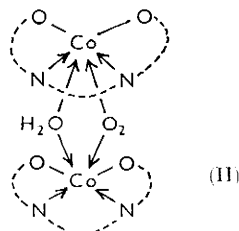
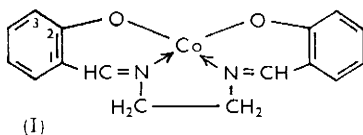


161. *Bridging Water in the Oxygen-carrying NN'-Ethylenebis-(salicylideneiminato)cobalt(II) Complex.*

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The suggestions that the compound *NN'*-ethylenebis(salicylideneiminato)-cobalt(II) contains an aquo bridge, and that this is essential for the complex to function as a synthetic oxygen-carrier, have not been confirmed by means of infrared and other investigations.

THE oxygen-carrying compound (I), *NN'*-ethylenebis(salicylideneiminato)cobalt(II), has been extensively studied by Calvin and by Diehl, and their co-workers.<sup>1</sup> The former assigned formula (I) to the compound, but the latter considered it to be binuclear, the two units being joined by an aquo bridge. In recent review articles,<sup>2-4</sup> Diehl's structure seems to be generally accepted, and the compound is quoted as the only one known to contain a bridging water molecule of this type.



Diehl's experimental evidence for the aquo bridge is as follows.<sup>3,4</sup> (1) After the compound had been refluxed with anhydrous pyridine, and the pyridine distilled off, an

<sup>1</sup> The references are collected together in Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, 1952, ch. 8, and in refs. 2, 3, and 4.

<sup>2</sup> "The Chemistry of the Coordination Compounds," ed. Bailar, Reinhold, New York, 1956, p. 391.

<sup>3</sup> Stewart, Estep, and Sebastian, *U.S. Bur. Min., Inform. Circ.*, No. 7906, 1959.

<sup>4</sup> Vogt, Faigenbaum, and Wiberley, *Chem. Rev.*, 1963, **63**, 269.

amount of water was found in the distillate (Karl Fischer titration) which corresponded to a single water bridge. Diehl considered that the pyridine had displaced the water bridge. Stewart *et al.*, have reported similar results.<sup>3</sup> (2) Compounds prepared under anhydrous conditions would not carry oxygen unless they had been pretreated with water; Diehl therefore considered that water was essential. (3) The oxygen-carrying capacity of the solid deteriorates on long cycling with oxygen. Diehl ascribed this to gradual removal of the bridge, and the rapid irreversible oxidation, in solvents such as pyridine, to rapid displacement of the water bridge by the solvent, to give a compound which would no longer combine reversibly with oxygen.

Since the compound cannot be recrystallized, Diehl considered that traces of impurities would mask the small analytical differences expected for compounds with and without a bridging water molecule. Poor solubility and reaction with the solvent prevent molecular-weight determinations.

During a study of the reaction of nitric oxide with oxygen-carrying compounds,<sup>5</sup> this compound has been reinvestigated, and new evidence supporting the monomer structure (I) has been obtained.

*Infrared Investigations.*—The infrared spectra of the unoxygenated and oxygenated compounds, prepared according to Diehl,<sup>6</sup> do not show the absorptions in the 3300 and 1600  $\text{cm}^{-1}$  regions expected for water. Bailes and Calvin have reported several substituted derivatives of (I), *e.g.*, that from 3-methoxysalicylaldehyde, to be monohydrates.<sup>7</sup> Such compounds were considered by Diehl to contain one water molecule per cobalt atom in addition to the water bridge. The 3-methoxy-compound shows a broad absorption at 3270  $\text{cm}^{-1}$  and a sharp absorption at 1650  $\text{cm}^{-1}$ , characteristic of water, both of which disappear on heating *in vacuo* to 170°, with a concomitant loss in weight corresponding to one water molecule. A sample of this compound was prepared in the presence of deuterium oxide and was found, from deuterium analysis, to contain 50% of deuterium oxide of hydration. The protium oxide bands at 3270 and 1650  $\text{cm}^{-1}$  were weakened, and the corresponding deuterium oxide bands appeared at 2410  $\text{cm}^{-1}$  and near 1220  $\text{cm}^{-1}$ , the latter only as a broadening of a band already present. The hydrate of the 3-methoxy-compound is not oxygen-sensitive although, after removal of the water molecule, it rapidly absorbs oxygen. This, and the high temperature required to remove the water, suggest that it is firmly bonded to the cobalt atom, presumably giving a five-co-ordinate structure. The water molecule is so readily detected by means of infrared techniques that it seems unlikely that a water bridge would be missed in (I). Ueno and Martell<sup>8</sup> make no mention of infrared absorptions due to water in their spectrum of (I).

*Other Investigations.*—On thermogravimetric analysis, (I) showed a small decrease in weight between 45 and 85°, which was due to the loss of a small amount of oxygen which had been reversibly absorbed between weighing and heating the sample. No more weight-loss occurred until about 240°, when decomposition began. There was no stable phase that could be attributed to loss of water.

A small amount of (I) was prepared, by Diehl's method, in deuterium oxide. The infrared spectrum was identical with that of the compound prepared in ordinary water, and deuterium analysis gave the D : H ratio as 0.8%, instead of 7.2% as expected for a fully deuterated water bridge.

In the following experiment, a water bridge, if present, should have been destroyed, and yet the oxygen-carrying capacity of the compound was not impaired, in contradiction of (2) above. A small sample of (I), of oxygen-carrying capacity 4.9% (theoretical, 4.9%), was refluxed with pyridine under nitrogen, and three-quarters of the pyridine was distilled off. According to Diehl, this should have removed any water in the compound. The

<sup>5</sup> Earnshaw, Hewlett, and Larkworthy, *Nature*, 1963, **199**, 483.

