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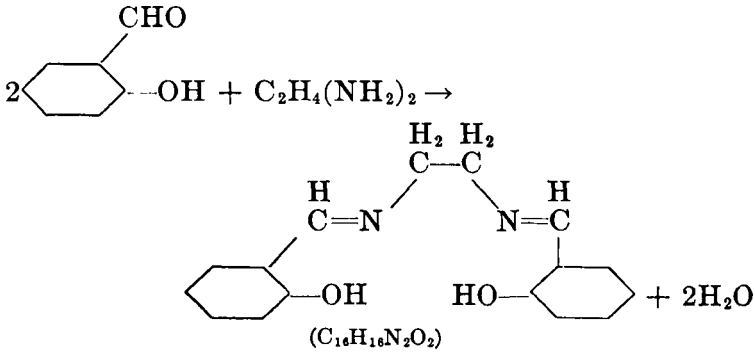
pered bottles to minimize atmospheric oxidation. The iodide is considerably less soluble in water than the bromide and both are sparingly soluble in liquid ammonia. Both salts are decomposed by bases and are converted to nickel(II) hydroxide by boiling with water. Thermal dissociation of the hexamminenickel(II) bromide yields successively compounds containing 2, 1, 0 mols of ammonia. The corresponding iodide is less stable and loses ammonia to form the diammine, and finally the unsolvated iodide.

References

1. Burgess and Eastes: *J. Am. Chem. Soc.*, **63**, 2674 (1941).
2. Watt and Davies: *ibid.*, **70**, 3753 (1948).
3. Richards and Cushman: *Z. anorg. Chem.*, **16**, 167 (1898).
4. Rammelsberg: *Pogg. Ann.*, **48**, 119, 155 (1839); **55**, 243 (1846).
5. Erdman: *J. prakt. Chem.*, [1] **1**, 266 (1834); [1] **7**, 249 (1836).

53. BIS(*N,N'*-DISALICYLALETHYLENEDIAMINE)-μ-AQUODICOBALT(II)

{Bis[*N,N'*-bis(*o*-hydroxybenzylidine)ethylenediamine]-μ-aquodicobalt(II)}



$$2C_{16}H_{16}N_2O_2 + 2CoCl_2 + 4NaOH \rightarrow \{[Co(C_{16}H_{14}N_2O_2)]_2H_2O\} + 4NaCl + 3H_2O$$

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The cobalt(II) derivative of *N,N'*-disalicylalethylenediamine, a Schiff base prepared from salicylaldehyde and ethylenediamine, was first described by Pfeiffer, Breith, Lübbe, and Tsumaki[1] and further studied by Tsumaki.[2] It was later investigated intensively by Diehl and coworkers,[3] who showed that it is a binuclear compound in which a molecule of water acts as a bridging group (μ-aquo) between two cobalt atoms, each of which is surrounded by the quadridentate, chelating molecule of the Schiff base. This material has the unique property of reversibly absorbing and releasing oxygen. The addition of the oxygen is thought to take place by the formation of a peroxo group, which makes a second bridge between the two cobalt atoms and fills the sixth coordination position of each cobalt atom. Thus, one oxygen molecule is absorbed for each two cobalt atoms, corresponding to a gain in weight of 4.79 per cent.

The compound was originally prepared by bringing cobalt acetate, ethylenediamine, and salicylaldehyde together simultaneously in an aqueous-alcohol reaction medium. Unless care is exercised in this procedure the product is relatively impure, but if all the factors mentioned below are controlled, a satisfactory material can be obtained by this direct mixing method. A much better procedure involves the preliminary formation of the Schiff base and its subsequent reaction with a cobalt salt. In this manner a product is obtained containing the correct stoichiometric ratio of salicylaldehyde to ethylenediamine; slight departure from the equivalent quantities or inadequate stirring in the direct mixing method leads to contamination of the product by the cobalt derivative of salicylaldehyde, by cobalt–ethylenediamine compounds, or by the Schiff base.

The recommended synthesis is complicated under certain conditions by the formation of three by-products, olive, black, and red in color, all of which are inactive toward oxygen. The olive by-product is formed on prolonged contact of the oxygen-carrying material with hot water,

either during the formation of the material or during drying. The presence of any free acid, especially when hot, promotes the formation of this olive by-product. A critical point in the procedure is, therefore, the drying step, which must be carried out as rapidly as possible.

The black by-product is formed from the oxygen-carrying compound by contact with oxygen, especially in the presence of alcohol; its formation is not observed in the procedure given here. It is soluble in water and removed by washing. The red by-product results from the action of alkali on the oxygen-carrying compound. In the procedure given below, a slight deficiency of alkali is used to avoid its formation. It is isomeric with the oxygen-carrying compound, but inactive toward oxygen.

Procedure

***N,N'*-Disalicylalethylenediamine.** The salicylaldehyde is purified by the process of shaking or by standing in contact with powdered calcium carbonate, followed by distillation. To a solution of 244 g. (2 mols) of the purified material in 1 l. of boiling 95 per cent ethyl alcohol is added 60.1 g. (1 mol) of ethylenediamine; this is measured by weighing out the appropriate amount of aqueous solution. If the concentration of the ethylenediamine is not known within a few per cent, a sample should be titrated against a standard acid, using methyl red as indicator. In 20 to 30 seconds the mass becomes solid with formation of a bright yellow, crystalline material. The reaction mixture is cooled and filtered on a Büchner funnel, and the precipitate is spread in thin layers on absorbent paper to dry. It may be recrystallized from 6 l. of hot 95 per cent alcohol or used without further purification. It will dissolve somewhat more readily in the next step if it is not allowed to dry completely. Yield, 255 g. (95 per cent). The compound melts at 123°.

