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## A General Synthesis of Cobalt(III) Complexes; A New Intermediate, $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$

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A general method of preparing symmetrical cobalt(III) complex compounds utilizing a new intermediate, sodium tris-carbonatocobaltate(III) trihydrate, is discussed with respect to its advantages over present methods. A representative number of symmetrical cobalt(III) complex compounds have been prepared. These include salts of cobalt amines, inner charge complexes and a variety of cobaltates. The intermediate is easily prepared and stored. It is reactive under mild conditions and gives good yields in most cases. Several new cobalt(III) complex compounds of easily oxidized ligands were prepared and identified.

### Introduction

Symmetrical cobalt(III) complex compounds generally have been prepared by the oxidation of cobalt(II) ion in the presence of the ligand, direct coordination of the ligand with freshly prepared hydrous cobalt(III) oxide or displacement of ammonia from hexamminecobalt(III) ion.

By far the largest number of complexes of cobalt(III) are prepared by oxidation of the cobalt(II) ion in the presence of the ligand. Such a procedure works well when applied to ligands which are inert toward oxidation and when the ligand shows a relatively strong coordinating ability. The preparation breaks down when applied to ligands which are sensitive to oxidation or when applied to ligands where solvent may be an effective competitor.

Cobalt(III) oxide is difficult to filter and cannot be utilized after storage. Its use has been restricted to the preparation of amino acid complexes.

The use of hexamminecobalt(III) ion as an intermediate is generally restricted to the preparation of amine chelates. Here, the increased stability which results from ring formation coupled with the volatility of ammonia is sufficient to drive the reaction to completion.

It should be noted also that in most cases syntheses require the basic form of the ligand. Basic conditions will, in general, increase the sensitivity of the ligand to oxidation, allow  $\text{CO}_2$  absorption by the ligand and increase volatility problems.

In an attempt to avoid the difficulties associated with other general methods of synthesis, we have investigated the utility of a new intermediate complex of cobalt(III). It is formed by the oxidation of cobalt(II) ion by hydrogen peroxide in the presence of excess sodium bicarbonate. Duval<sup>1</sup> has reported that such an oxidation results in the formation of the green, insoluble compound,  $\text{Co}_2(\text{CO}_3)_3$ . It is reported to be stable when dry. The compound isolated from a similar oxidation in the present investigation may best be represented as sodium tris-carbonatocobaltate(III) trihydrate,  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ . With our present data it is not possible to exclude the structure  $\text{Na}_3[\text{Co}(\text{HCO}_3)_3(\text{OH})_3]$ . It is important to notice, however, that the number of base equivalents per mole of intermediate is six in both assignments. Thus, the number of coordination positions per mole is equal to the number of base equivalents per mole. Ligands may be added in their acid form to liberate  $\text{CO}_2$  and produce the desired complex. Volatility of  $\text{CO}_2$  will drive the

reaction to completion. When the ligand does not carry a sufficient number of protons, additional acid may be added in the form of  $\text{HNO}_3$  or  $\text{HClO}_4$ .

Sodium tris-carbonatocobaltate(III) trihydrate is a stable compound which provides a reactive source of Co(III) in the presence of a proton donor.

A representative group of cobalt(III) coordination compounds has been prepared to illustrate the general applicability of the method. The following compounds, previously reported, were prepared using the intermediate  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ : tris-ethylenediaminecobalt(III) chloride,<sup>2</sup> tris-acetylacetonatocobalt(III)<sup>3</sup> and tris-benzoylacetonatocobalt(III).<sup>4</sup> The following new compounds also were prepared: tris-(1,3-diamino-2-propanol)-cobalt(III) nitrate (a cobalt(III) compound containing two tridentate molecules of 1,3-diamino-2-propanol has been reported<sup>5</sup>), tris (*o*-aminophenol)-cobalt(III), sodium tris-mercaptoacetatocobaltate(III), tris-ethylenediamine-cobalt(III) tris-salicylatocobaltate(III) and sodium tris-ethylenedimercaptocobaltate(III).

### Experimental

**Cobalt Analysis.**—Cobalt was determined spectrophotometrically as the thiocyanate complex of Co(II).<sup>6</sup>

**Sodium Tris-carbonatocobaltate(III) Trihydrate.**—A 50 ml. solution of 29.1 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.10 mole) and 10 ml. of 30% hydrogen peroxide (excess) was added dropwise with stirring to a cold slurry of 42.0 g. of sodium bicarbonate (0.50 mole) in 50 ml. of  $\text{H}_2\text{O}$ . The mixture was allowed to stand at 0° for 1 hr. with continuous stirring. The olive product was filtered, washed on the filter with three 10 cc. portions of cold water, then thoroughly washed with absolute alcohol and dry ether; yield: 33.3 g., 92% of theoretical; 93° dec.

