perfectly reversible after three cycles.

*Anal.* Calcd.: C, 60.92; H, 6.83; N, 8.20; Co, 11.52. Found: C, 61.03, 61.26; H, 6.81, 6.81; N, 8.36, 8.39; Co, 11.47, 11.87.

12. Cobalt di-(6-chlorosalicylal)-3,3'-diimino-di-*n*-propylamine, was a crystalline monohydrate which resembles the 3-chloro compound, loses 3.9% in weight when heated *in vacuo*; calculated 1 H<sub>2</sub>O = 3.73%.

*Analysis of anhydrous product.* Calcd.: C, 51.6; H, 4.52; N, 9.03; Co, 12.7; Cl, 15.26. Found: C, 50.1, 50.1; H, 4.35, 4.30; N, 8.47, 8.44; Co, 12.8, 12.3; Cl, 16.1, 16.2.

Samples when tested with oxygen at 200 p.s.i. pressure would absorb only 2.5%.

*Analysis of hydrate.* Calcd.: C, 49.7; H, 4.76; N, 8.70; Co, 12.2; Cl, 14.7. Found: C, 48.54, 48.4; H, 4.58, 4.56; N, 8.59, 8.49; Co, 12.3, 12.3; Cl, 15.0, 15.4.

13. Cobalt di-(4-nitrosalicylal)-3,3'-diimino-di-*n*-propylamine.—This brown crystalline unhydrated compound will absorb less than 1% oxygen.

*Anal.* Calcd.: C, 49.3; H, 4.32; N, 14.37; Co, 12.1. Found: C, 48.1, 47.9; H, 4.19, 4.17; N, 13.5, 13.4; Co, 12.1, 12.3.

14. Cobalt di-(3-chloro-5-*t*-butylsalicylal)-3,3'-diimino-di-*n*-propylamine was a crystalline compound which is probably not solvated. After drying in a vacuum desiccator a sample lost 2.25% in weight when heated *in vacuo*; calculated 1 H<sub>2</sub>O = 3.04%. It did not absorb oxygen.

*Anal.* Calcd.: C, 58.2; H, 6.42; N, 7.28; Co, 10.23; Cl, 12.30. Found: C, 58.2, 57.9; H, 6.25, 6.24; N, 7.39, 6.97; Co, 10.0, 10.4; Cl, 10.26, 10.22.

15. Cobalt di-(3-ethylsalicylal)-3,3'-diimino-di-*n*-propylamine was a beautiful orange crystalline compound which is unsolvated. Samples tested would absorb up to 3.6% of their weight of oxygen at high oxygen pressures. Calculated for two moles of chelate to one mole of oxygen 3.6%.

*Anal.* Calcd.: C, 63.7; H, 6.86; N, 9.30; Co, 13.05. Found: C, 63.2, 63.02; H, 6.65, 6.63; N, 9.64, 9.66; Co, 13.28, 13.30.

16. Cobalt Di-(3-fluorosalicylal)-3,3'-diimino-di-*n*-propylamine.—This yellow crystalline unsolvated compound would absorb up to 3.73% of its weight of oxygen at one atmosphere of oxygen, but rather slowly. It seemed fairly stable, undergoing little irreversible oxygenation under the conditions tested. Calcd.: C, 55.55; H, 4.86; N, 9.72; Co, 13.66. Found: C, 55.59, 55.51; H, 4.87, 4.83; N, 9.74, 9.82; Co, 13.95, 14.21.

### III. Miscellaneous Cobalt Chelates

1. Cobalt Di-(acetylacetone).—Precipitates as a pink dehydrate. Inactive to oxygen following removal of the solvated water.

*Anal.* Co(C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O. Calcd.: C, 41.0; H, 6.1; Co, 20.1. Found: C, 40.8, 40.6; H, 6.05, 6.04; Co, 18.2, 17.7.

2. Cobalt di-(acetoacetic ester) was prepared as a red monohydrate, inactive to oxygen after water was removed.

*Anal.* Co(C<sub>6</sub>H<sub>9</sub>O<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O. Calcd.: C, 43.0; H, 6.0; Co, 17.6. Found: C, 42.5, 42.3; H, 5.8, 5.7; Co, 18.5, 18.8.

3. Vortmann's Sulfate.—The green and red forms of this cobalt compound were prepared according to Vortmann.<sup>8</sup> Neither form could be made to absorb oxygen reversibly.

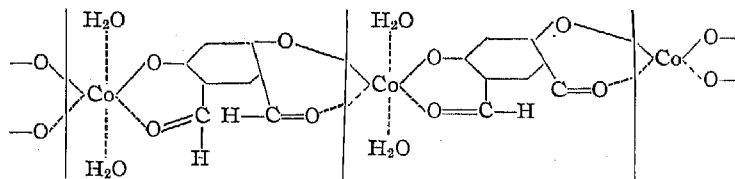
*Anal.* Green sulfate, Co<sub>2</sub>N<sub>8</sub>S<sub>2</sub>O<sub>10</sub>H<sub>26</sub>·2H<sub>2</sub>O. Calcd.: Co, 22.22; N, 23.8; H, 5.67. Found: Co, 22.3, 22.5; N, 22.2, 24.3; H, 5.44, 5.36.

