Several observations should be made at this point which have a bearing upon the success of the described process. A nitrogen flow through the hydrogen bromide jet is desirable if not necessary to prevent diffusion of uranium hexafluoride into the jet; reaction taking place within the jet tube when the hydrogen bromide is first admitted might plug the small opening of the jet with reaction product.

Varying the specific flow rates of the reactant gases so that the excess of uranium hexafluoride varies from 50 to 200% has little effect upon the quality of the unaged product; in all cases material sampled prior to the aging process is a gray to brown mixture, found by X-ray analysis to contain both $\alpha$- and $\beta$-uranium pentafluoride as well as some diuranium enneafluoride. Since the gross uranium hexafluoride pressure was at all times well above the disproportionation pressure of both forms of uranium pentafluoride, it is concluded that in the immediate zone of reaction (a) the partial pressure of uranium hexafluoride is sharply reduced by both hydrogen bromide and the gaseous reaction products and (b) the reaction temperature is probably somewhat above 65°, the measured gas temperature approximately 1.5 in. from the jet tip. Although reaction would occur at a lower temperature, 65° is the minimum operating temperature which will ensure complete removal of the bromine as a vapor. Higher temperatures would merely emphasize a deficiency in the uranium hexafluoride overpressure.

The presence of other intermediate uranium fluorides in the unaged product is a shortcoming which this preparative method has in common with previously developed methods. However, the high surface area and small particle size produced by the relatively low temperature gas phase reaction favor complete reconversion of the material to $\alpha$-uranium pentafluoride during the aging process. The tetravalent uranium equivalent was less than half the total uranium, probably because of adsorbed uranium hexafluoride. One expects this as a result of the short period of evacuation at room temperature employed before the product receiver was removed. Since some uranium hexafluoride pressure is necessary at all temperatures to prevent disproportionation, it is probably desirable not to remove the sorbed uranium hexafluoride too thoroughly if the product is to be stored for any length of time.

Both the product and the product receiver should be handled in a dry atmosphere at all times. The presence of any sorbed uranium hexafluoride merely enhances the susceptibility of the products to hydrolysis. If the receiver is exposed to moist air before reuse or if it is desirable to make a change in the isotopic concentration of the uranium hexafluoride feed, the receiver with its residual contents, when reinstalled at the bottom of the column, can be thoroughly decontaminated by exposure to fluorine at room temperature.

---

CONTRIBUTION FROM THE RESEARCH LABORATORY
OF ORQUIMA S.A., SÃO PAULO, BRAZIL

# A Tridentate Ligand from Pyridine-2-aldehyde and Ammonia

BY P. KRUMHOLZ

*Received June 15, 1964*

In the unsuccessful attempts to prepare an iron(II) complex of 2-pyridinalimine ($C_5H_4N{\cdot}CH{=}NH$) from pyridine-2-aldehyde, ammonia, and a ferrous salt, the formation of a strongly colored compound was observed in which apparently 1 mole of ammonia has reacted with 2 moles of the aldehyde. From a reaction mixture of ferrous chloride (1 mole), pyridine-2-aldehyde (4 moles), and ammonium bicarbonate (2 moles) in aqueous ethanol, sodium perchlorate precipitated a dark red, amorphous product. Analytical results are in agreement with the values calculated for bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) perchlorate (I, R = OH). A well-crystallized, hexahydrated chloride was obtained by allowing pyridine-2-aldehyde to react with ferrous chloride and ammonium chloride in aqueous solution. Part of the pyridine aldehyde is thereby transformed into the hydrochloride. Finally, the same complex species is formed on reaction of a ferrous salt with the 2-pyridinalimine trimer described by Harries and Lénárt.[1]

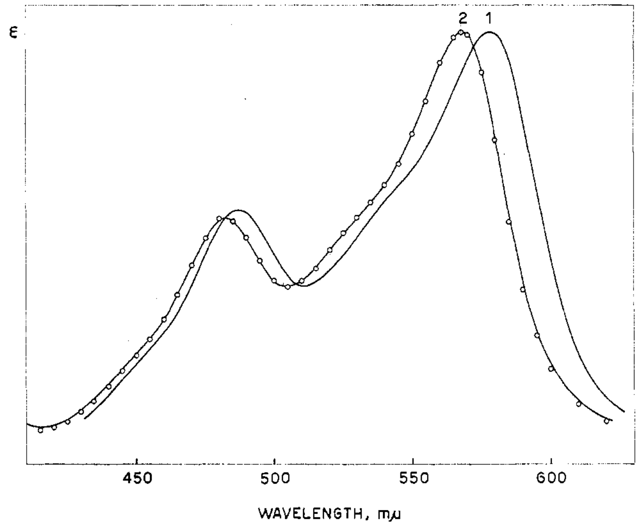
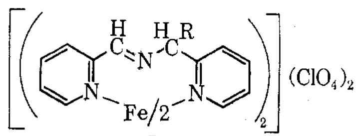


