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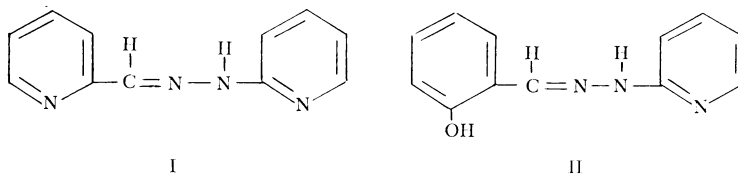
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Schiff's Bases of Pyridylhydrazine as Analytical Reagents for Cobalt

L. KEITH HUNT AND HARVEY DIEHL¹

Schiff's bases having functioned groups adjacent to the carbon-nitrogen bond so that chelation (ring formation) can occur with metal atoms are of interest because of the intense colors of the metal derivatives. Thus, the compound 1,3-bis(2'-pyridyl)-2,3-diaza-1-propene (I) abbreviated PDP reported by Lions and Martin (1) and Geldard and Lions (2) forms a compound with cobalt so intensely colored as to offer promise of use in the analytical chemistry of cobalt. We have now investigated the cobalt, iron and nickel derivatives of PDP in detail and have investigated also certain similar Schiff's bases such as 1-(2'-hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene (II), designated later as HPDP.



EXPERIMENTAL WORK

Apparatus and Materials. Absorption spectra were obtained on Beckmen DK2 and DU spectrophotometers. All spectrophotometric data used in determining combining ratios were obtained on the DU spectrophotometer.

Thermogravimetric analyses were made using the instrument described by Diehl and Wharton (3).

Karl Fischer titrations for water were carried out by addition of excess Karl Fischer reagent and back titration with a standard methanol-water solution. The reagent was standardized against analytical reagent grade sodium acetate trihydrate. The endpoint was determined by the "dead stop" method. The visual endpoint could not be used because of the dark color of the solutions titrated. The titration system was protected from moisture in the air by a calcium sulfate drying tube. The sample was added through a stopper in the top of the titration flask and the transfer of sample was made as rapidly as possible to prevent entrance of moisture. The dead stop electrodes were two bright platinum wires sealed into the bottom of the titration flask.

All pH measurements were made with a Beckman Model G

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pH meter standardized against commercial buffers. The constant ionic strength buffers used in spectrophotometric studies were prepared by the method of Bates (4).

Paper electrophoresis experiments were made with a horizontal type apparatus manufactured by the C-E Apparatus Co., Swarthmore, Penn. A 0.1 M potassium acid phthalate solution was used as buffer. The pH of this solution was approximately pH 7. A 500 volt, 10 mamp. current was applied.

Electrical conductance was measured on an Industrial Instruments Co. Conductance Bridge, Model RC16B2. The cell constant was determined with 0.01 M potassium chloride at 25° using the value 0.0014087 for the specific conductance, data of Jones and Bradshaw (5); the cell constant was 0.062.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Spectrometer Model HR60 with a 60 Mc field. Solutions of cobalt(II) perchlorate and PDP were purged of oxygen with pure nitrogen and mixed in a system free of atmospheric oxygen to form the cobalt-PDP complex. A sample of this solution was transferred to a glass NMR sample tube and the tube sealed with a torch. The spectrum of this solution was then run. The sample tube was opened and air bubbled in for a few minutes. The solution was again purged of oxygen by bubbling nitrogen into the sample tube. The NMR spectrum of the solution was then run.

Standard solutions of cobalt(II) were prepared from cobalt (II) sulfate prepared from hexamminecobalt(III) oxalate and thus free from iron and nickel impurities.

Iron(II) solutions were prepared from ferrous ethylenediammonium sulfate obtained from the G. Frederick Smith Chemical Co. Standard nickel(II) solutions were prepared by dissolving Mond nickel (International Nickel Co.) in a minimum amount of nitric acid.

2-Pyridinecarboxaldehyde and 2-chloropyridine were obtained from the Aldrich Chemical Co., and were used without further purification. Salicylaldehyde was obtained from Eastman Kodak Co.

