

Anal. Calcd. for $C_{14}H_{22}N_2O_8$: C, 48.54; H, 6.40; N, 8.09. Found: C, 48.57; H, 6.39; N, 8.03.

The levo acid prepared in the same manner from D-Ba-[Co(*l*-CDTA)]·9H₂O gave $[\alpha]_D = -53^\circ$.

Anal. Found: C, 48.41; H, 6.30; N, 8.06.

Acknowledgments.—The authors are indebted to the Geigy Chemical Corporation, Australia, for a gift of racemic cyclohexanediaminetetraacetic acid, and to Dr. J. Fildes, Department of Medical Chemistry for the analyses.

[CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN, AND THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

An Investigation of the Complexes of Platinum(II) with Pyridine-2-aldoxime. *cis-trans* Isomerism¹

BY CHUI FAN LIU AND C. H. LIU

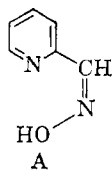
RECEIVED NOVEMBER 30, 1960

Chloride, bromide and tetrachloroplatinate(II) salts of the monohydrogen bis-pyridine-2-aldoxime platinum(II) ion have been prepared. The inner complex bis-pyridine-2-aldoxime platinum(II) dihydrate has also been obtained and has been shown to exist in both the *cis* or the *trans* configurations. The *cis* is converted to the *trans* by heating at 140° or by heating in 1 *N* hydrochloric acid followed by neutralization of the solution. The *trans* is converted into the *cis* by heating in 0.1 *N* hydrochloric acid, to form the intermediate monohydrogen bis-pyridine-2-aldoxime platinum(II) ion, and then neutralizing this ion with sodium hydroxide.

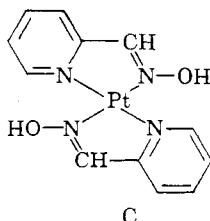
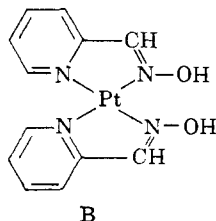
Introduction

Complexes of platinum(II) with both mono- and dioximes are known. The structure of the dimethyl glyoxime complex² of platinum(II) is probably similar to that of the inner complex nickel and palladium compounds. The two protons on the oxime groups are symmetrically located, and the complex affords a good example of intramolecular hydrogen bonding. Recently, Krouse and Busch³ reported the preparation of an inner complex between platinum(II) and pyridine-2-aldoxime. The present study is concerned with this same subject but particularly with the *cis-trans* isomerism of the inner complex.

Since pyridine-2-aldoxime(A) is an unsymmetrical chelating ligand, the two-to-one complex with platinum(II) can assume either the *cis*(B) or the



trans (C) form. These can lose their protons to give the corresponding inner complexes. Upon



losing one proton the *cis* configuration should be capable of intramolecular hydrogen bond formation. In fact, it might be expected that the formation

(1) Part of this work was done at the University of Connecticut, Storrs, Conn.

(2) J. Pech, M. Polster and A. Rezabek, *Chem. Listy*, **43**, 180-182 (1949).

(3) R. A. Krouse, and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960).

of this extra chelate ring may render the *cis*-configuration more easily obtainable than the *trans*.

Experimental

Starting Materials.—Potassium chloroplatinate(II) was obtained by a modified method of Cooley and Busch.⁴ Potassium hexachloroplatinate(IV) was reduced with hydrazine dihydrochloride. The resulting solution was evaporated until crystallization takes place, then cooled. The crystals obtained were washed with a small amount of water. Pyridine-2-aldoxime was obtained from the Aldrich Chemical Co. All the other chemicals used were of commercial reagent grade.

Infrared Spectra.—All spectra were obtained on a Perkin-Elmer Model 21 double beam instrument. Nujol Mulls were employed in all cases.

Analysis.—Platinum analyses were carried out by ignition. The microanalyses of carbon, hydrogen and nitrogen were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Preparation of Compounds. Monohydrogen-bis-(pyridine-2-aldoxime) Platinum(II) Chloride and Monohydrogen Bis-(pyridine-2-aldoxime) Platinum(II) Tetrachloroplatinate(II).—A solution of two grams of potassium tetrachloroplatinate(II) in approximately 100 ml. of water and a solution of 1.2 g. of pyridine-2-aldoxime in 50 ml. of 95% ethanol were mixed, and the mixture was heated on the steam-bath for 5 hr. During this time, orange crystals formed. After cooling, the crystals were filtered, washed thoroughly with distilled water, alcohol and ether and air dried. The product was found to be the tetrachloroplatinate(II) salt.