4. Cobalt Di-(*o*-hydroxyacetophenone)-ethylenediamine.—A fine red crystalline product was obtained when prepared in boiling propanol. After drying in a vacuum desiccator a sample lost 2.4% in weight and did not absorb oxygen. It is slightly soluble in cold 95% ethanol, chloroform, propanol, dioxane, benzene and acetone. It is very soluble in pyridine.

When prepared at lower temperatures in aqueous propanol a fine brown crystalline product results. One sample lost 3.72% in weight while another lost 3.65% when heated at 120° for one hour *in vacuo*, calculated for 1H<sub>2</sub>O, 4.85%. When exposed to one atmosphere of oxygen for one hour no absorption occurred. When treated for one-half hour with 150 p.s.i. oxygen pressure, the sample absorbed 4.71% of its weight of oxygen. A 2-1 absorption would be 4.54%.

*Analysis of hydrate.* Calcd.: C, 58.2; H, 5.40; N, 7.54; Co, 15.9. Found: C, 58.75, 58.93; H, 5.17, 5.16; N, 7.39, 7.34; Co, 16.5, 16.5.

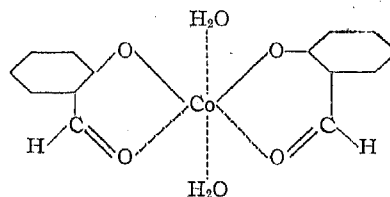
5. Cobalt 4-Hydroxy-5-formyl-salicylaldehyde (Polymer).—A yellow powder was formed when aqueous cobaltous acetate was added to an ethanol solution of 4-hydroxy-5-formyl-salicylaldehyde. It was filtered, washed with alcohol and ether and dried in a vacuum desiccator.



*Analysis of unit shown.* Calcd.: C, 37.05; H, 3.09; Co, 22.78. Found: C, 37.05; H, 3.11; Co, 22.59.

The compound should lose 13.9% when desolvated. A loss of 12.3% in weight was found experimentally.

The above structure is a reasonable one because of its relationship to cobalt disalicylaldehyde.



Both are yellow dihydrated solids.

6. Cobaltous Di-(picolinic Acid).—It was found possible to prepare this compound by heating a suspension of picolinic acid and cobaltous carbonate in water in the absence of air. A brown crystalline product formed. This was extracted with hot water from which beautiful yellow-orange crystals formed. These were washed with alcohol and ether and then dried. When heated *in vacuo* the color changed to pink and a weight-loss of 18.93% was observed, calcd. for 4H<sub>2</sub>O, 19.2%.

(8) Vortmann, *Ber.*, 40, 4609 (1907).

*Analysis of te*  
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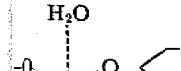
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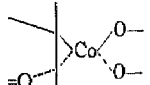
2H<sub>2</sub>O. Calcd.: Co, 22.3, 22.5;

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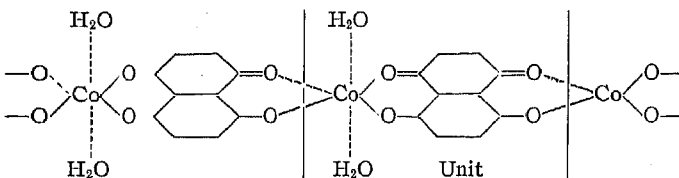
as found pos- suspension of water in the duct formed. hich beautiful e washed with eated *in vacuo* of 18.93% was

*Analysis* of tetrahydrate. Calcd.: C, 38.40; H, 4.26; N, 7.47; Co, 15.75. Found: C, 38.45, 38.60; H, 4.01, 3.93; N, 7.84, 7.84; Co, 15.70, 15.84.

When allowed to stand open to air the pink crystals slowly absorbed water and changed from pink back to yellow-orange. They would not absorb oxygen.

7. Cobalt Di-(*o*-aminobenzal)-ethylenediimine.—The Schiff base was prepared by mixing *o*-aminobenzaldehyde and ethylenediimine in a mixture of ethanol and dioxane. To this hot solution of Schiff base was added a hot aqueous solution of cobaltous acetate. A nicely crystallized red product was formed which was unsolvated. All efforts to solvate it with pyridine, etc., were in vain. The compound would not take up oxygen. Calcd.: C, 59.45; H, 4.96; N, 17.34; Co, 18.27. Found: C, 59.28, 59.28; H, 4.66, 4.56; N, 17.89, 18.09; Co, 17.8, 17.3.

8. Cobalt Naphthazarin (Polymer).—Excess naphthazarin was extracted off with ether.



*Anal.* Calcd.: C, 42.4; H, 2.83; Co, 20.85. Found: C, 41.5, 41.5; H, 3.00, 3.07; Co, 20.3, 20.2.

When heated a sample lost 10.0% in weight, calcd. for 2H<sub>2</sub>O per cobalt is 12.7%. Slowly absorbs water from the air following desolvation.

