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## The Cobalt-3,5-Dimethylpyrazole Reaction

By RONALD T. PFLAUM and LOWELL H. DIETER<sup>1</sup>

The reaction of 3,5-dimethylpyrazole with cobalt (II) ion in aqueous solution was first observed by Fischer in 1925 (1). He investigated a series of organic compounds as precipitants for the common metal ions and noted that aluminum, cobalt, iron, and zinc (among others) formed precipitates with 3,5-dimethylpyrazole. Surprisingly enough, precipitation was not observed with copper and nickel. A reagent capable of differentiating between cobalt and nickel was thus potentially available.

In 1930, Heim (2) used 3,5-dimethylpyrazole for the determination of cobalt ion in solutions of cobalt salts after separation of interfering ions. The blue-violet precipitate formed in basic solution was filtered, washed, dried, and weighed as  $\text{Co}(\text{C}_5\text{H}_7\text{N}_2)_2$ . More recently, the use of the reagent as a precipitant for cobalt has been advanced (7). Procedures are outlined for the determination of cobalt in organic compounds after destruction of the organic matter by sulfuric acid and peroxide oxidation.

Present interest in the cobalt-3,5-dimethylpyrazole system was concerned with the possible colorimetric determination of the metal ion with the reagent. Solubility of the colored material in a non-aqueous medium with retention of coloration would form the basis of such a method. Solubility to yield a colored solution (the precipitated species would remain as an undissociated species) might be expected from the similarity to the cobalt (1) acetylacetonate complex which is soluble in most organic solvents.

### EXPERIMENTAL PART

#### *Apparatus and Reagents*

All pH measurements were made with a Beckman Model G pH meter at room temperature of 25°. An automatic recording thermogravimetric balance was used for the thermogravimetric analyses. Electro-depositions were carried out with a WACO Electroanalyzer equipped with an A. C. rectifier.

The 3,5-dimethylpyrazole,  $\text{N}=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{NH}$ ,  
 $\text{C}_5\text{H}_7\text{N}_2$  was prepared by the condensation of acetylacetone with hydrazine sulfate in alkaline solution (8). One-half mole of hydrazine sulfate

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(6.5 grams) was dissolved in 400 ml. of 10% sodium hydroxide solution in a 1 liter 3-necked flask fitted with a thermometer, a stirrer, and a separatory funnel. The flask was cooled to 15° in an ice bath and 0.5 mole of acetylacetone (50 grams) was added dropwise at 15° with stirring. The mixture was stirred for an hour at 15° and then was transferred to a separatory funnel. The product was extracted from aqueous solution with one 125 ml. portion of ether and four 40 ml. portions of ether. The combined extracts were washed with sodium chloride and dried over anhydrous sodium carbonate. The ether was distilled off and the 3,5-dimethylpyrazole residue dried under reduced pressure. The yield was 38 grams (79%) of a slightly colored material with a melting point of 107-108° (literature value 107°). Recrystallization from ethanol yielded a colorless material of the same melting point. Recovery of purified product was low due to the high solubility in ethanol.

The 1-phenyl-3,5-dimethylpyrazole compound was prepared by the condensation of acetylacetone with phenyl-hydrazine (3). The 3,5-diphenylpyrazole compound was prepared by the reaction of hydrazine sulfate with 1,3-diphenyl-1,3-propanedione in aqueous ethanolic solution containing sodium carbonate (4). Attempts to prepare pure pyrazole by standard methods were unsuccessful (5).

A standard solution of cobalt (II) sulfate was prepared by the dissolution of cobalt sulfate heptahydrate in distilled water. Standardization was carried out by electrodeposition of cobalt. All other reagents used were of reagent grade quality.

### *The Precipitation Reaction*

A study of the precipitation reaction between cobalt (II) ion and 3,5-dimethylpyrazole was carried out as the initial step in this investigation. A stock solution containing 5.52 mg. of cobalt per ml. and a 2% aqueous stock solution of the reagent were prepared. Precipitations were effected at the proper pH from solutions which contained 0.34 mg. of cobalt per ml. and a 50% excess of the reagent. The pH of solutions was varied by the addition of dilute ammonium hydroxide, sodium hydroxide, or sulfuric acid. The effects of diverse ions were studied by the addition of the reagent to solutions of the particular ion in the presence of and in the absence of cobalt ion. The substituted pyrazole compounds mentioned above were investigated as precipitants.