2-Pyridylhydrazine was prepared by refluxing 2-chloropyridine with excess hydrazine hydrate in ethanol solution.

1,3-Bis(2'-pyridyl)-2,3-diaza-1-propene (PDP). PDP was prepared by refluxing 1 ml. of 2-pyridinecarboxaldehyde with 1 ml. of 2-pyridyl-hydrazine in 10 ml. of ethanol and several drops of glacial acetic acid. Pale yellow needles crystalized from ethanol, melting point 178-180°.

1-(2'-Hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene (HPDP). HPDP was prepared by refluxing 1 ml. of salicylaldehyde with

1 ml. of 2-pyridylhydrazine in 10 ml. of ethanol with several drops of glacial acetic acid. White needles recrystallized from ethanol, melting point 123.5-124.5°.

Cobalt Derivative of PDP. Cobalt(II) perchlorate was added to an ethanol solution of PDP. An ice cold, saturated solution of potassium bromide was added and the green precipitate filtered off. The material was recrystallized from ethanol-water mixture yielding iridescent green plates, melting point 303-304°. This compound gave a red-brown solution in water and crystals appeared red under a low power microscope. An aqueous solution of the compound gave a precipitate of silver bromide on the addition of silver nitrate solution. Found: C, 46.55; H, 4.10; N, 19.17; Br, 13.19; Co, 10.30; calculated for $C_{22}H_{18}N_8CoBr \cdot 3H_2O$: C, 45.00; H, 4.09; N, 19.20; Br, 13.56; Co, 10.01.

Variable results were obtained in an attempt to determine the water in the compound by Karl Fischer titration. Thermogravimetric analysis of the cobalt compound showed the progressive loss of water, bromide, and PDP with increasing temperature, water being lost initially at about 100°. Following the loss of water, there was no loss in weight up to 270°, at which temperature bromine was expelled. A final loss in weight from 320 to 560° corresponded to the loss of PDP, leaving only cobaltous-cobaltic oxide, Co_3O_4 . Apparently the PDP was not lost as an intact molecule but was degraded in several steps.

Absorption spectra for the cobalt compound were obtained using one centimeter square quartz cells. All solutions were blanked against distilled water. A preliminary spectrum of PDP in the absence of metal ions had so little absorbance in the 400 to 800 μ m region that no blank correction was necessary. The spectrum of the cobalt compound did not change appreciably on standing several days.

The conductance of the cobalt compound was determined in 0.001 M solution to determine the charge on the ion in solution. Migration of the compound in an electric field was also studied using paper electrophoresis. The migration of the highly colored compound in the electric field was easily followed.

The formation of the compound in aqueous solution was studied by Job's method of continuous variations. Eleven 100 ml. volumetric flasks were numbered consecutively from 0 to 10 and to each flask was added the same number of milliliters of 0.001 M PDP as the flask number. A standard 0.001 M cobalt (II) sulfate solution was then added to each flask such that the total number of milliliters of cobalt (II) plus PDP is 10 ml. The solutions were then diluted to mark with a constant ionic strength buffer of pH 4.6 and $\mu = 0.1$. Several hours were allowed for equilibration before reading the absorbance. A similar

continuous variations study using a pH 8.3, $\mu = 0.1$ buffer was also made.

Iron(II) Derivative of PDP. An aqueous solution of ferrous ammonium sulfate was added to a solution of PDP in ethanol and then a cold, saturated solution of potassium bromide was added. The iron compound of PDP crystallized in dark red-brown plates, from ethanol, melting point 189-191°.

A continuous variations study of the iron compound was made in the same manner as is described for the cobalt compound.

Water in the iron compound was determined by Karl Fischer titration using the same apparatus and technique as was described for the cobalt compound. Found: 8.88 per cent Fe; 8.28 per cent H₂O calculated for C₂₂H₂₀N₈FeBr₂·3H₂O; 8.4 per cent Fe; 8.12 per cent H₂O. The visual end-point could not be used because of the dark color of the solution titrated. The conductance of the iron compound was measured and the results are given in Table I. An NMR spectrum was obtained in the same manner as described for the cobalt compound.