*Anal.* Calcd. for  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ : C, 9.95; H, 1.66; Co, 16.3. Found: C, 8.72, 9.03; H, 1.39, 1.69; Co, 16.2.

**Tris-ethylenediaminecobalt(III) Chloride.**—A slurry of 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) was mixed with 4.0 g. of ethylenediamine dihydrochloride and warmed on a steam-bath for 30 minutes. Alcohol was added to precipitate an orange product which was recrystallized from an ethanol-water solution; yield: 3.13 g., 91% of theoretical.

*Anal.* Calcd. for  $[\text{Co}(\text{en})_3]\text{Cl}_3$ : C, 20.8; H, 6.95. Found: C, 20.9; H, 6.75.

**Tris-(1,3-diamino-2-propanol)-cobalt(III) Nitrate.**—A 25 ml. solution of 3.0 g. of 1,3-diamino-2-propanol (0.033 mole) and 4.5 ml. of 70% nitric acid (0.71 mole) was added slowly

(2) S. M. Jorgensen, *J. prakt. Chem.*, [2] **39**, 14 (1899).

(3) B. E. Bryant and W. C. Fernelius, "Inorganic Syntheses," Vol. V, McGraw-Hill, New York, N. Y., 1957, p. 188.

(4) B. Emmert and O. Schneider, *Ber.*, **69B**, 1316 (1936).

(5) J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Res.*, **17B**, 331 (1939).

(6) E. B. Sandell, "Determination of Traces of Metals," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 281.

(1) C. Duval, *Compt. rend.*, **191**, 615 (1930).

to 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) was warmed on a steam-bath for 30 minutes. The dark rose product was precipitated by evaporation to 10 ml., filtered and washed with acetone; yield: 4.1 g., 79% of theoretical; 122–124° dec.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_{10}\text{N}_2\text{O}_3)](\text{NO}_3)_3$ : C, 21.0; H, 5.82. Found: C, 20.4; H, 5.55.

**Tris-acetylacetonatocobalt(III).**—A mixture of 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole), 3.0 g. of acetylacetonone (0.03 mole) and 2.0 ml. of 70% nitric acid was refluxed for 30 minutes in a 60% acetone-water mixture. The solution was evaporated until a green precipitate appeared. The mixture was cooled and filtered. The product was recrystallized from acetone and water; yield: 3.4 g., 95% of theoretical; 220° dec.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3]$ : C, 50.5; H, 5.90. Found: C, 50.2; H, 6.08.

**Tris-benzoylacetonatocobalt(III).**—The procedure for tris-acetylacetonatocobalt(III) was employed; yield: 4.4 g., 81% of theoretical; 213° dec.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_{10}\text{H}_9\text{O}_2)_3]$ : C, 66.4; H, 4.98. Found: C, 65.9; H, 5.28.

**Tris-*o*-aminophenolcobalt(III).**—A slurry of 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) in 30 ml. ethanol was added to 4.4 g. of *o*-aminophenol hydrochloride (0.03 mole) and the mixture was refluxed for an hour. The NaCl was removed by filtration and the filtrate was concentrated to precipitate a brown product which was washed with cold water. The product was recrystallized from an alcohol-water solution; yield: 3.4 g., 88% of theoretical; 208–211° dec.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_6\text{H}_6\text{NO})_3] \cdot 1.5\text{H}_2\text{O}$ : C, 52.7; H, 5.14. Found: C, 52.9; H, 5.18.

**Sodium Tris-mercaptopacetatocobaltate(III).**—A 50 ml. aqueous solution of 2.8 g. of mercaptoacetic acid (0.03 mole) was added to 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) with stirring. The mixture was warmed on a steam-bath for 30 minutes. The dark green solid that separated upon cooling was washed with acetone; yield: 3.4 g., 85% of theoretical; 262° dec.

*Anal.* Calcd. for  $\text{Na}_3[\text{Co}(\text{C}_2\text{H}_3\text{OS})_3] \cdot 6\text{H}_2\text{O}$ : C, 14.25; H, 3.55. Found: C, 14.3; H, 3.45.

