[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Cobaltammines and Chlorostannic Acid

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It is well known that chlorostannic acid, $H_2SnCl_6\cdot 6H_2O$, forms stable compounds with certain complex cations.[1] We have prepared the following four well-defined crystalline compounds from cobaltammine and cobaltethylenediamine cations and chlorostannic acid, and also one compound with bromostannic acid.

$\left.\begin{array}{l}[Co(NH_3)_6]Cl\\ [Co(NH_3)_6]Cl\end{array}\right\rangle SnCl_6\cdot 2H_2O$ small amber needles (I)

$[Co\,en_3]^{Cl}_{SnCl_6}\cdot 2H_2O$ orange yellow plates (ethylenediamine = en) (II)

$(1.6)\left[Co^{Cl_2}_{en_2}\right]_2SnCl_6$ emerald green prisms, 4–6 mm. long (III)

$\left[Co^{C_2O_4}_{en_2}\right]_2SnCl_6\cdot\left[Co^{C_2O_4}_{en_2}\right]Cl\cdot SnCl_4 14H_2O$ small red plates (IV)

$2\left\{(1.6)\left[Co^{Br_2}_{en_2}\right]_2SnBr_6\right\}\cdot SnBr_4$ pale green plates (V)

These compounds may also be formulated as double salts

$[2Co(NH_3)_6]Cl_3\cdot SnCl_4\cdot 2H_2O$ (I)

$[Co\,en_3]Cl_3\cdot SnCl_4\cdot 2H_2O$ (II)

$2\ (1.6)\left[Co^{Cl_2}_{en_2}\right]Cl\cdot SnCl_4$ (III)

$3\left[Co^{C_2O_4}_{en_2}\right]Cl\cdot 2SnCl_4\cdot 14H_2O$ (IV)

$4\ (1.6)\left[Co^{Br_2}_{en_2}\right]Br\cdot 3SnBr_4$ (V)

The formulas containing a $SnCl_6^{=}$ anion are supported by the fact that these compounds could be made only from chlorostannic acid; attempts to substitute tin tetrachloride were unsuccessful.

All of these compounds are stable in air. Crystals have been kept for two years without any sign of alteration.

Recrystallization from pure water is impossible because of fairly rapid and complete hydrolysis. The cation dissolves and the anion changes to insoluble metastannic acid, which, in every instance, retains the shape of the original crystal. This behavior is best observed with the praseo compound (III), one of the most beautiful of the cobaltammines. When the long green prisms are covered with warm water, hydrolysis begins in a few minutes. The solution becomes violet, then red as the cobalt complex dissolves (formation of chloroaquo and diaquo), and a quantity of white prisms (metastannic acid) remain in the liquid, reproducing every detail of the original crystals except the color. Analysis proved the white material to be pure metastannic acid.

Experimental

$\left.\begin{array}{l}[Co(NH_3)_6]Cl\\ [Co(NH_3)_6]Cl\end{array}\right\rangle SnCl_6\cdot 2H_2O$ (I).—Five grams of hexammine carbonate (prepared from silver carbonate and hexammine cobalti-chloride) was warmed on the steam-bath with twenty grams of chlorostannic acid, $H_2SnCl\cdot 6H_2O$, and water was added, drop by drop, until all the material dissolved. Four grams of amber needles separated on cooling. The product was recrystallized from a concentrated solution of chlorostannic acid (5:1).

Anal. Calcd.: Co, 14.2; Sn, 14.3; Cl, 42.7. Found: Co, 14.2; Sn, 14.2; Cl, 42.5.

$[Co\,en_3]^{Cl}_{SnCl_6}\cdot 2H_2O$ (II).—Seven grams of triethylenediamine cobaltibromide was added to a solution of 4 g. of stannous chloride dihydrate in 35 ml. of concentrated hydrochloric acid. The solution was heated on the steam-bath and a rapid stream of chlorine was passed through the liquid for one hour. Orange plates (6 g.) separated on cooling. The compound was recrystallized from hydrochloric acid (1:1). The anhydrous salt was obtained by heating the dihydrate at 110°.

Anal. Calcd.: Sn, 19.58; Cl, 40.97; C, 11.89. Found: Sn, 19.55; Cl, 40.91; C, 11.97. Calcd. (for dihydrate): H_2O, 5.60. Found: 5.62.

$(1,6)\left[Co^{Cl_2}_{en_2}\right]_2SnCl_6$ (III).—This compound was made (1) by the method used for (II) (see above); (2) from pure chlorostannic acid and 1,6-dichloro-diethylenediamine-cobalti-chloride; (3) by warming carbonato-diethylenediamine-cobalti-chloride with excess of chlorostannic acid on the steam-bath. The compound was recrystallized from hydrochloric acid (1:1). Long emerald green prisms were obtained after standing for two days.

Anal. Calcd.: Co, 14.2; Sn, 14.3; Cl, 42.6. Found: Co, 14.31; Sn, 14.21; Cl, 42.40.

$\left[Co^{C_2O_4}_{en_2}\right]_2SnCl_6\cdot\left[Co^{C_2O_4}_{en_2}\right]Cl\cdot SnCl_4\cdot 14H_2O$ (IV).—A solution of oxalodiethylenediamine-cobalti-hydroxide (made from silver oxide and the chloride) was treated with an excess of pure chlorostannic acid. A nearly quantitative yield of small red plates was obtained. This compound is the most stable of the series; hydrolysis can be effected only by boiling water. When the dry crystals were heated in a test-tube, large amounts of water were evolved, together with some hydrochloric acid, due to hydrolysis of the anion; hence the pure anhydrous compound could not be made.

