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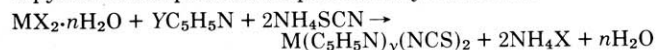
The Preparation and Analysis of Some Metal-Pyridine Complexes

A general chemistry experiment

We are in complete agreement with the statements by Snively and Yoder in a recent issue of THIS JOURNAL (1) that "the introduction of analytical techniques into the general chemistry laboratory has too often meant the addition of routine analysis of 'unknowns'. Chemists are generally more concerned with identification and characterization of their own preparations, and thus it would seem desirable to adopt the same approach in the student laboratory." The senior author subscribed to this philosophy in a general chemistry laboratory experiment published several years ago in THIS JOURNAL on syntheses and titrations of unknown acids, in which he stated that "when a student synthesizes a compound and then investigates his own product, the interest aroused is greater than that generated when the two experiments are performed separately (2)." To complement Snively and Yoder's experiment on "The Preparation and Analysis of Some Double Salts" (1), we now wish to add a similar experiment involving metal complexes.

The Experiment

The complexes formed by heterocyclic amines with halides and pseudohalides of dipositive first-transition-series metal ions have been known for many years, but recently there has been a resurgence of activity in the investigation of their properties. The most familiar of such insoluble compounds are those of pyridine. The pyridine isothiocyanate complexes are easily prepared by the reaction between a metallic salt, a soluble thiocyanate, and pyridine in aqueous solution. They are readily isolated in the pure state and can be analyzed by simple methods. Although the number of coordinated pyridine molecules varies, tetrapyridine and dipyridine compounds are particularly numerous



(For M = Mn, Fe, Co, or Ni, Y = 4; for M = Cu or Zn, Y = 2).

The thiocyanate ion is ambidentate and can coordinate to metals through either the nitrogen atom or the sulfur atom (3). Recent infrared absorption and X-ray diffraction studies have shown that metals of the first transition series normally form M-N bonds with the thiocyanate group (4), and hence the compounds prepared in this experiment are isothiocyanato complexes.

The colors and temperature stability ranges of the compounds, together with typical data on yields and analyses obtained by students, are shown in the table.

Preparation of the Complexes (5)

Dissolve 0.05 mole of the dipositive metal salt¹ in a solution of 300 ml of distilled water and 20 ml of pyridine (**Caution. Hood!**) contained in a 600-ml beaker. To the resulting solution add slowly with stirring a solution of 8.00 g of ammonium thiocyanate in 100 ml of distilled water². Allow the resulting mixture to stand in an ice bath until precipitation appears complete (about 1 hr). Collect the precipitate on an 8-cm Büchner funnel and wash it with three 10-ml portions of an ethanol-pyridine (9:1) solution. Air-dry the product for not longer than ten minutes³. Then powder it in a mor-

tar and dry it in a desiccator over potassium hydroxide until constant weight has been attained (about 24 hr).

Analyses

Pyridine (6). Dissolve a 0.5 g sample of product in 50 ml of standard 0.1 M hydrochloric acid and titrate the solution with 0.1 M sodium hydroxide to a pH of 3.00 as measured by a pH meter. In the cases of copper(II) and zinc(II), the dipyridine rather than tetrapyridine compounds are obtained.

Isothiocyanate (Reverse Volhard Method) (7). Dissolve a 0.5-g sample of product in 50 ml of 3 M aqueous ammonia and then make the solution slightly acidic to litmus paper with 6 M nitric acid. Add 50 ml of standard 0.1 M silver nitrate, 3 ml of nitrobenzene, and 10 drops of ferric alum indicator. Titrate the excess Ag⁺ with 0.1 M potassium thiocyanate to a brownish-red end point.

Additional Related Projects

The interesting properties and reactions of these colorful compounds suggest a number of projects for more ambitious students who have additional time available.

Metal Analysis. In addition to the analysis for pyridine and isothiocyanate described above, the student may be asked to devise an analytical procedure to determine the transition-metal content of his particular compound.

Gravimetric and Thermogravimetric Analysis. The formation of the complexes prepared in this experiment has been widely utilized in analytical chemistry (8, 9), and the student may wish to consult the original literature for specific details. For example, the compounds have been recommended for the gravimetric determination of manganese (10), nickel (11), and zinc (9). In some cases, the complexes have been employed not only for the determination of the metal but also for the determination of pyridine or thiocyanate.