### *Investigation of the Cobalt Precipitate*

The blue-violet precipitate formed in the reaction of cobalt with 3,5-dimethylpyrazole was obtained by filtration of the reaction solution in a medium porosity sintered glass crucible. After standard washing and drying procedures, the material was subjected to ele-

mental analysis of carbon, hydrogen, and nitrogen, to electroanalysis by deposition of cobalt from homogeneous acidic solution, and to thermogravimetric analysis. Solubility characteristics of the precipitate in a series of organic solvents were obtained by adding 0.1 mg. amounts of the material to 5 ml. of the solvent with vigorous agitation. Absorption characteristics of the precipitate and of the reagent were obtained spectrophotometrically.

## RESULTS AND DISCUSSION

The addition of 3,5-dimethylpyrazole to an acidic or neutral solution of a cobalt salt does not produce any visible reaction. Increase of the pH of the solution by the addition of sodium hydroxide or ammonium hydroxide results in the formation of a dense blue violet precipitate which rapidly settles out of solution. The material is much unlike the flocculent, light blue cobalt hydroxide which forms under identical conditions in the absence of the reagent. No reactions occur upon the addition of 1-phenyl-3,5-dimethylpyrazole or 3,5-diphenylpyrazole to solutions of cobalt (II) ion.

Inasmuch as the cobalt ion reacts with 3,5-dimethylpyrazole in basic solution, the investigation of the effects of diverse ions were carried out under basic conditions. It was found that a number of common metal ions are precipitated by the reagent. Heavy metal ions appear to be the most reactive. A summary of the results is shown in Table 1. Differences in the observations of this study and of those reported by Fischer (1) are noted.

Table 1  
Precipitates Formed with 3,5-Dimethylpyrazole and Metal Salts  
in Basic Solution

<i>Salt</i>	<i>Precipitate</i>	<i>Salt</i>	<i>Precipitate</i>
AlCl <sub>3</sub> .6H <sub>2</sub> O	— <sup>a</sup>	MgCl <sub>2</sub>	—
BaCl <sub>2</sub> .2H <sub>2</sub> O	White	MnCl <sub>2</sub> .4H <sub>2</sub> O	—
CaCl <sub>2</sub>	—	Hg(NO <sub>3</sub> ) <sub>2</sub>	White
CdCl <sub>2</sub>	—	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	— <sup>a</sup>
Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	Blue Violet	KCl	—
CrCl <sub>3</sub> .6H <sub>2</sub> O	— <sup>a</sup>	AgNO <sub>3</sub>	White
CuSO <sub>4</sub> .5H <sub>2</sub> O	— <sup>a</sup>	NaCl	—
FeCl <sub>3</sub> .6H <sub>2</sub> O	— <sup>b</sup>	SnCl <sub>2</sub> .2H <sub>2</sub> O	—
Pb(NO <sub>3</sub> ) <sub>2</sub>	White	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	White

<sup>a</sup>. . . . Hydroxide formation observed.

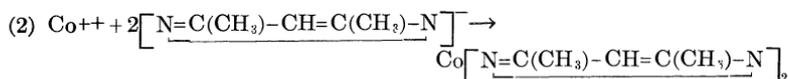
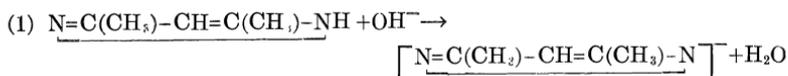
<sup>b</sup>. . . . A brown gold compound was reported by Fischer.

— No reaction with the organic reagent.

Since copper, iron, and nickel are commonly found together with cobalt in a sample and since these metals form insoluble hydroxides under conditions for the formation of the cobalt 3,5-dimethylpyrazole compound, it was desirable to eliminate the interferences due to these ions. It was found that the use of ammonium hydroxide in place of sodium hydroxide as the basic medium was satisfactory and

would eliminate the formation of copper hydroxide. Small amounts of nickel and iron could be kept in solution by the addition of tartrate and thiocyanate ions respectively.

