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Certain Metal Pyridine Methylnitramine Complexes

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If methylnitramine and pyridine are added to aqueous solutions of cobaltous, cupric and nickelous salts and the solutions are shaken with chloroform, the chloroform extracts the complex salts and assumes brilliant colors, purple in the case of the cobaltous salt, green and blue in the other cases, respectively. It has seemed interesting to isolate and characterize the complex compounds and to measure their dissociation pressures, in particular to determine whether the nickelous compound, like the nickelous pyridine cyanates¹ and thiocyanates, decomposes when it is cooled. We find that it does.

TABLE I
ANALYSES

Substance	Calcd. for			Metal. %		
	Mono-	Di-	Tri-	Found		
Cobaltous dipyridine methylnitramine	20.47	16.06	13.21	16.30	16.10	16.37
Cupric monopyridine methylnitramine	21.72	17.12	14.10	21.32		
Cupric tripyridine methylnitramine	For tetra-		11.99	14.06	14.20	14.45
Cupric dipyridine nitro-urea	18.13	14.79	12.49	14.65	14.82	
Nickelous dipyridine methylnitramine	20.49	16.00	13.16	16.04	16.10	

TABLE II

Temp., °C.	DISSOCIATION PRESSURES (MM. OF MERCURY AT 20°)												
	20	25	30	35	40	50	60	70	75	80	85	90	100
Co(CH ₃ NNO ₂) ₂ ·2Py	1.1	2.0	...	3.5	...	5.9	9.8
Cu(CH ₃ NNO ₂) ₂ ·Py	3.5
Cu(CH ₃ NNO ₂) ₂ ·2Py?	0.5	...	1.4	2.7	4.9	...	7.7	...	14.8	24.6
Cu(CH ₃ NNO ₂) ₂ ·3Py	...	2.3	3.2	12.2	31.2	...	56.3	...	98.5
Ni(CH ₃ NNO ₂) ₂ ·2Py	0.6	0.9	...	1.3	1.5	2.0	2.3

The complex salts may be prepared by extracting the aqueous solution with chloroform, but they are readily soluble in water and the chloroform extracts the excess pyridine with equal facility, and pyridine interferes with their crystallization from chloroform. We have, however, prepared them successfully by this method from solutions of cupric sulfate and cobaltous and nickelous nitrates. When cobaltous chloride was used, we were not able to secure a complex salt which was free from chlorine. The complexes were prepared more easily from the metal salts of methylnitramine by exposing them to a dry atmosphere

(1) Davis and Ou, *THIS JOURNAL*, **56**, 1061 (1934).

saturated with pyridine in a desiccator containing stick caustic and pyridine in separate vessels. The salts of methylnitramine were procured by adding freshly precipitated and washed cupric and nickelous hydroxide and cobaltous carbonate in excess to warm solutions of methylnitramine, filtering, evaporating almost to dryness in a current of warm air, and drying thoroughly in a desiccator over phosphorus pentoxide. The cobaltous and cupric salts of methylnitramine have already been described by Franchimont.² The nickelous salt crystallized with difficulty. Its sirupy solution after a few days in the desiccator hardened to a brittle scaly crust, which, powdered and dried in the oven for four hours at 85°, yielded the monohydrate, Ni(CH₃NNO₂)₂·H₂O.

Anal. Calcd. for monohydrate: Ni, 25.89; for dihydrate, Ni, 23.98. Found: Ni, 25.45.

Cobaltous dipyridine methylnitramine, dull red crystals, is stable in the air but deliquesces in an atmosphere of pyridine. It is sparingly soluble in chloroform alone, but readily soluble if an excess of pyridine is present and does not crystallize readily from such a solution.

Nickelous dipyridine methylnitramine, bluish-green crystals, is moderately stable in the air and moderately soluble in chloroform.

Cupric tripyridine methylnitramine exists in the form of dark blue indigo-colored crystals and yields a deep blue-green solution in chloroform. The monopyridine compound, a light bluish-green powder, less readily soluble in chloroform than the tripyridine compound, was prepared by heating the latter at 100° for several hours. We have measured the dissociation pressure of the monopyridine compound at 100° only. The routine of measuring the dissociation pressure

(2) Franchimont, *Rec. Trav. Chim.*, **13**, 324 (1894).

showed the existence of a cupric derivative, a light purplish-blue powder, evidently cupric dipyrindine methylnitramine, intermediate between the mono- and tripyridine compounds. We have not secured it in the pure condition for analysis.

We have also prepared cupric dipyrindine nitrourea, small lilac-colored rhomb-shaped crystals, by the interaction of a cold aqueous solution of nitrourea with copper sulfate and an excess of pyridine. It is sparingly soluble in water. It decomposes overnight when in contact with water, and in the dry state gives off an appreciable amount of gas at 70°. We have not been able to measure its dissociation pressure. On standing for a year at ordinary temperature, the dry material decomposed completely into cupric dipyrindine cyanate.

Results of analysis are shown in Table I, where the calculated values for the substances containing one more and one less molecule of pyridine than the found substances are included for comparison. The dissociation pressures, determined as described in an earlier paper, are reported in Table II and are represented graphically in the semi-logarithmic chart, Fig. 1.

The curves of the dissociation pressures of the cobaltous and cupric compounds approach the curve of the vapor pressure of pyridine at elevated temperatures, and these substances decompose when they are heated. The curve of the nickelous compound, on the other hand, approaches the pyridine curve at the lower temperature, and the nickelous compound decomposes when it is cooled.

Cobaltous dipyrindine methylnitramine, cupric tri- and mono- and probably dipyrindine methylnitramine, cupric dipyrindine nitrourea and nickel-

ous dipyrindine methylnitramine have been prepared. The dissociation pressures of the methylnitramine complexes have been measured.

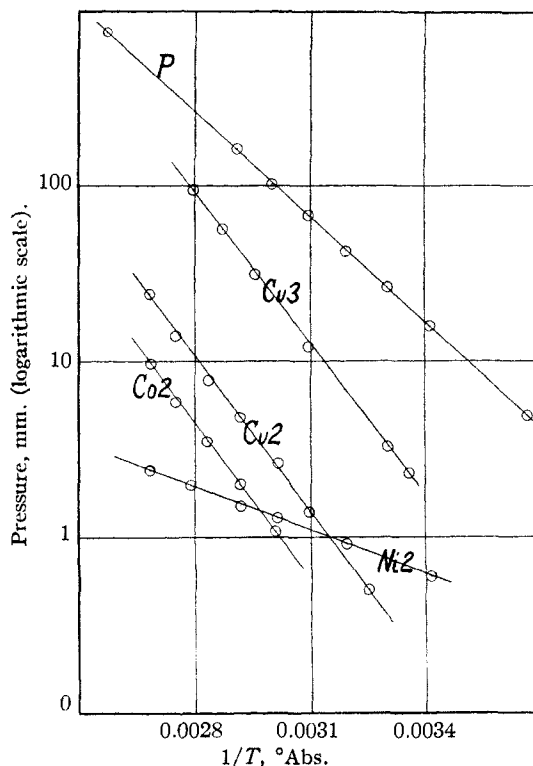


Fig. 1.—Dissociation pressures of metal pyridine methylnitramine complexes. P, pyridine (vapor pressure); Co2 cobaltous dipyrindine methylnitramine; Cu2 cupric dipyrindine ?; Cu3 cupric tripyridine; Ni2 nickelous dipyrindine.

The affinity which holds the pyridine in nickelous dipyrindine methylnitramine decreases at the lower temperatures.

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