

from *p*-bromobenzenediazomorpholide was refluxed for ten minutes with 1 g. of sodium hydroxide in 10 cc. of water. Ten cc. more of water was added and the solution filtered from a small amount of tar. On making the filtrate acid with concentrated hydrochloric acid, cream-colored needles separated. These needles dissolved in hot concentrated sulfuric acid to give a blue color; a mixed m. p. with a sample of *p*-bromobenzenesulfonic acid showed no depression.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON RECEIVED NOVEMBER 19, 1942

The Preparation of Cholesteryl *p*-Aminobenzoate

By DAVID KRITCHEVSKY

In the preparation of cholesteryl *p*-aminobenzoate by reduction of cholesteryl *p*-nitrobenzoate, Shriner and Ko¹ were unable to effect reduction using iron, tin and amalgamated zinc with hydrochloric acid and finally reduced the nitro compound catalytically.

The reduction by chemical means was re-investigated and a suitable procedure using iron powder and acetic acid was found.

Experimental Part

Cholesteryl *p*-Nitrobenzoate.—The esterification was carried out by the method of Einhorn and Hollandt.² Cholesterol (25 g.) and *p*-nitrobenzoyl chloride (14.5 g.) (purified by vacuum distillation) were weighed into a 400-cc. beaker and 50 cc. of pyridine was added. The mixture was slowly heated to boiling; the acid chloride and the cholesterol dissolving during the heating. The solution was allowed to boil for one minute and then allowed to cool. A light brown solid began to crystallize instantly. Two recrystallizations from boiling methyl cellosolve gave large, white almost transparent plates, 25.7 g. (74% based on cholesterol used). The purest compound obtained melted at 190.5–191.5° and possessed a specific rotation in chloroform, $[\alpha]^{20}_D -6.97^\circ$.

Cholesteryl *p*-Aminobenzoate.—Cholesteryl *p*-nitrobenzoate (6 g.) was placed in a 200-cc. round-bottomed flask with 80 cc. of glacial acetic acid, 3.5 g. of 100 mesh iron filings was added and the mixture allowed to boil under gentle reflux. The color of the solution changed from colorless to dark brown within the first half hour. After one and one-half hours all the *p*-nitrobenzoate had dissolved. The solution was allowed to boil under reflux for one hour longer. The solution was then poured into a beaker and allowed to cool, crystals separating instantly. The crystals were washed with 1 *N* hydrochloric acid until the washings were colorless and then with water until the washings were neutral to litmus. The crude product weighed 5 g. Two recrystallizations from boiling amyl acetate yielded large tan needles, 4.2 g. (76% calculated). The purest compound obtained melted at 237.8–238.8°

(1) Shriner and Ko, *J. Biol. Chem.*, **80**, 1 (1928).

(2) Einhorn and Hollandt, *Ann.*, **301**, 95 (1898).

and possessed a specific rotation in chloroform, $[\alpha]^{20}_D +3.68^\circ$.

Saponification.—For the saponification of the cholesteryl *p*-aminobenzoate 0.1508 g. of the compound was boiled under reflux with 16 cc. of 0.9864 *N* alcoholic sodium hydroxide for two and one-half hours. A titer of 30.95 cc. of 0.5000 *N* hydrochloric acid was required to neutralize the excess alkali. Saponification equivalent found, 503; calculated, 505. The cholesterol recovered weighed 0.1086 g. (90% recovery based on *p*-aminobenzoate used) and melted at 147–148°. The melting point of the cholesterol used in these experiments was 145–146°. The *p*-aminobenzoic acid recovered from the saponification melted at 183° and did not depress the melting point of a known sample of *p*-aminobenzoic acid.

GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO RECEIVED NOVEMBER 30, 1942
CHICAGO, ILLINOIS

Hydrate Isomerism in the Hydrated Chromic Chlorides. Preparation of Triethylenediamine Chromium(III) Chloride from Hexaquo Chromium(III) Chloride¹

By LOUIS E. MARCHI² AND JAMES P. McREYNOLDS

Triethylenediamine chromium(III) chloride, $[\text{Cr}(\text{en})_3]\text{Cl}_3$,³ may be prepared from the violet hexaquo-chromium(III) chloride by reaction with anhydrous ethylenediamine.

Procedure

Triethylenediamine Chromium(III) Chloride.—The violet hexaquo-chromium(III) chloride was prepared by the method of Biltz and Biltz.⁴ Forty grams of the violet chloride was added to 100 ml. of anhydrous toluene in a 3-necked, 500 ml., round-bottomed flask equipped with a stirrer, thermometer and separatory funnel. The flask and its contents were cooled to 0° and anhydrous ethylenediamine⁵ added slowly at first. The temperature was never allowed to rise above 15°. During the course of the reaction the mixture became red colored, due to the formation of some red dichlorodiethylenediamine chromium(III) chloride monohydrate, $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$, which masked the yellow color of the $[\text{Cr}(\text{en})_3]\text{Cl}_3$. The mixture was stirred for one-half hour after the addition of the ethylenediamine, after which time the toluene layer was poured off. The thick red aqueous solution was diluted to twice its volume and treated with "Super-cel."

(1) Abstracted from a thesis presented to the Faculty of the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in August, 1942.

(2) Present address: Department of Chemistry, Indiana University, Bloomington, Indiana.