Thermogravimetric analysis gave weight losses at about the same temperature as those for the cobalt compound.

Nickel Compound of PDP. The nickel(II) derivative of PDP was prepared using the same procedure used in preparing the iron and cobalt compounds. The compound crystallized from ethanol to give red-bronze plates, melting point 264-265°. A water solution of the nickel compound gave a yellow solution. No precipitate of silver bromide was observed when silver nitrate was added. Addition of a few drops of nitric acid and then silver nitrate gave a silver bromide precipitate. Electrophoresis experiments were run to determine the charge on the ions formed in aqueous solution.

RESULTS AND DISCUSSION

The continuous variations data show that the combining ratio of cobalt and PDP is 1:2. This is confirmed by the analytical data. The formula calculated from this data is C₂₂H₁₈N₈CoBr. Thermogravimetric analysis shows the loss of three molecules of water per cobalt and also one bromide with increasing temperature. Although the PDP is not lost as a whole molecule, the total weight lost from the loss of bromide to the final residue of Co₃O₄ corresponds to the loss of two molecules of PDP. The conductance of a 0.001 M solution of the cobalt compound is that of a 1:1 electrolyte. Addition of silver nitrate gave a precipitate of silver bromide indicating the bromide is ionic and does not occupy a position in the coordination sphere about the cobalt atom. Further evidence of this is given by paper electrophoresis experiments. The colored cobalt compound migrated

toward the negative electrode indicating that the ion is positively charged.

The broad peaks in the NMR spectrum of the cobalt compound formed in the absence of oxygen indicate that the cobalt is present as cobalt(II). When the NMR sample tube was opened and air bubbled through the sample for a few minutes and the spectrum run again, the peaks were very sharp indicating the presence of diamagnetic cobalt(III). The cobalt(II) compound is apparently formed first and then immediately air oxidized to cobalt(III).

The variable results obtained in the Karl Fischer titration for water in the cobalt compound probably result from instability of the cobalt(III) compound in the pyridine-methanol solution used as solvent in the titration, some of the Karl Fischer reagent being oxidized by the cobalt(III).

All these data lead to the conclusion that the cobalt compound formed in the presence of air and the solid is $(C_{11}H_9N_4)_2Co(III)Br \cdot 3H_2O$. In the formation of this compound two hydrogen atoms must be lost from the organic part of the molecule during formation; the hydrogen on nitrogen number three in 2,3-diaza-1-propene seems to be the most likely one to be lost.

The absorption spectrum of the cobalt compound has maximum absorption at 470 $m\mu$. The molar extinction coefficient is about 28,000.

The combining ratio of iron to PDP was shown to be 1:2 by the continuous variations method. The determination of water by the Karl Fischer titration and the thermogravimetric analysis showed the presence of three molecules of water. The thermogram also showed the loss of two bromide atoms per iron. A further loss in weight corresponding to the loss of two PDP molecules was also observed.

Conductance measurements on 0.001 M solutions of the iron compound were typical of a 2:1 electrolyte. The data are given in the following table:

Table 1. Conductance of the Cobalt and Iron Derivatives of 1,3-Bis(2'-pyridyl)-2,3-diaza-1-propene

	specific conductance	molar conductance
$Co(NH_3)_6Cl_3$	4.575×10^{-4}	457.5
$Co(PDP)_2Br \cdot 3H_2O$	1.065×10^{-4}	106.5
$Fe(PDP)_2Br_2 \cdot 3H_2O$	2.02×10^{-4}	202.0

The NMR spectrum for the iron compound showed no broadening of the peaks due to paramagnetism. The iron is thus present as iron(II). The spectrophotometric data, thermogravimetric analysis, NMR spectrum, and conductance data lead to the

conclusion that the iron compound is $(C_{11}H_{10}N_4)_2Fe(II)-Br_2 \cdot 3H_2O$. The iron compound has maximum absorbance at $520 m\mu$ and molar extinction coefficient of about 12,500.

