TABLE I

TABLE OF ARYL RHODANAL-$\Delta^{5,3'}$-5'-NITRO-OXINDOLES ANALYSIS (SALICYL-SULFONIC ACID METHOD)

Aryl group	M. p., °C.	Weight	0.1 *N* acid, cc.	N found, %	N calcd., %
Phenyl	260–267	0.1731	13.6	11.01	10.97
o-Anisyl	247	.1289	9.1	9.89	10.17
p-Anisyl	370	.1277	9.2	10.09	10.17
ψ-Cumyl	245	.1293	9.0	9.75	9.88
β-Naphthyl	330	.1053	7.3	9.71	9.70

Summary

Phenyl, *o*- and *p*-anisyl, *ψ*-cumyl and *β*-naphthyl rhodanic acids have been condensed with 5-nitro-isatin to form the corresponding aryl rhodanal-$\Delta^{5,3'}$-5'-nitro-oxindoles.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 27 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

CHLOROFORM SOLUBLE METAL PYRIDINE CYANATES

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

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Many compounds of pyridine with inorganic salts have been prepared and described.[1] The first mention that any of these substances is soluble in chloroform appears to be in the paper of Spacu,[2] in which the author described a delicate qualitative test in which cupric pyridine thiocyanate was precipitated from a water solution of cupric thiocyanate by the addition of pyridine. Chloroform dissolved the substance more readily than water and yielded an emerald green solution which served for the detection of one part of copper in 300,000–800,000, one of pyridine in 2000 and one of thiocyanate in 50,000. Spacu, on the basis of copper and nitrogen determinations, assigned to his substance the composition, $Cu(NCS)_2\cdot 2C_5H_5N$. E. A. Werner[3] later developed a similar test for cyanate. The

[1] Pyridine compounds with the cadmium halides, zinc iodide and cyanide and nickel bromide, Varet, *Compt. rend.*, **115**, 464 (1892), **124**, 1155 (1897); with the permanganates of silver, copper, cadmium, zinc and nickel, Klobb, *Compt. rend.*, **118**, 1271 (1894); with the sulfates and halides of iron, cobalt, nickel, cadmium, lead, copper, and manganese, Reitzenstein, *Ann.*, **282**, 267 (1894); *Z. anorg. Chem.*, **18**, 253 (1898); with copper sulfate, nitrate and acetate, Tombeck, *Ann. chim. phys.*, **21**, 433 (1900), **22**, 113 (1901); with cupric and cuprous thiocyanate, Litterscheid, *Arch. Pharm.*, **239**, 336 (1901), **240**, 74 (1902); with the thiocyanates of silver, lead, copper, manganese, nickel, cadmium, zinc, mercury, cobalt and iron, Grossmann, *Ber.*, **37**, 559 (1904); with copper nitrate, Pfeiffer and Pimmer, *Z. anorg. Chem.*, **48**, 98 (1905); and with the halides of cobalt and chromium, Werner, Feenstra and Osann, *Ber.*, **39**, 1538 (1906), etc.

[2] Spacu, *Bull. soc. Stiinte Cluj.*, **1**, 284 (1922).

[3] Werner, *J. Chem. Soc.*, **123**, 2577 (1925).

azure blue chloroform solution on evaporation yielded a bluish-lilac colored substance to which, on the basis of a copper determination, he assigned the composition, $Cu(NCO)_2 \cdot 2C_5H_5N$.

Since cupric pyridine sulfate, nitrate, chloride, etc., are insoluble in chloroform, it seems probable that the solubility of the cyanate and thiocyanate in that solvent is due to the organic nature of their acid constituents. We have found that the cupric, cobaltous and nickelous salts of the aliphatic nitramines and the cupric derivatives of biuret and various related substances combine with pyridine to form complex salts which are soluble in chloroform. Before studying these substances further, it has seemed best to gain a fuller knowledge of the metal pyridine cyanates.