(3) en = ethylenediamine, $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$.

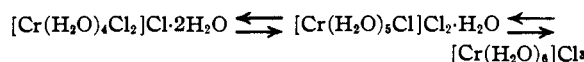
(4) Biltz and Biltz (trans. by Hall and Blanchard), "Laboratory Methods of Inorganic Chemistry," 1928, p. 200.

(5) The ethylenediamine was prepared by the method of Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938). The round-bottomed flask recommended was replaced by an iron container, the use of which circumvented the etching encountered by the contact of hot concentrated solutions of sodium hydroxide with glass.

The subsequent filtration completely removed the finely divided $\text{Cr}(\text{OH})_3$ which was formed during the course of the reaction. The clear red filtrate was cooled to 0° and neutralized carefully with concentrated hydrochloric acid; the temperature of the mixture was not allowed to rise above 25° . When the solution had been only partially neutralized, a considerable amount of ethylenediamine hydrochloride precipitated, and was removed by filtration after the solution had been neutralized. This filtrate was placed in a vacuum desiccator over phosphorus pentoxide; the solution was left there for twelve hours and the precipitate formed was removed by filtration. This procedure was repeated twice more; in all three cases the material was colorless ethylenediamine hydrochloride. The next two 12-hour evaporations yielded impure $[\text{Cr}(\text{en})_3]\text{Cl}_3$. This product was purified according to Pfeiffer's⁶ method. The yields were never over 25% of the theoretical.

Triethylenediamine chromium(III) chloride, at least in worthwhile yields, does not result from a similar treatment of ordinary hydrated chromic chloride, which contains dichlorotetraquo chromic chloride and chloropentaquo chromic chloride.

A question as to validity of the simple hydrate isomerism as shown by the formulas



seems to arise. To produce $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ it is necessary to have a very high concentration of HCl (a saturated solution at 0°).⁴ In the substitution of ethylenediamine for water and for chloride ion the chloride ions are normally more readily replaced. In dilute solutions of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and of $[\text{Cr}(\text{en})_3]\text{Cl}_3$ the final product on standing is $[\text{Cr}(\text{en})_2(\text{H}_4\text{O}_2)]\text{Cl}_3$. The dichloro compound reacts with water more rapidly than the triethylenediamine.

It does not seem logical that a compound of the formula $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ should result in a different product with anhydrous ethylenediamine than one of the formula $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. The explanation of this more or less classical example of hydrate isomerism proposed by Werner and others⁷ is undoubtedly more complicated than was supposed. The molecular conductivity and the molecular weight determinations on the tetrahydrate are in agreement with the simplest formula but the chemical properties seem difficult to explain on the basis of the simplest formula.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

RECEIVED OCTOBER 21, 1942

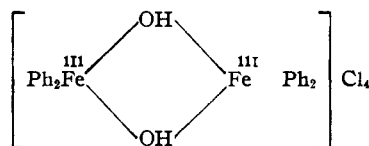
(6) Pfeiffer, *Z. anorg. Chem.*, **29**, 113 (1901).

(7) See Thomas, "Complex Salts," D. Van Nostrand Co., Inc., New York, N. Y., 1924, pp. 28 ff., and Schwarz (translation by Bass) "The Chemistry of the Inorganic Complex Compounds," John Wiley and Sons, Inc., New York, N. Y., 1923, pp. 45 ff.

The Magnetic Susceptibility of the Brown Ferric Phenanthroline Complex

BY L. MICHAELIS AND S. GRANICK

During the study of the magnetic properties of some complex iron compounds of biological interest the problem arose as to how much the mutual interaction of closely packed iron atoms in a polynuclear complex may influence the susceptibility. It seems unavoidable to postulate an iron-iron bond for $\text{Fe}_2(\text{CO})_9$,^{1,2} but, beside this rather exceptional case, no iron complex has been known in which the value of the susceptibility would compel the assumption of Fe-Fe interaction of any appreciable magnitude, except for one case published by Gaines, Hammett and Walden.³ These authors have described a brown well-crystallizable complex of ferric iron with *o*-phenanthroline which they proved to be binuclear with the following structure (Ph = Phenanthroline)



They have reported a susceptibility of this complex corresponding to an effective magnetic dipole moment of as little as 1.4 Bohr magnetons per gram atom of iron. Since the moment of any ferric complex in which there is no appreciable Fe-Fe interaction can according to theory never be smaller than 1.73 BM even upon the assumption of complete absence of orbital contributions, the authors have suggested an Fe-Fe interaction due to the closeness of the two iron atoms within the binuclear complex. In view of the importance of this case for more general conclusions, we undertook to repeat this measurement. The complex can be easily prepared according to those authors. It forms brown crystals which, when thoroughly dried, having no water of crystallization, should contain 11.1% iron. All of our various samples, prepared independently, showed exactly 11.1% iron, as an average of many well-agreeing analyses. We recommend especially for this analysis the precipitation of iron hydroxide from the complex with alkali, collecting it on an asbestos mat filter, washing with a dilute salt

(1) H. M. Powell and R. V. S. Ewens, *J. Chem. Soc.*, 286 (1939).

(2) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 238.

(3) A. Gaines, L. P. Hammett and G. H. Walden, *THIS JOURNAL*, **58**, 1668 (1936).