

ribonucleotides were separated by ion-exchange chromatography.<sup>11</sup> The polysaccharide impurity was not adsorbed, and was washed off the column before the first nucleotide was eluted. Cytidylic acid, in a thin layer on a planchet, showed 750 counts/min./micromole. Adenylic and guanylic acids were separately hydrolyzed with hydrochloric acid, the purines isolated on cation-exchange columns, precipitated as copper salts, and converted to barium carbonate for counting. Cytidylic and uridylic acids were hydrolyzed with perchloric acid,<sup>12</sup> the free bases isolated on cation and anion exchange resins, respectively, precipitated as silver salts, and converted to barium carbonate. (The uracil is believed to have contained some carbohydrate impurity.) Approximately 0.25 mg. of uracil was diluted with 5 mg. of non-labeled uracil and degraded.<sup>2</sup> The results shown below indicate incorporation of the carbamyl carbon of citrulline into carbon 2 of pyrimidines.<sup>13</sup>

	Counts/min./mg. C <sup>a</sup>	
Citrulline-carbamyl-C <sup>14</sup>	66,000	
Carbon dioxide, 2nd day	29	
Carbon dioxide, 3rd day	16	
Carbon dioxide, 4th day	11	
Protein	20	
Nucleic acid	Guanine	9
	Adenine	8
	Cytosine	800
	Uracil	670
	CO <sub>2</sub> <sup>b</sup>	2
	Oxalate	0
Urea (carbon 2)	185	

<sup>a</sup> BaCO<sub>3</sub> plates, counted in a gas-flow counter, and corrected to infinite thickness. <sup>b</sup> Uracil degradation products, not corrected for approximately 20-fold dilution.

(11) W. E. Cohn, *THIS JOURNAL*, **72**, 1471 (1950).

(12) A. Marshak and H. J. Vogel, *J. Biol. Chem.*, **189**, 597 (1951).

(13) While this manuscript was in preparation, the abstract by M. P. Schulman and S. J. Badger appeared (*Fed. Proc.*, **13**, 292) showing a similar incorporation in pigeons.

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### SYNTHESIS OF THE TRIS-(DIMETHYLGLYOXIMO)-COBALTATE(III)

Sir:

Since the work of Tschugaeff,<sup>1</sup> a number of dimethylglyoximo-cobalt(III) complexes have been prepared. However, the complex compound having the internal tri-salt structure, *i.e.*, the complex compound which is formed by the coordination of three ions<sup>2</sup> of dimethylglyoxime about a cobalt atom, has never been described. Thus it has been a definite opinion that dimethylglyoxime cannot fill more than four coordination positions even when introduced into the six-coördinate complex.<sup>3,4,5</sup>

(1) L. Tschugaeff, *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **39**, 2692 (1906); **40**, 3498 (1907); **41**, 2226 (1908).

(2) The ion of dimethylglyoxime (DMG) = CH<sub>2</sub>C(NO)C(NO)H-CH<sub>3</sub>.

(3) F. G. Mann, *J. Chem. Soc.*, 412 (1933).

(4) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 2nd ed., George Routledge and Sons, Ltd., London, 1952, p. 125.

(5) L. Cambi and C. Coriselli, *Gazz. chim. ital.*, **66**, 91-96 (1936).

This concept is no longer valid since the present authors have succeeded in preparing the tris-dimethylglyoximo-cobaltate(III).

Six grams of dimethylglyoxime was dissolved completely in 60 ml. of hot water containing 6 g. of potassium hydroxide. After the solution was cooled to 40-50°, 5 g. of crystalline cobaltous nitrate hexahydrate was added. The mixture was shaken vigorously and thoroughly, and to this 12 ml. of 50% acetic acid was added. Then the air was bubbled vigorously through the reaction mixture for about three hours. Beautiful orange-yellow acicular crystals gradually were deposited. The mixture was allowed to stand for several hours, and then filtered by suction. The crude substance was recrystallized from water containing a small amount of acetic acid. Four grams of pure substance was obtained.

It is quite stable in the solid state and hardly decomposes below 180°. The crystal appears orange-yellow or brownish-yellow. It is almost insoluble in benzene and acetone, and is soluble in water, alcohol, chloroform and dioxane. It is soluble in dilute acetic acid.

In place of the potassium hydroxide and cobaltous nitrate in the above described procedure, sodium hydroxide and cobaltous chloride, respectively, may be used. Analyses were: Calcd. for [Co(DMG)<sub>3</sub>]·2.5H<sub>2</sub>O: Co, 13.12; C, 32.08; H, 5.83; N, 18.71; H<sub>2</sub>O, 10.02. Found: Co, 12.90; C, 32.51; H, 5.98; N, 18.80; H<sub>2</sub>O, 9.75.

Furthermore, it will also be concluded that three ions of dimethylglyoxime coordinate about a cobalt atom as the chelate ligands, similar to the ethylenediamine in the tris-(ethylenediamine)-cobalt(III) complex ion. If this proves to be the case the complex molecule must be optically active. Since the compound, however, could not be resolved by ordinary methods, we adopted the method of asymmetric adsorption by quartz.<sup>6</sup> From the results of this experiment a poor but definite optical activity was confirmed, supporting the above conclusion.

(6) R. Tsuchida, M. Kobayashi and A. Nakamura, *J. Chem. Soc. Japan*, **66**, 1339 (1935); *Bull. Chem. Soc. Japan*, **11**, 38 (1936).

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### THE ISOLATION OF PODOPHYLLOTOXIN GLUCOSIDE

Sir:

It has hitherto been found possible to isolate several crystalline compounds from the resin fraction of certain species of *Podophyllum* (*Berberidaceae* family) which are characterized by a noteworthy biological activity. The most important and the one occurring in the greatest quantity is podophyllotoxin.<sup>1</sup> This is present in the American species *Podophyllum peltatum* L. and in the Indian species, *P. emodi* Wall. The Indian plant also contains a compound which has one methyl

(1) V. Podwyssotzki, (a) *Arch. Exp. Path.*, **13**, 29 (1880); (b) *Ber.*, **15**, 377 (1882).