Analysis of Chloroform Solutions. The complexes are soluble to varying degrees in chloroform, and this property has found use in analysis (12). For example, the emerald-green chloroform-soluble copper(II) complex has been suggested for the detection of copper, pyridine, or thiocyanate (13). The student may wish to devise qualitative tests as well as quantitative colorimetric procedures.

Thermal Decomposition. The complexes may be decomposed by heat into dipyridine complexes or in some cases into the anhydrous thiocyanates. The student may wish to measure dissociation pressures for these complexes (12, 14), investigate them by differential thermal analysis (15), or determine heats of decomposition (16) or kinetic parameters (17). In most cases stability trends in conformity with the Irving-Williams series (18) will be found.

Clathration. Selective clathration of the cobalt(II), nickel(II), and copper(II) complexes has been employed to separate and purify organic compounds, especially certain hydrocarbons in petroleum research (19). The student may wish to reproduce this work

¹ The nitrates, sulfates, or chlorides of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) are satisfactory. If desired, the preparation can be carried out on a smaller scale, e.g., 0.005 mole. In the case of Fe(II), add about 0.1 g of ascorbic acid in order to prevent oxidation by the atmosphere (see The Iron(II) Compound Under Additional Related Projects).

² In the case of zinc, first add the NH₄SCN solution to the solution of the zinc salt and then add the pyridine. Addition of pyridine to a solution of zinc salts produces a white gelatinous precipitate.

³ Prolonged drying in air may result in loss of pyridine.

Typical Student Results

Compound	Starting material (g)	Yield (g)	Analyses				Color (12, 14)	Stability range, °C (9)	Reference
			% Pyridine		% Isothiocyanate				
			Calcd.	Found	Calcd.	Found			
Mn(C ₅ H ₅ N) ₄ (NCS) ₂	MnSO ₄ ·H ₂ O (8.45)	17.56–20.72 (72–85%)	64.90	64.97	23.83	23.91	White	<40 (9, 10, 12, 20)	
Fe(C ₅ H ₅ N) ₄ (NCS) ₂	FeSO ₄ ·7H ₂ O (13.90)	22.00–24.20 (90–99%)	64.78	64.54	23.78	24.03	Yellow	(12, 20–23)	
Co(C ₅ H ₅ N) ₄ (NCS) ₂	Co(NO ₃) ₂ ·6H ₂ O (14.55)	22.60–24.31 (92–99%)	64.37	64.32	23.63	23.79	Pink	(12, 20)	
Ni(C ₅ H ₅ N) ₄ (NCS) ₂	Ni(NO ₃) ₂ ·6H ₂ O (14.54)	24.31 (99%)	64.40	64.22	23.64	23.52	Blue	<63 (11, 12, 20)	
Cu(C ₅ H ₅ N) ₂ (NCS) ₂	CuSO ₄ ·5H ₂ O (12.49)	15.5 (92.8%)	46.81	46.50	34.38	34.02	Green	<46 (9, 12–14)	
Zn(C ₅ H ₅ N) ₂ (NCS) ₂	Zn(NO ₃) ₂ ·6H ₂ O (14.87)	16.2 (95.5%)	46.57	46.41	34.21	White	<70 (9, 12)	

^a Easily oxidized to the violet form (see section on Additional Related Projects).

or extend it to other hydrocarbons or to the complexes of other metals.

The Iron(II) Compound. Fe(C₅H₅N)₄(NCS)₂, first synthesized in 1904 (20), was for many years believed to exist in two geometrically isomeric forms—a yellow (α) and a violet (β) form (21)—and the composition and structure of the violet form have long been a subject of controversy (22). The yellow form, the one obtained in this experiment, has finally been identified as the trans octahedral compound, whereas the violet form is merely the yellow form contaminated with traces of iron(III)(23). The student may wish to compare the two forms. He can readily obtain the violet form by evaporating a chloroform solution of the yellow form.

The Cobalt(II) and Zinc(II) Compounds. All the complexes prepared in this experiment possess an octahedral configuration except for the zinc(II) complex, which is tetrahedral. According to Graddon (24), the pink cobalt(II) and green copper(II) complexes prepared in this experiment can be obtained in tetrahedral blue and violet forms, respectively, by incorporating them in host crystals of the tetrahedral zinc(II) complex.

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