Anal. Calcd. for $[Pt(C_6H_5N_2O)_2H]_2[PtCl_4]$: C, 23.74; H, 1.81; N, 9.23; Pt, 48.2. Found: C, 23.73; H, 1.90; N, 9.15; Pt, 47.6.

The mother liquor from the above preparation was evaporated on the steam-bath until crystallization began. On cooling, fine dark needles formed. These were washed successively with a small amount of cold water, 95% alcohol and ether and were dried in vacuum at room temperature. This compound proved to be the monochloride.

Anal. Calcd. for $[Pt(C_6H_5N_2O)H]Cl$: C, 30.44; H, 2.31; N, 11.8; Pt, 41.2. Found: C, 29.3; H, 2.65; N, 11.1; Pt, 41.0.

Monohydrogen Bis-(pyridine-2-aldoxime) Platinum(II) Bromide.—Two tenths of a gram of monohydrogen bis-(pyridine-2-aldoxime) chloride was dissolved in about 30 ml. of water. Excess sodium bromide was added and crystals immediately formed. These were filtered, washed with distilled water and recrystallized from water.

(4) W. E. Cooley and D. H. Busch, "Inorganic Synthesis," Vol. V, McGraw-Hill Book Co., New York, N. Y., p. 208.

Anal. Calcd. for $[\text{Pt}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2\text{H}]\text{Br}$: C, 27.80; H, 2.12; N, 10.81; Pt, 37.64. Found: C, 27.82; H, 2.15; N, 10.92; Pt, 37.44.

cis-Bis-(pyridine-2-aldoxime) Platinum(II) Dihydrate.—To a solution of 0.948 g. of bis-(pyridine-2-aldoxime) platinum(II) chloride in 10 ml. of water was added 20 ml. of 0.1 *N* sodium hydroxide solution. The light brown crystals that formed were washed with water, alcohol and ether and dried in vacuum at room temperature.

Anal. Calcd. for $[\text{Pt}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$: C, 30.44; H, 2.96; N, 11.84; Pt, 41.22. Found: C, 30.43; H, 2.97; N, 11.84; Pt, 41.22.

trans-Bis-(pyridine-2-aldoxime) Platinum(II) Dihydrate.—Tetrammine platinum(II) chloride (0.334 g.) was dissolved in 20 ml. of water, and 5 ml. of concentrated aqueous ammonia was added. To this solution was added 0.244 g. of pyridine-2-aldoxime in about 10 ml. of alcohol. The mixture was heated on the steam-bath for two days. During this time long, fine dark brown needles formed. These were filtered, washed and dried as above.

Anal. Calcd. for $[\text{Pt}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$: C, 30.44; H, 2.96; N, 11.84; Pt, 41.2. Found: C, 30.18; H, 2.95; N, 11.55; Pt, 41.2.

This compound was also prepared as follows: The mother liquor from the preparation of monohydrogen bis-(pyridine-2-aldoxime) platinum(II) chloride was neutralized with 0.1 *N* sodium hydroxide to pH 8. Dark brown crystals slowly separated. These were washed and dried the usual way.

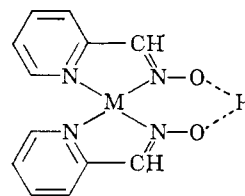
Anal. Found: Pt, 40.5%.

cis-trans Isomerization.—The *cis*-bis(pyridine-2-aldoxime) platinum(II) dihydrate was heated in an oven at 140° for 10 minutes during which time it was completely transformed into the *trans* configuration, as shown by its infrared spectrum. The same isomerization was carried out by a different method. A solution of *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate in about 20 ml. 1 *N* hydrochloric acid was heated in the steam-bath for 3 hr. and after cooling, was neutralized with sodium hydroxide to pH 8. Crystals separated slowly. These were washed and dried in vacuum at room temperature. The product so obtained was *trans*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate. For the isomerization of the *trans* compound to the *cis* the following method was used: Crystals of *trans*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate were suspended in 0.1 *N* hydrochloric acid. The mixture was heated on the steam-bath for a long period of time (sometimes one week was needed). The crystals eventually dissolved. The monohydrogen bis-(pyridine-2-aldoxime) platinum ion was then isolated as the bromide, iodide or tetrachloroplatinate(II) salt by adding the corresponding anion to the solution. The chloride was obtained by evaporating the solution till crystallization began. Then, after cooling, the crystals were filtered, purified and dried as usual. The *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate was then prepared by neutralizing a solution of the chloride with 0.1 *N* sodium hydroxide.

