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Complexes between Palladium(II) and Pyridine-2-aldoxime

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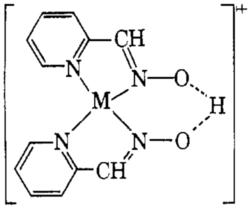
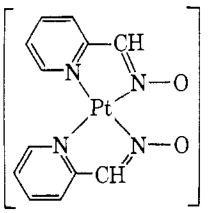
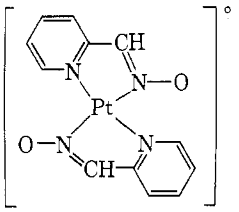
Salts of monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) ion have been prepared and compared to the analogous platinum(II) and copper(II) compounds. The inner complex between pyridine-2-aldoxime and palladium(II) also has been prepared. In contrast to the platinum(II) inner complex only the *trans* isomer of the palladium(II) compound has been obtained.

In previous publications,[1,2] it has been shown that copper(II) and platinum(II) form one to two pyridine 2-aldoxime complexes with the structure



Furthermore, platinum(II) forms the inner complex, which may assume either the *cis* or the *trans* configuration.





cis–trans-Isomerization could be easily effected by changing the experimental conditions.[2] The present investigation is concerned with the similarities and differences exhibited by the corresponding palladium(II) compounds. Complexes between palladium(II) and pyridine-2-aldoxime were first reported by Krause and Busch.[3] The structures of these complexes however, were not examined.

Experimental

Starting Materials.—Pyridine-2-aldoxime was obtained from Aldrich Chemical Co., Milwaukee, Wis. Palladium(II) chloride was supplied by Fisher Scientific Co., New York, N. Y. 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.

Analyses.—Palladium was determined by first igniting the compound; the resulting mixture of palladium–palladium oxide then was reduced with formic acid. The metallic palladium obtained was dried at 200° and weighed. Microanalysis of carbon, hydrogen, and nitrogen was performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Preparation of Compounds. Monohydrogen Bis-(pyridine-2-aldoxime)-palladium(II) Tetrachloropalladadate(II).—To 200 ml. of 0.01 *M* potassium tetrachloropalladate(II) was added 2.44 g. of pyridine-2-aldoxime in 70 ml. of alcohol. A yellow precipitate immediately formed. After filtration the yellow precipitate was washed with 0.1 *N* hydrochloric acid until the washings became colorless, then with alcohol and ether, and then dried under vacuum over magnesium perchlorate.

Anal. Calcd. for $[Pd(C_6H_5N_2O)_2H][PdCl_4]$: C, 30.5; H, 2.32; N, 11.9; Pd, 33.8. Found: C, 30.4; H, 2.46; N, 11.9; Pd, 33.1.

Monohydrogen Bis-(pyridine-2-aldoxime)-palladium(II) Chloride.—To 200 ml. of 0.01 *M* potassium chloropalladate(II) was added 2.44 g. of pyridine-2-aldoxime in 70 ml. of alcohol. After heating for 4 hr. on the steam bath the mixture was filtered, and the filtrate was evaporated on the steam bath until crystallization began. Upon cooling, large crystals formed which were washed successively with small amounts of water, alcohol, and ether and dried under vacuum over magnesium perchlorate.

Anal. Calcd. for $[Pd(C_6H_5N_2O)_2H]Cl$: C, 37.8; H, 2.85; N, 14.5; Pd, 27.8. Found: C, 37.1; H, 2.24; N, 14.6; Pd, 27.6.

Monohydrogen Bis-(pyridine-2-aldoxime)-palladium(II) Nitrate.—A small amount of monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) chloride was dissolved in 2.0 ml. of 0.1 *N* hydrochloric acid and a solution of potassium nitrate was added. The light yellow precipitate which formed immediately was filtered, washed thoroughly with water, and dried over magnesium perchlorate.

Anal. Calcd. for $[Pd(C_6H_5N_2O)_2H]NO_3$: C, 34.9; H, 2.66; N, 17.0. Found: C, 34.7; H, 2.78; N, 16.7. Using similar procedures, the bromide, iodide, and perchlorate also were prepared.

***trans*-Bis-(pyridine-2-aldoxime)-palladium(II) Dihydrate.**—A solution of 0.5 g. of monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) chloride in 100 ml. of water was left standing overnight. The fine crystals formed during this time were filtered, washed with water, and air dried.

Anal. Calcd. for $[Pd(C_6H_5N_2O)_2]\cdot 2H_2O$: C, 37.3; H, 3.62; N, 14.5; Pd, 27.8. Found: C, 37.7; H, 3.77; N, 14.7; Pd, 27.6.

The same compound was prepared by treating 200 ml. of an ammoniacal solution 0.01 *M* in tetraamminepalladium(II) ion with 2.44 g. of pyridine-2-aldoxime in 70 ml. of alcohol. After standing overnight, fine yellow needles separated which were washed with water and air dried.

The attempted preparation of *cis*-bis-(pyridine-2-aldoxime)-palladium(II) chloride with sodium hydroxide yielded the *trans*-bis-(pyridine-2-aldoxime)-palladium(II) dihydrate at either room temperature or 0°. The neutralization also was carried out at Dry Ice temperature *via* the following procedure. Monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) iodide was suspended in ethanol. The mixture was cooled in a Dry Ice bath and treated with alcoholic potassium hydroxide solution, also cooled to Dry Ice temperature. A brown product formed. When the mixture was warmed to −10° the brown precipitate rapidly turned into a light yellow product which was identified by

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(1) C. H. Liu and C. F. Liu, *J. Am. Chem. Soc.*, **83**, 4169 (1961).
(2) C. F. Liu and C. H. Liu, *ibid.*, **83**, 2615 (1961).
(3) R. A. Krause and D. H. Busch, *ibid.*, **82**, 4830 (1960).