Figure 1.—Absorption spectra of: (1) bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) chloride; and (2) bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) perchlorate (solid line refers to authentic sample (3A), points to product (3B) obtained by reduction of the hydroxymethyl derivative). Solvent water. Curves are drawn to equal height at the main absorption maximum. The numerical values of the molar absorbancy indices at these maxima are: 1, 1.05 × $10^4$; 2, 1.1 × $10^4$.



I

In solution and even in the solid state the new iron(II) complex slowly decomposes or changes otherwise, as shown by distinct changes of its absorption spectrum. This spectrum ($\lambda_{max}$ 578 and 487 m$\mu$) is very similar to that of the iron(II) complex of the tridentate ligand 2-(2′-pyridylmethyleneaminomethyl)pyridine (I, R = H) obtained by Lions and Martins[2] from pyridine-2-aldehyde and 2-aminomethylpyridine (see Figure 1). Spectroscopic evidence thus supports the proposed structure.

In order to provide chemical structural proof, an attempt was made to reduce the >CH·OH grouping to

---

[1] C. Harries and G. H. Lénárt, *Ann. Chem.*, **410**, 115 (1915).

[2] F. Lions and K. V. Martins, *J. Am. Chem. Soc.*, **79**, 2733 (1957).

$>CH_2$, in order to obtain the known derivative of Lions and Martins. Reduction with zinc dust in dilute acetic acid yielded a product, the analysis of which closely agreed with that calculated for bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) perchlorate. Its absorption spectrum ($\lambda_{max}$ 568 m$\mu$), however, was slightly different from the spectrum of an authentic sample of the complex ($\lambda_{max}$ 569 m$\mu$) prepared according to the Lions and Martins[2] procedure. When this preparation was repeated, small changes in the absorption spectrum were again observed, suggesting formation of more than one and possibly isomeric species. Experimental conditions were finally found by which the condensation of pyridine-2-aldehyde, 2-aminomethylpyridine, and ferrous salt yielded a product whose absorption spectrum was practically identical with that of the product obtained by reduction of the hydroxy derivative (see Figure 1). The constitution of the latter therefore seems definitively established.

### Experimental

(1) **Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]-iron(II) Perchlorate.**—To 2.14 g. (20 mmoles) of pyridine-2-aldehyde in 10 ml. of ethanol, kept under nitrogen, was added 15 ml. of 0.4 *M* ferrous chloride (6 mmoles) followed by 5 ml. of 2 *M* ammonium bicarbonate (10 mmoles). Copious amounts of carbon dioxide were evolved and the mixture turned dark violet. After standing for 5 min. at room temperature, 5 g. of sodium perchlorate was added and the mixture kept at 0° for 3 hr. The amorphous precipitate was filtered off and washed with a solution of sodium perchlorate and finally with water; yield, 3 g.

*Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3O)_2](ClO_4)_2$: Fe, 8.20; N, 12.35. Found (dried over $P_2O_5$ *in vacuo*): Fe, 8.4; N, 12.6, 12.3.

(2) **Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]-iron(II) Chloride 6-Hydrate.**—To 2.14 g. (20 mmoles) of pyridine-2-aldehyde in 20 ml. of water, kept under nitrogen, was added 2.5 ml. of 2 *M* ferrous chloride (5 mmoles) followed by 2 g. of solid ammonium chloride. The dark violet solution was kept at 25° for 15 min. and then at 0° for 1 hr. The crystalline product was filtered off, washed with a few ml. of a solution of ammonium chloride, and air-dried; yield, 1.9 g.

*Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3O]_2)Cl_2 \cdot 6H_2O$: $H_2O$, 16.35. Found: $H_2O$, 16.85, 16.6. Calcd. for $[Fe(C_{12}H_{11}N_3O)_2]Cl_2$: Fe, 10.09; N, 15.19; Cl, 12.82. Found (dried over $P_2O_5$ *in vacuo*): Fe, 10.0, 10.1; N, 15.2, 15.3; Cl, 12.75.