Results and Discussion

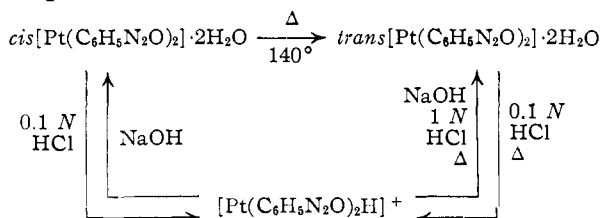
The reaction between pyridine-2-aldoxime and $\text{K}_2[\text{PtCl}_4]$ in water proceeds smoothly to yield the monohydrogen-bis-(pyridine-2-aldoxime) platinum(II) tetrachloroplatinate(II) when the mixture is heated on the steam-bath. This salt is quite insoluble in water and conversion to the chloride is difficult. However, prolonged heating on the steam-bath with a solution of excess pyridine-2-aldoxime and a few drops of concentrated hydrochloric acid in a water-alcohol mixture eventually dissolved this compound and yielded the chloride salt. The infrared spectrum of the tetrachloroplatinate(II) salt is virtually identical with that of the bis-(pyridine-2-aldoxime) platinum(II) chloride. To confirm the fact that the compound obtained is actually the tetrachloroplatinate(II) salt of the monohydrogen ion, some bis-(pyridine-2-aldoxime) platinum(II) chloride was dissolved

in water and potassium tetrachloroplatinate(II) was added. The precipitated material was found to show identical infrared spectrum and platinum analysis with the compound obtained in the original reaction between potassium tetrachloroplatinate(II) and pyridine-2-aldoxime. When the reaction between pyridine-2-aldoxime was carried out at room temperature over a long period of time, a mixture resulted. The infrared spectrum indicated this to be a mixture of *trans*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate and monohydrogen bis-(pyridine-2-aldoxime) platinum(II) tetrachloroplatinate(II). The monohydrogen bis-(pyridine-2-aldoxime) platinum(II) ion probably has a *cis* configuration with intramolecular molecular hydrogen bonding analogous to that of the monohydrogen bis-(pyridine-2-aldoxime) copper(II) ion, which has been shown to possess the *cis*-configuration and intramolecular hydrogen



bonding by infrared studies of both the normal and the deuterated complexes.⁵ The infrared spectra of the monohydrogen bis-(pyridine-2-aldoxime) platinum(II) chloride and of the bromide are virtually identical.

If the assumption is correct that the monohydrogen bis-(pyridine-2-aldoxime) platinum(II) ion has the *cis* configuration, then it is not unreasonable that neutralization of this ion should yield the inner complex with the *cis* configuration. The *cis-trans* isomerization can be summarized in this diagram.



The *cis* and *trans* inner complexes have different infrared spectra. The *cis* complex is appreciably soluble in water and instantly soluble in 0.1 *N* hydrochloric acid to yield the monohydrogen bis-(pyridine-2-aldoxime) platinum(II) ion as evidenced by the isolation of the bromide, chloride and tetrachloroplatinate(II) salts from the solution. Neutralization of the solution with 0.1 *N* sodium hydroxide yields the original *cis* inner complex. The *trans* inner complex, on the other hand, is virtually insoluble in water, and 0.1 *N* hydrochloric acid will dissolve it only upon prolonged heating. This solution yields the same monohydrogen bis-(pyridine-2-aldoxime) platinum(II) bromide, chloride and tetrachloroplatinate as those isolated from the solution of the

(5) C. F. Liu, C. H. Liu, work presented at the 138th Meeting of the American Chemical Society.

cis compound in dilute hydrochloric acid. This is shown by the fact that the infrared spectra of the corresponding pairs are identical, and in turn these spectra are identical with those of the original preparations described in the Experimental section. The neutralization of the 0.1 *N* hydrochloric acid solution of the *trans* inner complex yields an inner complex whose infrared spectrum is identical with that of the *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate. The *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is easily isomerized to the *trans* compound simply by heating for 15 minutes at 140°. The *trans* compound thus obtained has the same infrared spectrum as the one from the original preparation. When the *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is dissolved in 1 *N* hydrochloric

acid, heated on the steam-bath for 15 minutes, and neutralized with sodium hydroxide, the *trans*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is isolated as is evidenced again by its characteristic infrared spectrum.