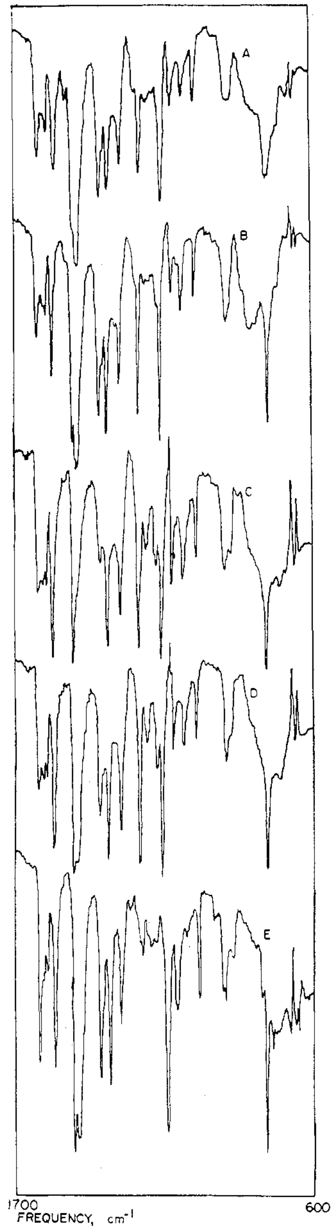

Fig. 1.—Infrared spectra of the monohydrogen compounds: A, $[Pt(C_6H_5N_2O)_2H]Cl$; B, $[Pt(C_6H_5N_2O)_2H]Br$; C, $[Pd(C_6H_5)N_2O)_2H]Cl$; D, $[Pd(C_6H_5N_2O)_2H]Br$; E, $[Cu(C_6H_5N_2O)_2H]Br$.

its infrared spectrum as *trans*-bis-(pyridine-2-aldoxime)-palladium(II) dihydrate. The brown product was filtered, washed with ethanol, and dried by a stream of nitrogen pulled through the filter by suction while the system was kept in a Dry Ice bath. When warmed to room temperature, the dried brown product quickly turned into a light yellow solid which gave the characteristic infrared spectrum of the *trans*-bis-(pyridine-2-aldoxime)-palladium(II) dihydrate.

Results and Discussion

The reaction between pyridine-2-aldoxime and the tetrachloropalladate(II) ion is very much faster than that between the aldoxime and tetrachloroplatinate(II) ion. The former reaction is essentially instantaneous, yielding a yellow precipitate. Examination of the infrared spectrum of this precipitate showed that all the absorption bands characteristic of both the monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) tetrachloropalladate(II) and the *trans*-bis(pyridine-2-aldoxime)-palladium(II) dihydrate were present. Therefore, it was concluded that the precipitate was a mixture of the two palladium compounds. Since *trans*-bis-(pyridine-2-aldoxime)-palladium(II) dihydrate is easily soluble in 0.1 *N* hydrochloric acid, pure monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) tetrachloropalladate(II) can be obtained simply by washing the mixture with the acid solution. The product after washing gave an infrared spectrum which was virtually identical with the spectrum of the corresponding platinum compound. The infrared spectra of the monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) chloride, bromide, iodide, nitrate, and perchlorate also were almost identical with the corresponding platinum(II) complexes and very similar to the analogous copper(II) salts (Fig. 1).

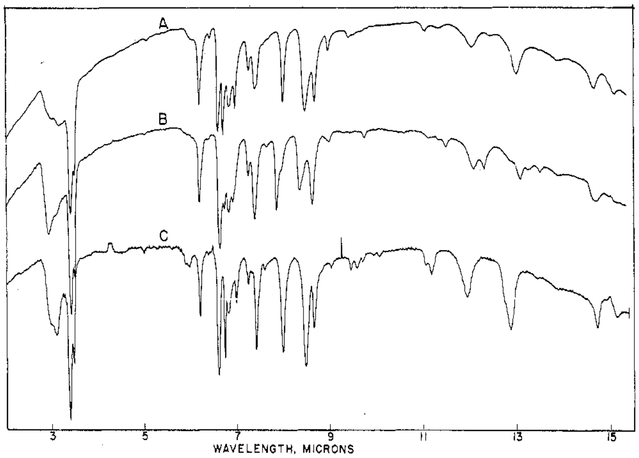

Fig. 2.—Infrared spectra of the inner complexes: A, *trans*-$[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$; B, *cis*-$[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$; C, *trans*-$[Pd(C_6H_5N_2O)_2]\cdot 2H_2O$.

The configuration of the light yellow inner complex may be deduced from its infrared spectrum, which is quite different from that of the *cis*-bis-(pyridine-2-aldoxime)-platinum(II) dihydrate but is virtually identical with that of the *trans* isomer (Fig. 2). While both the *cis* and the *trans* isomers of the platinum(II) inner complex are easily isolated,[2] *trans*-bis-(pyridine-2-aldoxime)-palladium(II) dihydrate alone has been successfully prepared. It appears that the inner complex of palladium(II) is much more easily isomerized. The *cis* isomer is very quickly converted to the *trans* at room temperature in the same way *cis*-bis-(pyridine-2-aldoxime)-platinum(II) dihydrate changes into the *trans* configuration at 140°.[2] The ease of isomerization of the palladium inner complex also is evidenced by the fact that it dissolves instantly in 0.1 *N* hydrochloric acid to yield the monohydrogen bis-(pyridine-2-aldoxime)-palladium(II) ion which must assume the *cis* configuration.