We have found that copper, nickel, cobalt, cadmium, zinc and silver all form pyridine cyanates which are soluble in chloroform, and have established the composition of the complex salts by analysis for the metal and for pyridine. Cupric, nickelous, cobaltous and cadmium cyanates each form two pyridine compounds, one with more and one with less pyridine, one stable only in an atmosphere saturated with pyridine and one fairly stable in open vessels in the laboratory. Zinc dipyridine cyanate and silver monopyridine cyanate deliquesce in an atmosphere saturated with pyridine, evidently forming compounds with more of that material. These metal pyridine cyanates are insoluble in petroleum ether and carbon tetrachloride, insoluble or slightly soluble in ether, benzene and toluene, and varying from very slightly to very readily soluble in methyl and ethyl alcohol and acetone.

Cobaltous hexapyridine cyanate forms rose-colored crystals which lose pyridine rapidly in the open to leave a bright blue mass of the dipyridine compound. In chloroform solution the hexapyridine compound apparently dissociates to form the dipyridine compound and free pyridine, for the solution possesses an intense blue color. On strong cooling the solution becomes violet or lilac or pink-colored according to the degree of cold, and the same color changes are produced at room temperature by the addition of pyridine—which evidently retards the dissociation. When the pink or almost colorless solution is heated to boiling, it takes on an intense blue color even if a large excess of pyridine is present. By the careful addition of pyridine to a chloroform solution of cobaltous hexapyridine cyanate we have obtained a liquid which shows a striking change of color between the temperature of tap water, room temperature and the temperature of the body. Similar color changes occur in water solution and to a less striking degree in various organic solvents. Solutions in methyl or ethyl alcohol, acetone or xylene are purple, lavender, light blue or pale dirty brown, respectively, at low temperatures or when an excess of pyridine is present.[4]

[4] Schönn, *Z. anal. Chem.*, **9**, 209 (1870), used sodium thiocyanate as a qualitative test for cobalt. If the amount of cobalt is very small, the blue color appears only on warming.

Cobaltous hexapyridine cyanate and cupric hexapyridine cyanate[5] raise the boiling point of chloroform more than would be expected if they were completely dissociated in the solution into pyridine and the metal dipyridine cyanate. The solutions do not appear to contain ions, for they have no action on a piece of metallic zinc.

Preparation of the Compounds.—One-tenth of a mole of potassium cyanate and an equivalent amount of the metal salt were dissolved separately in water and the solutions were mixed. Pyridine was added until no further change occurred and then a little more so that a slight excess was present. The precipitated metal pyridine cyanate was extracted with 100–200 cc. of chloroform. The solution was filtered through paper previously wet with chloroform and allowed to evaporate spontaneously. The deposited crystals were freed from superficial pyridine by means of filter paper and were kept in a desiccator which contained pyridine and sticks of caustic potash in separate vessels. This procedure yielded the pyridine saturated compounds. The compounds containing less pyridine were obtained by leaving the saturated compounds uncovered in watch glasses for periods varying from two days to a week. After the samples had assumed the appearance of homogeneity they were bottled for analysis.

Determination of Pyridine.—For the determination of pyridine the samples were decomposed by boiling with caustic soda and the pyridine was distilled off and titrated. Since the pyridine was accompanied by ammonia from the hydrolysis of the cyanic acid, it was necessary to use a procedure which would take account of ammonia, and that of A. C. Houghton[6] for the determination of pyridine in ammonia liquors was finally adopted. The accuracy of the method was tested by blank determinations on weighed samples of purified pyridine, b.p. 114–115°. The pyridine was dissolved in 100 cc. of water, a few drops of ammonia added, the whole neutralized with sulfuric acid and then made alkaline with 5 cc. of normal sodium hydroxide solution and steam distilled from a 1000-cc. round-bottomed flask. The vapors passed through a 500-cc. Erlenmeyer flask containing sodium hypobromite solution (from 2.5 cc. of bromine and 100 cc. of 10% sodium hydroxide solution) which destroyed the ammonia, thence through a Kjeldahl bulb into the condenser and finally into a known amount of $N/10$ sulfuric acid solution. Best results were secured by collecting 100–125 cc. of distillate during thirty to forty minutes. Methyl red, Congo red, cochineal, methyl red-methylene blue mixture and methyl orange were all tried as indicators; none gave a very sharp end-point but methyl orange proved to be the best. After the method had been worked out, blank determinations were made as follows.