It has been stated that cobalt precipitates with the reagent in basic solution. Presumably the reaction proceeds as follows:



The two step reaction involves removal of a proton by the base to form the organic anion with subsequent coordination of cobalt (II) ion to form the neutral complex.

It was found that the complex isolated from strongly basic solution was not identical with that obtained at a lower pH value. Precipitate isolated at pH 13 was dried for 6 hours at 110° and analyzed.

Anal. Calcd, for  $\text{Co}(\text{C}_5\text{H}_7\text{N}_2)_2$ : C, 48.10%; H, 5.64%

Found: C, 33.61%; H, 3.96%

Thermal decomposition of 27.9 milligrams of the material yielded 13.4 grams of  $\text{Co}_3\text{O}_4$  at 800°. It is evident that the precipitate cannot be  $\text{CoR}_2$  as has been reported, but is a mixture in which  $\text{Co}(\text{OH})_2$  is one of the components.

Precipitate isolated from solution of pH 7.5-9.0 was analyzed after drying in an oven at 110° for 8 hours.

Anal. Calcd. for  $\text{Co}(\text{C}_5\text{H}_7\text{N}_2)_2$ : C, 48.10%; H, 5.64%; N, 22.40%. Found: C, 48.01%; H, 5.71%; N, 22.59%.

Thermogravimetric analysis gave 7.9 milligram of  $\text{Co}_3\text{O}_4$  for a 26.9 milligram sample of precipitate, the theoretical amount for a 2:1 ratio of reagent to cobalt ion. Electro-deposition yielded 16.5 milligram of cobalt from 70.7 milligram of precipitate as compared to the 16.7 milligram of cobalt present in the 2:1 compound. Thus, the analytical precipitate formed in a solution of controlled pH has the formula of  $\text{CoR}_2$ .

The solubility of the cobalt compound in non-aqueous media was ascertained. A number of solvents including acetic acid, acetone, acetonitrile, benzene, carbon tetrachloride, chloroform, cyclohexane, dimethylformamide, dioxane, ethanol, ethylenediamine, hexane, isoamyl alcohol, methanol, methyl cellosolve, morpholine, nitrobenzene, pyridine, and tetrahydrofuran were investigated. No dissolution was observed except in the case of the most basic solvents. Only a

partial solubility at best was observed with ethylenediamine, morpholine, and pyridine. The colorations which resulted were characteristic of the amine complexes of cobalt rather than the 3,5-dimethylpyrazole compound.

The insolubility of the colored compound precluded an investigation of 3,5-dimethylpyrazole as a colorimetric reagent for cobalt. A spectrophotometric study of the reagent itself showed absorption characteristics that were unsuited to the determination of the organic compound after decomposition of the complex in acidic solution. An absorption maximum at 322  $m\mu$  has a molar absorptivity of less than 25. Other maxima at lower wavelengths were not observed. Thus, a colorimetric procedure for cobalt with the reagent is not a feasible undertaking.

The insolubility of the cobalt compound in organic solvents is rather unexpected in view of the solubility of other somewhat similar cobalt complexes. As a comparison, the cobalt acetylacetonate complex,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$ , formed from the reaction of cobalt hydroxide and the diketone, is soluble in water and in most organic solvents. The hexacovalent coordination sphere of the cobalt atom is unsaturated being quadricovalent due to the bidentate nature of the acetylacetonate ligand. Saturation of the coordination sphere by solvation with the solvent is the driving force behind dissolution in practically all solvents. Thus, the acetylacetonate complex readily forms diamines with ammonia and pyridine (6).

The 3,5-dimethylpyrazole complex of cobalt has a higher degree of coordination unsaturation than has the acetylacetonate compound. A study of the organic ligand, 3,5-dimethylpyrazole, shows that it must be unidentate with respect to the cobalt ion. Thus only two coordination positions on the cobalt atom are filled and a high degree of coordination unsaturation exists. However, it is difficult to solvate these unfilled positions even with strongly basic organic ligands. Such behavior suggests a unique configuration for the complex.