<sup>6</sup> Diehl and Hach, *Inorg. Synth.*, 1950, **3**, 196.

<sup>7</sup> Bailes and Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

<sup>8</sup> Ueno and Martell, *J. Chem. Phys.*, 1956, **60**, 1270.

orange monopyridinate, which crystallized from the residue, was filtered off under nitrogen and dried *in vacuo*. Once dry, it was stable to air. On activation, by heating under reduced pressure at 170°, it lost 19.2% by weight (1 pyridine  $\equiv$  19.5%) to give a product of oxygen-carrying capacity 4.9%. The formation of solvates containing one solvent molecule is common in this type of compound.

*Evidence from Other Sources.*—X-Ray results<sup>1</sup> show that molecules of (I) are stacked parallel in the crystal; however, the expected approximately tetrahedral disposition of bonds about the oxygen atom of an aquo bridge would prevent this, and would cause molecules of (I) to clash unless the Co-O bond distance was uncommonly large.

Calvin has reported the preparation of inactive forms of (I) and related compounds. However, his fully active (I) was prepared by recrystallizing an inactive form from pyridine under nitrogen, and then activating the pyridinate as above. We have obtained similar results. Apparently, the inactive isomer has a crystal structure which does not allow access of the oxygen molecule. Once the pyridine has been removed, a more open structure remains, which will allow reaction with oxygen. The effect of water on Diehl's inactive compounds is perhaps similar.

Diehl's experiment for the detection of water [(I) above] was carried out under anhydrous conditions, but not under nitrogen. On exposure to air, a solution of (I) in pyridine immediately turns black, and a pyridinate peroxide can be isolated.<sup>7</sup> It is believed that, in air at the temperature of boiling pyridine, oxidation of the complex occurred to form water, which reacted with the Karl Fischer reagent. In solution, irreversible oxidation soon occurs.<sup>1</sup> The oxygen-carrying capacity of the solid compound is known to deteriorate on long cycling with oxygen even at room temperature and below, and water is among the products. Stewart *et al.*<sup>3</sup> found that about twice as much water was produced during deterioration of the solid as the removal of a water bridge alone would warrant. Acid gases, presumably including carbon dioxide, were also produced, so that the deterioration would seem more likely to be due to oxidation of the compound, as suggested by Calvin,<sup>1</sup> than to removal of a water bridge [(3) above].

Mitchell and Smith<sup>9</sup> found that (I) will react directly with the Karl Fischer reagent, but this was ascribed to oxidation of cobalt(II) to cobalt(III) by the reagent, and not to the presence of water in the molecule.

Calvin's analyses and those reported here agree more closely with the monomer structure.

Diehl believed that, on oxygenation, the cobalt(II) atom should become six-co-ordinate, *i.e.*, co-ordinatively saturated, by the formation of a "peroxide" bridge, as depicted in (II). Intermolecular bonding of the oxygen molecule would seem more feasible.

However, it is now known that a metal such as cobalt(II) with a spin-paired  $d^7$  configuration, as in these complexes,<sup>1</sup> is unlikely to form regular octahedral complexes, and five-co-ordination is very common.<sup>5,10</sup> The oxygenated compound and the solvates which are inactive towards oxygen are then not unusual in being five-co-ordinate, and the postulation of a water bridge to make the cobalt atom six-co-ordinate in the oxygenated compound is unnecessary.

#### EXPERIMENTAL

Compound (I) was prepared under nitrogen by Diehl's method<sup>6</sup> (Found: Co, 18.2. Calc. for  $C_{16}H_{14}N_2O_2Co$ : Co, 18.1%. Calc. for  $C_{16}H_{14}N_2O_2Co, \frac{1}{2}H_2O$ : Co, 17.6%). The compound was prepared in small quantity in deuterium oxide by the same method. Separate solutions of the reactants were heated, in deuterium oxide on a water-bath for several hours before mixing, to allow complete exchange. Compared with the amount of deuterium oxide used, the protium oxide introduced in the reactants was negligible.

NN'-Ethylenebis-(3-methoxysalicylideneiminato)cobalt(II) hydrate was prepared by Diehl and Liggett's method,<sup>11</sup> using aqueous alcohol. The loss in weight on heating to 170° *in vacuo*

<sup>9</sup> Mitchell and Smith, "Aquametry," Interscience, New York, 1948, p. 393.

<sup>10</sup> Nyholm, *Proc. Chem. Soc.*, 1961, 292.

<sup>11</sup> Diehl and Liggett, *Iowa State Coll. J. Sci.*, 1947, **21**, 326.

was 5.1% (Calc. for  $1\text{H}_2\text{O}$ : 4.5%) (Found: Co, 14.5. Calc. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Co}, \text{H}_2\text{O}$ : Co, 14.6%. Calc. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Co}, 1\frac{1}{2}\text{H}_2\text{O}$ : Co, 14.3%). The compound with the water of hydration partly replaced by deuterium oxide was prepared by adding cobalt acetate, in deuterium oxide, to the ligand in a minimum quantity of hot dimethylformamide which had been dried and distilled under reduced pressure.

*Physical Measurements.*—The infrared spectra were recorded, in Nujol and hexachlorobutadiene mulls, on the Grubb-Parsons GS 2A grating instrument. The thermal decomposition of (I) was studied by using an automatic direct-reading Stanton thermobalance, model HT-D, between room temperature and 650°.

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