From these results it seems that intramolecular hydrogen bonding and the resultant extra chelate ring formation tend to stabilize the *cis* configuration and serve to isomerize the *trans* inner complex to the *cis* inner complex through the formation of the intermediate monohydrogen compound. The fact that the *cis* compound is converted to the *trans* in more concentrated acid seems to indicate that both oximate oxygens may be protonated and that the resulting dihydrogen species loses the stabilizing influence of the extra chelate formation and thus rearranges to the *trans* configuration.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Polymerization in Cobaltic Periodate Solutions^{1a}

BY C. J. NYMAN^{1b} AND R. A. PLANE

RECEIVED DECEMBER 10, 1960

Acidified solutions of $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$ show the presence of two types of periodate ions as evidenced by the fact that a portion, but not all, of the periodate may be removed by precipitation or reduction without changing the absorption spectra. Polymerization of the cobalt species to form a soluble polynuclear complex having a cobalt(III) to periodate ratio of 4:3 occurs at a measurable rate which increases with increasing hydrogen ion concentration. From a 2 *M* perchloric acid solution, a dark green crystalline solid is obtained which has 3 strongly ionized hydrogen ions and 3 iodine atoms per four cobalts. The crystals are soluble in water and have an elemental analysis and equivalent weight leading to a postulated formula $\text{H}_2[\text{Co}_4\text{I}_3\text{O}_{36}\text{H}_2]$ for their composition.

Recently, Lister and Yoshino² have described the preparation and properties of some most interesting compounds, which apparently contain periodate ions coordinated to cobalt (III). Such complex ions should be of general interest because complexes containing strong oxidizing agents as ligands are quite rare, and due to the possible octahedral configuration of the periodate ion, these complexes might show structural resemblance to polynuclear species. For these reasons and because the compounds have not been fully characterized, further investigation seems appropriate.

The sodium salt has been formulated previously as $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$ or alternatively as $\text{Na}_5[\text{Co}(\text{H}_2\text{IO}_6)_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$. By passing solutions of this salt through hydrogen-form cation exchange resins, Lister and Yoshino have prepared solutions of the corresponding free acid. However, they have shown by spectral studies that in acid solutions the compound undergoes changes at measurable rates. A primary goal of the present work is to elucidate the nature of these changes in order to gain a more detailed knowledge of the structure and properties of the compound.

Experimental

The sodium salt, $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$, readily was prepared by using a variation of the Lister and Yoshino pro-

cedure as described: 0.01 mole of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was mixed with 0.02 mole of NaIO_4 in 900 ml. of water; 0.2 mole of NaOH was dissolved in 100 ml. of water and added to the mixture. Immediately, 0.02 mole of NaOCl was added with stirring. An emerald green color appeared in the solution and an olive green solid formed. The solution was separated by centrifugation, and the olive colored solid discarded. On treatment of the solution with one-half of its own volume of ethanol, added in small amounts and with constant stirring, the $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$ precipitated. This precipitate (which was oily if the alcohol was added too rapidly) was dissolved in 200 ml. of water and then 200 ml. of 4 *M* NaOH was added. After standing 12 to 24 hr., the green crystalline material was collected on a coarse fritted glass filter funnel, washed two times with small portions of cold water, two times with 50% alcohol water mixture and two times with absolute alcohol. The sample was dried by sucking air through, transferred to a desiccator and stored over anhydrous calcium chloride. It was found that 50 ml. of ethanol can be used as a precipitant in place of the NaOH .

While a complete analysis of the solid was not obtained, the iodine/cobalt ratio was determined to be 2.0. Furthermore, the spectrum of aqueous solutions of the solid prepared by this procedure is identical with that reported by Lister and Yoshino.

Cobalt Determination.—Cobalt was determined spectrophotometrically using an aliquot portion of a solution of known weight of sample. In a typical analysis, one ml. of cobalt solution was pipetted into a 10 ml. volumetric flask, 0.2 ml. of 1 *M* H_2SO_4 , 0.2 ml. of 1 *M* Na_2SO_3 and 8 ml. of conc. (12 *M*) HCl were added. The absorption spectrum then was determined and the optical density at 6900 Å., the long wave length maxima in the $\text{Co}(\text{II})$ spectra were used to determine the concentration of the unknown by comparison with a calibration curve prepared from known samples.

Iodine Determination.—Iodide analysis was carried out using a method outlined by Willard and Furman.³ Thirty-

(1) (a) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States government. (b) Department of Chemistry, Washington State University Pullman, Wash.

(2) M. W. Lister and Y. Yoshino, *Canadian J. Chem.*, **38**, 45 (1960).

(3) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 320-321.