NOTES

A New Method for the Preparation of Hydroxoaquobis-(ethylenediamine)-cobalt(III) and Hydroxoamminebis-(ethylenediamine)-cobalt(III) Salts

By Fred Basolo and D. H. Steninger

The replacement of chloro (likewise bromo and iodo) ligands coördinated to cobalt(III) in the "Werner-type" complex compounds by hydroxide ion has in general been accomplished either by treatment of the complex with potassium hydroxide[1] or with a slurry of silver oxide.[2] Although both methods give satisfactory results it was found during a recent study[3] that hydroxoaquobis-(ethylenediamine)-cobalt(III) bromide, free of potassium chloride and potassium bromide, could be obtained in no greater than 65% yield from the reaction of *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride and excess potassium hydroxide. The use of silver oxide instead of potassium hydroxide results in the formation of the desired product in almost the theoretical yield. However, this procedure is not convenient since it requires that the reaction mixture be ground in a mortar for approximately one hour followed by subsequent extraction of the product from the silver chloride and excess silver oxide.

It would appear that one of the strongly basic anion exchange resins[4] recently developed may be readily employed for the displacement of chloro ligands by hydroxide ion without the introduction of any impurities. The ionic chloride should be removed from solution and held by the resin as the hydrochloride. This then results in the formation of the complex hydroxide which is a strong base comparable to potassium hydroxide, and thus the hydroxide ion displaces the coördinated chloro groups which are in turn removed by the resin—the final product being the hydroxo hydroxide. This procedure was carried out successfully using Amberlite IR-A-400 resin for the synthesis of hydroxoaquobis-(ethylenediamine)-cobalt(III) and hydroxoamminebis - (ethylenediamine) - cobalt(III) salts in almost theoretical yields.

Experimental

Hydroxoaquobis-(ethylenediamine)-cobalt(III) Bromide.—A column of Amberlite IR-A-400 resin, in its original chloride form, 2 cm. in diameter and 60 cm. in length, is treated with 3 l. of 4% sodium hydroxide solution and then washed with distilled water to a *p*H of 8. A solution containing 5 g. of *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in 100 cc. of water is then added to the column and followed by distilled water until the elutriant is only very faintly pink. The green color of the *trans*-dichloro compound readily changes to red as the salt progresses down the column. A total volume of 175 cc. of elutriant is collected in 30 min. and this solution has a *p*H of 12.5. Concentrated hydrobromic acid (approximately 4 cc.) is then added carefully adjusting the *p*H of the solution to 7. This solution is concentrated on a steam-bath to about 15 cc. and the concentrate is added slowly with vigorous stirring to 200 cc. of ice-cold absolute ethanol. The precipitate is collected on a filter, washed with alcohol and ether and dried at 75° to give 6 g. or 92% yield of the desired product.

Anal. Calcd. for $[\mathrm{Co\,en_2H_2O(OH)}]\mathrm{Br_2}$: Br, 42.74. Found: Br, 42.62.

Hydroxaquobis-(ethylenediamine)-cobalt(III) Sulfate.—This compound is prepared as described above except that the elutriant is neutralized with sulfuric instead of hydrobromic acid. A 90% yield of the desired sulfate was obtained.

Anal. Calcd. for $[\mathrm{Co\,en_2H_2O(OH)}]$: S, 10.34: Found: S, 10.53.

Hydroxoamminebis-(ethylenediamine)-cobalt(III) Bromide.—By this same procedure 5 g. of *cis*-chloroamminebis-(ethylenediamine)-cobalt(III) chloride was converted in 95% yield to the hydroxoamminebis-(ethylenediamine)-cobalt(III) bromide.

Anal. Calcd. for $[\mathrm{Co\,en_2NH_3OH}]\mathrm{Br_2}$: Br, 42.85. Found: Br, 42.78.

Hydroxoamminebis-(ethylenediamine)-cobalt(III) Sulfate.—Similarly a 94% yield of the corresponding sulfate was obtained by neutralizing the elutriant with sulfuric acid and precipitation of the desired product with absolute ethanol.

Anal. Calcd. for $[\mathrm{Co\,en_2NH_3OH}]\mathrm{SO_4}$: S, 10.37. Found: S, 10.11.

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(1) Werner, *Ber.*, **40**, 282 (1907).

(2) Werner, *Ann.*, **386**, 186 (1912); Lamb and Yngve, This Journal, **43**, 2352 (1921).

(3) Basolo, *ibid.*, **72**, 4393 (1950).

(4) Davies and Nancollas, *Nature*, **165**, 237 (1950).

Critical Solution Temperatures for Sulfur and Butyl Phthalate

By Maxey Brooke

In an attempt to extend the rather limited data on solubility of sulfur in organic solvents, several experiments were made.

The chemicals were Eastman Kodak Company *n*-butyl phthalate, b. p. 203–206° (20 mm.). No attempt at purification was made. The sulfur was a very pure specimen of natural brimstone having the analysis: S, 99.983; carbonaceous matter, 0.015; ash, 0.002. The determinations were made in a modified aniline point apparatus (ASTM designation D 611-47T) consisting of a 20 × 175 mm. test-tube for a mixing chamber, loosely stoppered. Holes were bored in the stopper to admit a thermometer meeting ASTM specification 1C-49 and a stirring device. This assembly was heated in a glycerol-bath and illuminated from behind with a fluorescent light. Dibutyl phthalate and sulfur were weighed into the test-tube. The thermometer and stirrer were immersed in the mixture. The test-tube was placed in the cold glycerol-bath which was then heated at a rate not exceeding 5° per minute. The sulfur–dibutyl phthalate mixture was constantly stirred manually until it was clear and homogeneous. The heat source was removed from the bath and the mixture was allowed to cool. A distinct cloud-point marked the separation of the two materials. Temperature measurements were taken at this point. On reheating and recooling it was possible to duplicate the