A sandwich type structure, with the cobalt atom between the two organic ligands, provides a convenient picture of the complex. It serves to explain the insolubility of the compound inasmuch as the cobalt atom is essentially covered up by the layers of ligand. Solvent molecules apparently cannot penetrate to the inner coordination sphere. The nonreactivity of 3,5-diphenylpyrazole is likewise explained since steric requirements of the phenyl groups are prohibitive to complex formation.

Any procedure for the gravimetric determination of cobalt as its insoluble 3,5-dimethylpyrazole complex necessitates attention to drying conditions for the precipitated material. Existing procedures call

for drying at as low a temperature as possible (2) or for drying at 110° for 5-8 hours (7). Differential thermal analysis of the blue violet compound showed thermal stability to 205°. The compound undergoes an exothermic decomposition at 298° with only a small loss in weight. A gradual loss in weight occurs over the temperature range of 365-440°. The very stable cobaltous oxide,  $\text{Co}_3\text{O}_4$ , is present over the temperature range of 550-1000°.

The following method for the determination of cobalt with 3,5-dimethylpyrazole is proposed as the result of this study.

Preliminary treatment of the sample to yield a solution of cobalt (II) ion may be carried out by any of the standard methods. A sample in the form of an ore or alloy may be treated with hydrochloric and nitric acids. An organic compound containing cobalt may be digested with perchloric or sulfuric acid to destroy all organic matter. For all cases, the solution is diluted with distilled water and adjusted to pH 5 with dilute sodium hydroxide.

Separation of cobalt as cobalt (II)-3,5-dimethylpyrazole is effected by the addition of 10 ml. in excess of the calculated volume of a 2% aqueous solution of the reagent. Dilute sodium hydroxide is added dropwise with stirring to pH 7.5-9.0. (Dilute ammonium hydroxide is added in the presence of copper. Ammonium thiocyanate is added to prevent precipitation of iron if present. The tartrate ion is added in the presence of nickel.) The reaction mixture is allowed to stand for 20 minutes.

The precipitate is collected on a previously weighed medium porosity sintered glass crucible. Washing is effected with one 10 ml. portion of water followed by a 10 ml. portion of acetone. The crucible and precipitate are dried in an oven at 150° for 30 minutes.

Measurement is carried out by weighing the dried precipitate as  $\text{Co}(\text{C}_5\text{H}_7\text{H}_2)_2$ . The gravimetric factor, 0.2365, yields the weight of cobalt in the precipitate.

Results obtained with the preceding method are summarized in Table 2. The feasibility of the proposed method is demonstrated. The data indicate that satisfactory determinations can be carried out in the shortened time period.

Table 2  
Summary of Cobalt Determinations

Sample	Mg. Co Taken	Mg. Co Found
CoSO <sub>4</sub>	0.0234	0.0232
	0.0234	0.0233
	0.0702	0.0701
	0.0702	0.0700
	0.1170	0.1168
	0.1170	0.1166
CoSO <sub>4</sub> + NiCl <sub>2</sub>	0.0234	0.0228
	0.0234	0.0229
CoSO <sub>4</sub> + CuSO <sub>4</sub>	0.0234	0.0226
	0.0234	0.0227

## SUMMARY

The following items of interest have been ascertained as a result of this investigation.

1. The reagent, 3,5-dimethylpyrazole, reacts with cobalt (II) ion in basic solution. Other substituted pyrazole reagents do not react.
2. The reagent is not a specific precipitant for cobalt.
3. Quantitative precipitation of cobalt ion from aqueous solution occurs over the pH range of 7.5-9.0.
4. The blue-violet precipitate has been shown to be the bis-3,5-dimethylpyrazole-cobalt (II) compound.
5. The cobalt (II)-3,5-dimethylpyrazole complex is insoluble in most organic solvents.
6. The complex is thermally stable at 200°. Decomposition to  $\text{Co}_3\text{O}_4$  occurs over the temperature range of 300-550°.
7. A modified procedure for the determination of cobalt involving a great saving of time is proposed.

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