Bis(*N,N'*-disalicylalethylenediamine)-μ-aquodicobalt. One mol (268 g.) of finely ground disalicylalethylenedi-

amine, 79.5 g. (2 mols less 0.5 g.) of sodium hydroxide and 5 g. of sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, are dissolved in 3 l. of boiling water. Solution of the disalicylalethylenediamine requires from 10 to 20 minutes and depends on the state of subdivision of the material and the agitation given the mixture. Stirring is continued subsequently while a solution of 238 g. (1 mol) of hexahydrated cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$) in 500 ml. of hot water is added, until the mixture sets up to a reddish-brown paste. The mass is covered with ½ in. of water and allowed to stand for at least 15 minutes. It is then centrifuged* until most of the mother liquor has been removed and a hard cake remains. Three portions of water (each about 250 ml.) are added, the liquid being removed by centrifugation after each addition. The cake is removed from the centrifuge basket and mixed thoroughly with 1.5 l. of water so that no large particles remain and a uniform slurry is obtained. It is centrifuged again, and is finally washed with a few hundred milliliters of water. The filtrate will never be colorless, but will be light brown. The cake is finally centrifuged as dry as possible. If a letter press† is available, the cake should be wrapped in a few thicknesses of towel and pressed. It is then broken into small pieces and dried at 100° in a good vacuum. The final vacuum drying apparatus need not be complicated but should be provided with a large gas outlet and a condenser to allow adequate facility for the escape of steam. Direct connection to a water pump is poor inasmuch as a water pump cannot handle a sufficiently large volume of vapor. A satisfactory drier may be constructed from pyrex tubing, 2 in. in diam-

* If a centrifuge is not available, suction filtration may be substituted. However, the residual water left on the cake is less when a material is centrifuged than when filtered by suction, so the use of a centrifuge is much to be preferred. The centrifuge of the International Equipment Company, No. 418, with a bronze basket is ideal for the purpose.

† The use of a hydraulic press is desirable if the material has been separated by centrifuging and almost necessary if it is separated by suction filtration.

eter and 36 in. long. This tube is surrounded by a second pyrex tube 3 in. in diameter and just slightly shorter, which serves as a jacket through which steam can be passed. The inner tube can be supported concentrically in the outer tube at one end by a few turns of rubber tubing of suitable diameter, which also serves as a steam inlet. At the other end, a single turn of rubber tubing can be used, leaving a gap at the bottom for the condensate to escape. The material is placed in the inner tube on a tray made by bending a strip of tin plate into a semicircular cross section. One end of this tube is stoppered and the other connected through a tube 0.75 in. in diameter to a condenser, receiver, and water pump. The condenser and receiver may consist simply of a 1-l. round-bottomed flask cooled by a stream of running water. The yield is 300 g., or 90 per cent; oxygen-carrying capacity, 4.7 to 4.8 per cent; theoretical capacity, 4.79 per cent.*

Properties

Bis(N,N'-disalicylalethylenediamine)-μ-aquodicobalt is a maroon-colored, microcrystalline material, which is somewhat soluble in pyridine, chloroform, and benzene. It crystallizes from pyridine and chloroform with solvent of crystallization that can be removed by heating at 120° in a vacuum; the resulting product, however, is of low oxygen-carrying capacity. The material absorbs oxygen in the dry state, turning from maroon to black in color. The rate of oxygenation of the material is greatly affected by pressure and temperature, being a maximum with respect to tem-

* The oxygen-carrying capacity of the material is determined by exposing a weighed sample on a boat to oxygen or air at increased pressure and obtaining the increase in weight. This is best carried out in a metal tube equipped with a screw cap, pressure gage, line to oxygen tank or air line, and release valve. A period of 10 minutes in oxygen at 100 pounds pressure is sufficient to saturate the compound, after which the pressure may be released and the boat weighed rapidly. It is usually necessary to deoxygenate the material at 100° in a vacuum to secure a correct initial weight of the sample. The maximum oxygen-carrying capacity is obtained after two or three cycles of oxygenation and deoxygenation.

perature at about 20°. The oxygen is expelled by heating the material to 65°. It also absorbs nitrogen(II) oxide and nitrogen(IV) oxide, but irreversibly. It does not absorb carbon monoxide, nitrous oxide, or sulfur dioxide. The deoxygenated form of the material is paramagnetic, the oxygenated form diamagnetic. It catalyzes the luminescence of 3-aminophthalhydrazide (luminol) in alkaline solution containing hydrogen peroxide. The compound is quite toxic; inhalation of the finely divided dust should be avoided.

References

1. PFEIFFER, BREITH, LÜBBE, and TSUMAKI: *Ann.*, **503**, 84 (1933).
2. TSUMAKI: *Bull. Chem. Soc. Japan*, **13**, 252 (1938).
3. DIEHL and co-workers: "Studies on Oxygen-carrying Cobalt Compounds," Iowa State College, Ames, Iowa, (1946).