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[5] The only ones which we have tried.

[6] Houghton, *J. Ind. Eng. Chem.*, **1**, 698 (1909).

TABLE I

BLANK DETERMINATIONS

Pyridine taken, g.	Pyridine found By titration of aliquot					Average	Error, %
0.4493	0.4475	0.4450	0.4440			0.4455	−0.85
.5206	.5240	.5180	.5280	0.5230		.5232	+ .50
.5546	.5610	.5640	.5540	.5450	0.5550	.5577	+ .22
.4960	.4974	.4960	.5050	.4920	.4950	.4971	+ .09
.6047	.6045	.6035	.6050	.5960		.6023	− .39
.5567	.5458	.5475	.5410			.5475	−2.10
.6073	.6200	.6210				.6205	+2.17
.4855	.4890	.4870	.4900	.4840	.4790	.4858	+ .06
						Average error, %	0.798

The results show that the method is accurate to about 1%. The metal pyridine cyanates were analyzed by treating a sample of about 1 g. with water and 5 cc. of normal sodium hydroxide solution, and proceeding as described above.

Description of the Compounds.—Cupric hexapyridine cyanate[7] crystallizes from chloroform in azure blue prisms which retain their color and form as long as they remain in an atmosphere of pyridine. Exposed to the air for a short time the crystals change to a pale blue or bluish-lilac colored powder of cupric dipyridine cyanate, described by Werner.[3] After exposure to the air for several months, or after heating at 100° for a few hours, the latter substance changes to a pale green powder of cupric cyanate.

Nickelous hexapyridine cyanate[8] crystallizes from chloroform in blue prisms of a lighter color than those of the cupric compound. It loses pyridine to form a pale blue powder of nickelous tetrapyridine cyanate and finally an apple green powder of nickelous cyanate.

When pyridine is added to the bright blue solution which results from the interaction of potassium cyanate and cobaltous chloride, a blue precipitate forms at once and changes to one of a pink color when an excess of pyridine is added. This dissolves in chloroform and the solution, which contains free pyridine, deposits rose-colored hexagonal prisms of cobaltous hexapyridine cyanate. That substance in the open loses pyridine rapidly to yield bright blue cobaltous dipyridine cyanate, which on long exposure or heating yields lilac-colored cobaltous cyanate, which in a moist atmosphere changes in part to carbonate and oxide.

Cadmium hexapyridine cyanate[9] is considerably less soluble in chloro-

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[7] Pfeiffer and Pimmer (Ref. 1) found cupric pyridine nitrates which contained two, three, four and six molecules of pyridine.

[8] Grossmann (Ref. 1) obtained a nickelous tetrapyridine thiocyanate and Varet (*ibid.*) nickelous di- and tetrapyridine bromides.

[9] Grossmann (Ref. 1) and Varet (*ibid.*) have obtained hexa- and dipyridine compounds of cadmium thiocyanate and of the halides, as well as some compounds containing one and four molecules of pyridine.

form than the corresponding copper and nickel compounds. It crystallizes in small white crystals which lose pyridine to form a white powder of cadmium cyanate.

Zinc dipyridine cyanate[10] was more difficult to prepare than the other compounds, for it was not easily extracted by chloroform from water solution and an excess of pyridine interfered with its crystallization. It crystallizes from chloroform in granular white crystals which do not lose

TABLE II

RESULTS OF ANALYSES[a]