Anal. Calcd.: Co, 10.5; Sn, 14.1; Cl, 23.2. Found: Co, 10.6; Sn, 14.2; Cl, 23.1.

$2\left\{(1,6)\left[Co^{Br_2}_{en_2}\right]_2SnBr_6\right\}\cdot SnBr_4$ (V).—Solid carbonato-diethylene-diamine-cobalti-bromide was covered with an excess of bromostannic acid, H_2SnBr_6. The fine precipitate which separated was dissolved in a saturated solution of ammonium bromide. After two days, pale green plates were obtained in fair yield. This compound hydrolyzed more readily than any of the derivatives of chlorostannic acid.

Anal. Calcd.: Co, 7.8; Sn, 11.9; Br, 64.2. Found: Co, 7.8; Sn, 11.7; Br, 63.9.

Summary

Well-defined, crystalline compounds have been

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[1] R. Weinland, *Ber.*, **41**, 32 (1908).

prepared from cobaltammines and halogenostannic acids, and a novel form of metastannic acid has been obtained by the hydrolysis of these compounds.

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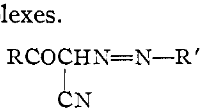
Chromium Complexes of Azo Dyes Derived from Acylacetonitriles[1]

BY ROBERT S. LONG

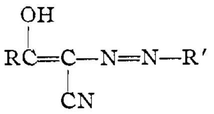
This work was initiated to determine whether azo dyes of type I, derived from acylacetonitriles and certain specific types of diazo compounds to be described later, could be converted to stable chromium complexes.



$\mathrm{RCO}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{C}}\mathrm{HN{=}N{-}R'}$

I

Certain types of active methylene compounds such as β-diketones and β-ketoesters had been used for this purpose, but there was no record of the use of β-cyanoketones. Although several of the acylacetonitriles recorded in the literature had been reported to be alkali-soluble and to couple with diazo compounds, it was not certain whether the activating effect of the cyano group on the methylene group would be sufficient to promote enolization in the azo dye (I) to give the enolic form (II) believed necessary for metallization.



$\mathrm{R}\overset{\substack{\mathrm{OH}\\ |}}{\mathrm{C}}{=}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{C}}\mathrm{{-}N{=}N{-}R'}$

II

The presence of a metallizable group in ortho position at each end of the azo linkage has been shown to be necessary for the formation of stable metal complexes. This necessitates the use of an *o*-aminophenol or an anthranilic acid derivative as the diazo component if the azo dye is to be metallized by simple procedures. The diazo compounds derived from anthranilic acid and its derivatives are fairly active couplers, but the diazo compounds derived from *o*-aminophenols are very weak couplers—much weaker than the corresponding diazo compounds without the hydroxyl group. The coupling of acetoacetonitrile with diazo sulfanilic acid[2] and of several aromatic acylacetonitriles with various diazo compounds[3] has been reported previously. However, none of the diazo compounds used contained an hydroxyl or carboxyl group ortho to the diazo group.

Preparation of the Chromium Complexes.—A number of acylacetonitriles have now been prepared, many of them new compounds. They have been found to couple readily with diazo compounds containing hydroxyl and carboxyl groups ortho to the diazo group. The dyes described in this paper were mostly prepared by coupling in aqueous sodium hydroxide solution, but the coupling may also be carried out, in most cases equally satisfactorily, in sodium carbonate solution, although the reaction is somewhat slower.

The azo dyes were found to be easily converted to the corresponding chromium complexes. The procedure consists of refluxing the dye in water solution with a small excess of basic chromic acetate. A rapid conversion to partially metallized dye takes place as evidenced by complete solution of the dye and a marked deepening in the color of the solution. When the *p*H is lowered to the range 1–4 and refluxing is continued, a gradual conversion takes place to the fully metallized dye containing one atom of chromium per molecule of dye. Usually this complex is much less soluble and precipitates from the reaction mixture in a well-defined crystalline form.

The over-all yield for the coupling and metallization is usually at least 80% of theory under optimum conditions. In a number of the examples reported in this paper the yield is lower because it varies considerably with small changes in *p*H and concentration of the metallization and no effort has been made as yet to determine the optimum conditions for the preparation of most of these complexes.

The structure of the chromium complexes of azo dyes has not been studied extensively and the correct structure has not been established. The complex which is generally the most stable and the one most easily isolated contains one atom of chromium combined with one molecule of dye, based on the analytical data. This is the type of complex dealt with in this paper. It is also apparent from the analytical data that the complexes must contain an appreciable amount of water which is not removed by drying at 60°. The amount of water seems to vary from one complex to another.

Since the conversion to this complex often requires refluxing the dye in aqueous solution of *p*H 1–4 for as long as twenty-four hours, it is particularly gratifying that no decomposition of

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(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Chicago, Ill., Sept. 13, 1946. A portion of this work has also appeared in U. S. Patents 2,366,633 and 2,392,167 (Long to American Cyanamid Company).

(2) Justoni, *Gazz. chim. ital.*, **70**, 804–812 (1940); *C. A.*, **35**, 5110 (1941).

(3) McNally and Dickey, U. S. Patent 2,211,339 (1940).