9. Cobalt Di-(1-*o*-hydroxyphenyl)-isoquinoline.—Precipitates as a monohydrate which is inert to oxygen after removal of the hydrated water.

*Analysis* of hydrate. Calcd.: C, 69.62; H, 4.26; N, 5.42; Co, 11.42. Found: C, 69.65, 69.78; H, 4.27, 4.32; N, 5.48, 5.53; Co, 11.61, 11.74.

10. Cobalt Di-(*o*-hydroxyacetophenone)-propylenediimine was a red crystalline unsolvated compound; inert to high pressure oxygen. Calcd.: C, 62.15; H, 5.45;

N, 7.63; Co, 16.1. Found: C, 62.11, 62.05; H, 5.62, 5.65; N, 7.82, 7.92; Co, 16.1, 16.4.

11. Cobalt Di-(2-hydroxy-3-ethoxyacetophenone)-ethylenediimine.—This one exists in two forms, one a red crystalline unsolvated form which is inert to high pressure oxygen. The other form is a yellow material which may be hydrated as a sample lost 8.34% in weight when heated one and one-half hours at 170° *in vacuo*; calcd. for 2H<sub>2</sub>O, 7.54%. A sample absorbed 2.04% oxygen when exposed at 125 p.s.i. oxygen pressure for half an hour. Calcd.: C, 59.90; H, 5.90; N, 6.35; Co, 13.38. Found: C, 59.9, 59.7; H, 6.14, 6.19; N, 6.40, 6.54; Co, 13.5, 13.2.

12. Cobalt Di-(acetylacetone)-ethylenediimine.—This orange-red compound was prepared according to Morgan.<sup>9</sup> It would absorb huge quantities of oxygen but most of it was of an irreversible nature. Frequently the chelate compound would burn in oxygen, particularly under high pressures of oxygen.

13. Cobalt Di-(salicylaldehyde)-ethylenediimine.—Prepared in aqueous alcohol, and red crystals were formed. They were washed with water, alcohol and ether, then dried in a vacuum desiccator. A sample lost 3.4% in weight when heated to 125° *in vacuo*, and turned black. When exposed to high pressure oxygen the sample increased slightly in weight.

*Analysis* of red form. Calcd.: C, 50.8; H, 3.63; N, 8.46; Co, 17.83. Found: C, 50.87, 50.93; H, 3.71, 4.01; N, 8.45, 8.62; Co, 17.84, 17.74.

*Analysis* of black crystals. Found: C, 51.40, 51.47, 51.64; H, 3.39, 3.42, 3.58; N, 8.41, 8.21; Co, 18.01, 18.07, 18.08.

### Summary

A group of fifty-seven chelate compounds have been prepared, characterized, and tested for the oxygen carrying properties.

(9) Morgan, *J. Chem. Soc.*, 117, 1457 (1920).

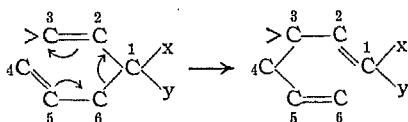
BERKELEY, CALIFORNIA RECEIVED DECEMBER 23, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN AND THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

## Activation Energies and Entropies of Activation in the Rearrangement of Allyl Groups in Three Carbon Systems<sup>1</sup>

BY E. GORDON FOSTER,<sup>2</sup> ARTHUR C. COPE<sup>3</sup> AND FARRINGTON DANIELS

The rearrangement of allyl groups in three-carbon systems was first reported by Cope and Hardy.<sup>4</sup> The general reaction reported was as follows



where x and y are CN or COOC<sub>2</sub>H<sub>5</sub> groups.

The belief was expressed that the reaction was

(1) An abstract of a thesis presented by E. G. Foster to the faculty of the University of Wisconsin as partial fulfillment for the requirements of the Master of Science degree, June, 1942.

(2) Present address: E. I. du Pont de Nemours & Co., Wilmington, Del.

(3) Present address: Massachusetts Institute of Technology, Cambridge, Massachusetts.

(4) Cope and Hardy, *THIS JOURNAL*, 62, 441 (1940).

analogous to the Claisen rearrangement and occurred by the same cyclic mechanism.<sup>4,5</sup> According to this mechanism, the number 4 carbon atom approaches the number 3 carbon atom and simultaneously electron pairs shift from the 1-6 position to the 1-2 position, from the 4-5 position to the 5-6 position, and from the 2-3 position to the 3-4 position. This cyclic mechanism was substantially confirmed when it was shown that the reaction was intramolecular and proceeded with an inversion of methyl substituted allyl groups.<sup>6</sup>

In a series of kinetic studies<sup>7</sup> it was demonstrated that the reaction was first order. It was also shown that the more electronegative the

(5) Hurd and Pollack, *J. Org. Chem.*, 3, 550 (1939).

(6) Cope, Hofmann and Hardy, *THIS JOURNAL*, 63, 1852 (1941).

(7) Cope, Hoyle and Heyl, *ibid.*, 63, 1843 (1941).