Compound	Pyridine, % Calcd.	Pyridine, % Found	Metal, % Calcd.	Metal, % Found
$Cu(NCO)_2\cdot 1C_5H_5N$	34.89	.....	28.05	.....
$Cu(NCO)_2\cdot 2C_5H_5N$	51.70	52.33, 52.05 51.00	20.85	21.7, 21.8, 21.8, 21.5
$Cu(NCO)_2\cdot 3C_5H_5N$	61.60	.....	16.53	.....
$Cu(NCO)_2\cdot 5C_5H_5N$	72.80	.....	11.72	.....
$Cu(NCO)_2\cdot 6C_5H_5N$	76.26	76.82, 75.93	10.23	10.78, 10.42, 10.74, 10.65
$Cu(NCO)_2\cdot 7C_5H_5N$	78.94	.....	9.07	.....
$Ni(NCO)_2\cdot 3C_5H_5N$	62.42	.....	15.45	.....
$Ni(NCO)_2\cdot 4C_5H_5N$	68.89	67.60, 68.33	12.79	13.04, 12.74, 12.70
$Ni(NCO)_2\cdot 5C_5H_5N$	73.46	.....	10.95	.....
$Ni(NCO)_2\cdot 6C_5H_5N$	76.86	76.50, 77.36	9.51	9.38, 9.57, 9.47
$Ni(NCO)_2\cdot 7C_5H_5N$	79.49	.....	8.44	.....
$Co(NCO)_2\cdot 1C_5H_5N$	35.59	.....	26.56	.....
$Co(NCO)_2\cdot 2C_5H_5N$	52.49	51.88, 52.09	19.59	19.68, 19.59
$Co(NCO)_2\cdot 3C_5H_5N$	62.37	.....	15.52	.....
$Co(NCO)_2\cdot 5C_5H_5N$	73.42	.....	10.96	.....
$Co(NCO)_2\cdot 6C_5H_5N$	76.82	76.43, 76.96	9.56	9.16, 9.25, 9.58, 9.64
$Co(NCO)_2\cdot 7C_5H_5N$	79.46	.....	8.47	.....
$Cd(NCO)_2\cdot 1C_5H_5N$	28.68	.....	40.81	.....
$Cd(NCO)_2\cdot 2C_5H_5N$	44.58	43.54, 43.27	31.72	32.13, 31.75
$Cd(NCO)_2\cdot 3C_5H_5N$	54.68	.....	25.93	.....
$Cd(NCO)_2\cdot 5C_5H_5N$	66.83	.....	19.00	.....
$Cd(NCO)_2\cdot 6C_5H_5N$	70.70	70.38, 70.78	16.77	16.60, 16.90, 16.77, 16.57
$Cd(NCO)_2\cdot 7C_5H_5N$	73.79	.....	15.00	.....
$Zn(NCO)_2\cdot 1C_5H_5N$	34.60	.....	28.06	.....
$Zn(NCO)_2\cdot 2C_5H_5N$	51.40	51.64, 52.18	20.80	21.08, 21.14, 20.93,[b] 20.66[b]
$Zn(NCO)_2\cdot 3C_5H_5N$	61.34	.....	16.53	.....
$AgNCO\cdot 1C_5H_5N$	34.53	35.36, 34.80	47.12	46.75, 46.70
$AgNCO\cdot 2C_5H_5N$	51.33	.....	35.31	.....

[a] In order that it may be evident that the analyses really fix with certainty the amount of pyridine in the complexes, the calculated values for the substances containing one more and one less molecule of pyridine than the found substances are included in the table. The figures reported for pyridine are in each case the average results from the titration of four or five aliquots.

[b] Analyzed after exposure for a week to the open air.

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[10] Grossmann (Ref. 1) and Varet (*ibid.*) obtained zinc thiocyanates, cyanides and halides with two, three and four molecules of pyridine.

their form on exposure to the air and which retain their pyridine rather strongly, for analysis showed no appreciable loss of pyridine after a week's exposure. In an atmosphere saturated with pyridine it deliquesces to form a sirupy liquid, a phenomenon which suggests that a compound containing more than two molecules of pyridine is formed.

Silver monopyridine cyanate[11] crystallizes from chloroform in very thin, silky, white needles which deliquesce in an atmosphere of pyridine and are but little affected by light. On exposure to the air it loses pyridine to form silver cyanate which is markedly more sensitive to the action of light.

Effect on Boiling Point of Chloroform.—An attempt was made to determine the extent to which cobaltous hexapyridine cyanate dissociates in chloroform solution by observation of its effect in raising the boiling point of that solvent. Preliminary experiments showed that pyridine alone in chloroform solution, even as much as 9 g. in 80 g. of solvent, behaved as a non-volatile solute and had the normal effect in raising the boiling point. The results of a typical experiment, in which 64.2 g. of chloroform was used, are tabulated below.