**Tris-ethylenediaminecobalt(III) Tris-salicylatocobaltate(III).**—A solution of 4.3 g. of salicylic acid (0.03 mole) and 4.2 g. of tris-ethylenediaminecobalt(III) nitrate (0.01 mole) in 500 ml. of  $\text{H}_2\text{O}$  was prepared. With stirring, 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) was added in small portions and the mixture heated to boiling. The insoluble residue was discarded and the filtrate was evaporated at room temperature to 20 ml. A rose-beige product was collected and washed with ethanol; yield: 0.9 g., 15% of theoretical; 223–229° dec.

*Anal.* Calcd. for  $[\text{Co}(\text{C}_2\text{H}_3\text{N}_2)_3][\text{Co}(\text{C}_7\text{H}_4\text{O}_3)_3]$ : C, 45.9; H, 5.10; N, 11.88. Found: C, 46.9; H, 5.41; N, 10.83. The analysis indicated contamination with a small amount of salicylic acid.

**Sodium Tris-ethylenedimercaptocobaltate(III).**—To a warm solution of 3.1 g. of ethylenedimercaptan (0.033 mole), 3.6 g. of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (0.01 mole) was added with stirring. A black precipitate appeared immediately. The mixture was warmed for 30 minutes and filtered. The product was washed repeatedly with hot water, washed with acetone and dried at 110° for 8 hr.; yield: 4.2 g., 95% of theoretical.

*Anal.* Calcd. for  $\text{Na}_3[\text{Co}(\text{C}_2\text{H}_4\text{S}_2)_3] \cdot 2\text{H}_2\text{O}$ : C, 16.4; H, 3.64. Found: C, 15.9; H, 3.06.

### Discussion

The structural formula  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  is the simplest formula to fit available analytical data. Since no weight was lost after drying at 80° over  $\text{P}_2\text{O}_5$  *in vacuo* for 10 hr., an alternate structure  $\text{Na}_3[\text{Co}(\text{HCO}_3)_3(\text{OH})_3]$  is possible. The decom-

position temperature of 93° precludes further attempts to elucidate the structure by dehydration.

There has been some controversy as to whether carbonate can form a stable four-membered ring in carbonato complexes or whether a molecule of water is needed for a bicarbonato-hydroxo structure. The fact that carbonate can indeed fill two coordination sites has been shown unequivocally by McCutcheon and Schuele<sup>7</sup> in their isolation of  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO}_3)_3]$ . Moreover, Lamb and Mysels found<sup>8</sup> that one may remove water from  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$  without destruction of the complex. A chelate structure, similar to that proposed for  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ , has been postulated for the analogous potassium compound<sup>9</sup> on the basis of analytical data and absorption spectra.

A striking solubility difference is responsible for the increased utility of sodium tris-carbonatocobaltate(III) trihydrate over the potassium analog. Sodium tris-carbonatocobaltate is water insoluble. It may be easily separated from the reaction mixture, and when completely dry it can be stored on the shelf for future use. In contrast, potassium tris-carbonatocobaltate(III) trihydrate is water soluble and difficult to isolate from the potassium bicarbonate impurity. Its aqueous solution is somewhat unstable in the absence of excess bicarbonate, forming hydrous cobalt(III) oxide. Yet once isolated, it too can be used for the synthesis of cobalt(III) compounds.<sup>10</sup>

The use of tris-carbonatocobaltate(III) trihydrate offers several desirable features. An oxidant need not be present, for a source of cobalt(III) ion is available. The acid form of ligands may now be used. The intermediate is easily prepared, storable for later use and reactive under mild conditions.

Because the source of cobalt(III) ion obviates the need for an oxidant, the reaction of compounds such as *o*-aminophenol, mercaptoacetic acid and ethylenedimercaptan is possible without the usual accompanying oxidative decomposition.

Basic forms of ligands such as amines are susceptible to contamination with carbonate from the air as well as oxidation. The presence of six basic equivalents per mole of intermediate which are replaceable and volatile in acid allows the use of acid forms of ligands such as amine hydrochlorides, carboxylic acids, phenols and mercaptans.

Conditions for the preparation of the intermediate are not critical or time consuming. The starting materials are readily available and purification is simple. The intermediate is stable on storage if kept dry and may be prepared in quantity. If sufficient acid is present during the reaction the evolution of  $\text{CO}_2$  gas drives the reaction to completion even under relatively mild conditions.

(7) T. P. McCutcheon and W. J. Schuele, *THIS JOURNAL*, **75**, 1845 (1953).

(8) A. B. Lamb and K. J. Mysels, *ibid.*, **67**, 468 (1945).

(9) M. Mori, *et al.*, *Bull. Chem. Soc. Japan*, **29**, 883 (1956).

(10) M. Mori, *et al.*, *ibid.*, **31**, 291 (1958).