The nickel compound of PDP was not completely characterized. Tests with silver nitrate seem to indicate that bromide is present in the coordination sphere. Nitric acid displaces the bromide which then reacts with silver nitrate. Electrophoresis experiments showed that the colored part of the molecule is positively charged. Thermogravimetric analysis indicate a loss of three molecules of water per nickel.

1-(2'-hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene(II). Compound II, designated as HPDP, differs from 1,3-bis(2'-pyridyl)-2,3-diaza-1-propene (PDP), compound I, only in having a 2'-hydroxyphenyl group in place of a 2-pyridine group on carbon one of 2,3-diaza-1-propene. Structural formulas I and II show this similarity. Metal derivatives of PDP and HPDP should have similar structures, differences being due to the relative bonding abilities of nitrogen and oxygen with the metal.

The combining ratio of HPDP with cobalt has been shown to be 2:1 by the method of continuous variations. This cobalt compound has intense absorption of possible analytical use in the $430 m\mu$ region of the spectrum. Other compounds of HPDP with iron, nickel, manganese, copper, palladium, and platinum have also been prepared.

It is particularly interesting that Schiff's bases of salicylaldehyde like HPDP form fluorescent calcium and magnesium complexes in solution. This is not unexpected since the Schiff's bases formed from salicylaldehyde and o-aminophenol is similar in overall structure to o,o'-dihydroxyazobenzene used by Diehl and coworkers (6) in the fluorometric determination of magnesium. Unfortunately, all the Schiff's bases investigated formed alkaline earth compounds only with very large excess of metal ion. None appear to offer possibilities as analytical reagents.

The spectrophotometric data gives promise that PDP may be a very useful colorimetric reagent for cobalt(II), iron(II), and nickel(II). The molar extinction coefficients are extremely high and no other elements interfere. Both cobalt and iron can be determined in the presence of nickel since the nickel compound does not form below pH 6 as do the iron and cobalt complexes. The iron and cobalt compounds have overlapping spectra and the problem of determining one in the presence of the other is much more difficult. Some experimental work not yet finished indicates that the differences in extractability into immiscible solvents will make it possible to extract the cobalt compound leaving the iron compound in the aqueous phase.

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The Treatment of a Cesium Ore by Sulfur Chloride and Chlorine¹

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Abstract. A Southern Rhodesian cesium ore containing essentially pollucite was chlorinated by a gaseous mixture of sulfur chloride and chlorine at temperatures between 500 and 700°C. The reaction products consisted principally of SiCl_4 , AlCl_3 , CsCl , and $\text{CsCl} \cdot \text{AlCl}_3$. Under favorable conditions for chlorination, 17 wt % of the ore remained unreacted. The optimum conditions were the fixed bed reactor used in this study were chlorination at 650°C for 4½ hr with an ore particle size that passes a 150 mesh sieve.

For a number of years cesium metal has been used as a "getter" for scavenging residual gases from vacuum tubes, as the light sensitive element in photo-electric cells, and as a reactant in certain organic syntheses. Cesium is currently receiving consideration for a number of potential applications. In the development of an ion rocket motor for deep-space propulsion systems, this metal is being tested and conditions for its use are being studied (1). Other anticipated uses for cesium are in magnetohydrodynamic and thermionic methods of power generation (1). If these applications develop as desired, the demand for the pure metal can be expected to increase sharply in atomic energy and space programs. It is estimated that a single trip of a deep-space vehicle using ion engine power will require approximately 300 lb of cesium, an amount roughly equal to the entire domestic production for the year 1962 (2). Consequently, interest in the development of new cesium production methods has increased. The work presented here deals with one aspect of the extractive metallurgy of cesium.

Bunsen and Kirchoff in 1860 discovered the element cesium by observing its spectrum in a Dürkheim mineral water (3). Twenty-one years later, Setterberg prepared the metal in Bunsen's laboratory by electrolysis of a molten salt mixture (3,4).

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