TABLE III

RESULTS OF EXPERIMENT

$Co(NCO)_2 \cdot 6C_5H_5N$, g.	Observed ΔT, °C.	Expected ΔT if no dissociation	Apparent number of molecules
0.1740	0.11	0.016	6.87
.2255	.14	.021	6.67
.2085	.11	.019	5.79
.6080	.36	.056	6.43

When pyridine was added to the solution which remained at the end of the experiment, it acted normally in its effect in raising the boiling point still farther.

Sixty-eight one-hundredths g. of cupric hexapyridine cyanate raised the boiling point of 76.6 g. of chloroform 0.34°, or 6.54 times as much as the amount (0.052°) which would be expected if no dissociation had occurred. The abnormal results deserve further study.

Summary

Cupric hexapyridine and dipyridine cyanate, nickelous hexapyridine and tetrapyridine cyanate, cobaltous hexapyridine and dipyridine cyanate, cadmium hexapyridine and dipyridine cyanate, zinc dipyridine cyanate and silver monopyridine cyanate have been prepared and characterized by analysis for pyridine and for the metal.

Cobaltous hexapyridine cyanate and cupric hexapyridine cyanate raise the boiling point of chloroform about six and one-half times as much as would be expected if they were undissociated molecules.

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[11] Grossmann (Ref. 1) prepared silver monopyridine thiocyanate.

Cobaltous hexapyridine cyanate yields a blue solution in chloroform which turns lilac-colored or pink if the temperature is lowered or if pyridine is added. By adjusting the amount of excess pyridine in such a solution, a liquid may be secured which changes color with very moderate changes of temperature.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

STUDY OF THE POSSIBLE ISOMERISM OF CERTAIN ANALOGS OF RESOLVABLE DIPHENYL COMPOUNDS[1]

BY J. F. HYDE AND ROGER ADAMS

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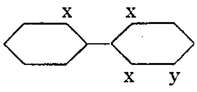
A configuration in which the two aromatic nuclei are coaxial and not in the same plane apparently accounts for all of the known facts concerning the optical activity in certain diphenyl compounds. It is generally accepted that the asymmetry arises from the influence which the groups located in the ortho position to the connecting bond have in preventing free rotation of the two nuclei. The exact nature of the interference to free rotation remains still to be determined.

Mills[2] considers it to be entirely mechanical in nature. The groups are unable to get by each other due to their size and proximity in space. Meisenheimer[3] has offered additional evidence to favor mechanical interference and has pointed out that spacings of the groups from the nucleus as well as between the two rings must be considered.

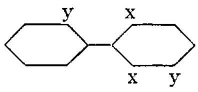
Turner and Le Fèvre[4] consider the problem from the point of view of residual affinity on each ring and the influence of the electrical nature of the ortho substituted groups.

It seems reasonably certain that the isomerism is not due to the specific effect of any particular group on the nuclei.[5]

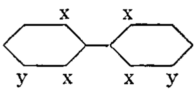
Diphenyl derivatives of the general types Ia, Ib, Ic, in which the ortho



Ia



Ib



Ic

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[1] This communication is a portion of a thesis submitted by J. F. Hyde in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Mills, *Chemistry Industry*, **45**, 883, 905 (1926).

[3] Meisenheimer and Höring, *Ber.*, **60**, 1425 (1927).

[4] Turner and Le Fèvre, *Chemistry Industry*, **45**, 831 (1926).

[5] Christie and Kenner, *J. Chem. Soc.*, **121**, 614 (1922); *ibid.*, **123**, 779 (1923); Christie, James and Kenner, *ibid.*, **123**, 1948 (1923); Christie, Holderness and Kenner, *ibid.*, **129**, 671 (1926); Bell and Kenyon, *Chemistry Industry*, **45**, 864 (1926); Turner and Le Fèvre, *ibid.*, **46**, 218 (1927).