The filtrate, which contained unreacted pyridine-2-aldehyde as the hydrochloride, was treated with sodium bicarbonate and then sodium perchlorate. The precipitated product (1.2 g.) had the same composition and spectrum as the product obtained under (1).

(3) **Bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) Perchlorate.** (**A**).—A solution of 1.07 g. (10 mmoles) of pyridine-2-aldehyde in 5 ml. of ethanol was mixed with 1.08 g. (10 mmoles) of 2-aminomethylpyridine, and the mixture was kept at 25° for 20 min.; 25 ml. of 0.2 *M* ferrous chloride (5 mmoles) was then added under nitrogen and the mixture kept at 0° for 1 hr. The crystalline chloride was filtered off and dissolved in 20 ml. of water, and the perchlorate of the complex was precipitated by slowly adding a solution of sodium perchlorate. The amorphous product was filtered off, washed with a diluted solution of sodium perchlorate and then with water, and air-dried; yield, 1.2 g.

*Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3)_2](ClO_4)_2$: Fe, 8.60; N, 12.95. Found (dried over $P_2O_5$ *in vacuo*): Fe, 8.5; N, 13.05. (The air-dry product contained 3.35% $H_2O$.)

Addition of sodium perchlorate to the filtrate from the complex chloride precipitated 2 g. of a less pure product. *Anal.* Found: Fe, 8.8; N, 12.2. Its absorption spectrum had slightly shifted and broadened toward longer wave lengths, but was otherwise very similar to the spectrum of the first fraction.

(**B**).—Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) chloride 6-hydrate (1 g.) was dissolved in 40 ml. of 4 *M* acetic acid. Under vigorous stirring 1 g. of zinc dust was added, the temperature being kept at 30–35°. After 10 min., 1 g. of zinc dust was added, and stirring was continued for 10 min. Excess zinc dust was filtered off and washed with 50 ml. of water. The combined filtrates were treated with sodium perchlorate, thereby precipitating a red, amorphous product. After 1 hr. the precipitate was filtered off, washed with a solution of sodium perchlorate and then with water, and air-dried; yield, 0.5 g.

*Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3)_2](ClO_4)_2$: Fe, 8.60; N, 12.95. Found (dried over $P_2O_5$ *in vacuo*): Fe, 8.55, 8.6; N, 13.0, 13.05. (The air-dry product contained 3.5% $H_2O$.)

---

Contribution from the Chemistry Department, Reaction
Motors Division of the Thiokol Chemical
Corporation, Denville, New Jersey

## The Chemistry of Alane. III.[1] Quaternary Ammonium Aluminohydrides[2]

By Robert Ehrlich, Archie R. Young, II,
and Donald D. Perry

*Received October 26, 1964*

The first compound containing the aluminohydride group, $LiAlH_4$, was prepared by Finholt, Bond, and Schlesinger[3] in 1947. Since that time many metal aluminohydrides have been prepared, but no report has been made of the synthesis of nonmetallic aluminohydrides such as the quaternary ammonium salts. We wish to report the synthesis of two quaternary ammonium aluminohydrides, tri-*n*-octyl-*n*-propylammonium aluminohydride, $(C_8H_{17})_3(C_3H_7)NAlH_4$ (I) and tetramethylammonium aluminohydride, $(CH_3)_4NAlH_4$ (II). The former is very soluble in benzene, toluene, and diethyl ether, and slightly soluble in hexane and pentane, while the latter is insoluble in all organic solvents. Both exhibit considerably greater hydrolytic stability than lithium aluminum hydride.

### Experimental

Reagents were handled in a nitrogen-atomosphere vacuum drybox and all reactions were conducted under dry nitrogen. Filtrations were also conducted in the drybox. Solvents were purified and dried by refluxing over $LiAlH_4$; after distillation they were stored over $LiAlH_4$ (benzene, hexane, pentane, and toluene) or LiH (diethyl ether and tetrahydrofuran). Commercial grade $LiAlH_4$ (Metal Hydrides, Inc., Beverly, Mass.) was used without further purification. Quantitative hydrolyses were performed on a Toepler pump system.

Tri-*n*-octyl-*n*-propylammonium bromide was specially prepared by Distillation Products Industries, Division of Eastman

---

[1] Paper II: *Inorg. Chem.*, **3**, 628 (1964).

[2] This research was supported by the Advanced Research Projects Agency under ARPA Order No. 24. Additional support was provided by the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, Calif., under Contracts AF33(616)-5935 and AF04(611)-7046. Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).