3.26 Å., nearly identical with metal distances in complexes of Ni, Pd and Pt. Here, however, the chains are alternately Au(I) and Au(III). Figure 1 shows one layer of the structure. In the layer above the one shown, cation and anion positions are interchanged and both ions rotated approximately 90° in the plane. The gold bonds are between layers. The configuration about Au(III) is octahedral, counting metal bonds, as in Ni(II), Pd(II) and Pt(II). The configuration about Au(I) is square, counting the metal bonds.

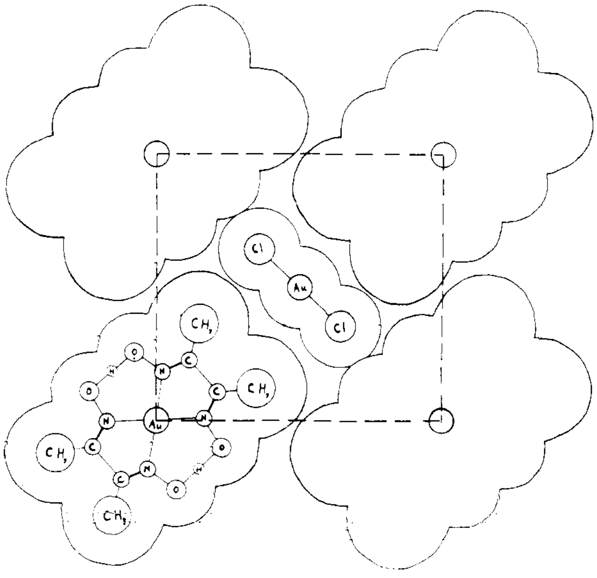

Fig. 1.—Structure for layer at $z = 0$. Layer at $z = {}^1/_2 c$ is identical except that cation and anion exchange positions are reflected through dashed line (a horizontal, b vertical).

It now appears that metals forming linear sp bonds, and possessing vacant p-orbitals, can similarly form weak metal bonds, presumably through some contribution of a dsp^2 state, illustrating anew the principle that atoms tend to use all low energy orbitals in bond formation.[3]

Though further examples of this type of interaction should be found, promotional energies are high, and the contribution of the metallic bond, small. Differences in the solubility of Ni(DMG) and $Cu(DMG)_2$[4] suggest that the Ni–Ni bond energy is approximately 10 kcal./mole. Moreover, such weak bonds can be destroyed by steric influences.

Preparation.—Aqueous $HAuCl_4$ and alcoholic dimethylglyoxime were mixed in the molar ratio 1:2. During several hours the solution deepened from yellow to red-amber, crystals separating subsequently. (Base causes immediate precipitation of lighter yellow crystals, composition as yet unknown.)

Analysis.—Au:DMG:Cl = 1:1:1. The amber crystals are notable for their stability to strong acid. (I am indebted to Dr. C. V. Banks for this analysis.)

X-Ray Data.—Orthorhombic needles, $a = 11.52$, $b = 10.59$, c (needle) $= 6.52$ Å. $\rho_{obsd} = 2.93$ g./cc., $\rho_{calcd} = 2.92$ for $z = 2$. Probable space group, Pnnm. 4Au at 000, $\frac{1}{2}\frac{1}{2}0$, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Structural Derivation.—Infrared spectra of crystalline mull is nearly identical with that of $Ni(DMG)_2$ and $Pd(DMG)_2$, establishing $Au(DMG)_2{}^+$ ion. Packing considerations plus gold positions are then straightforward. The extreme importance of gold scattering renders a complete X-ray determination nearly impossible. (Dr. Marvin Margoshes kindly obtained the infrared spectrum.)

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[3] R. E. Rundle, THIS JOURNAL, **69**, 1327 (1947); *J. Chem. Phys.*, **17**, 671 (1949).

[4] H. Christopherson and E. B. Sandell, *Anal. Chim. Acta*, **10**, 1 (1954).

CITRULLINE AS A PRECURSOR OF PYRIMIDINES[1]

Sir:

The incorporation of carbon dioxide into carbon-2 of pyrimidines in the rat was demonstrated in 1950.[2] The location of this carbon in a ureide group in the pyrimidine suggested that the mechanism of synthesis may be related to that of urea. Ratner and Pappas[3] demonstrated a condensation product of citrulline and aspartic acid (later identified as argininosuccinic acid[4]) to be an intermediate in arginine synthesis. This suggested that such a compound might be an intermediate in pyrimidine synthesis also; this would account for the appearance of carbon dioxide in carbon-2 of uracil, ~~as well as utilization of aspartic acid.~~[5]

Carbamyl-labeled L-citrulline was synthesized[6] from urea-C^{14} and L-ornithine. Administration of the citrulline-C^{14} to rats and a chick resulted in some labeling of proteins, practically no label in nucleic acid components, and excretion of the greatest portion of activity. The loss of active material by conversion to arginine was avoided by using an arginine-requiring strain of *Neurospora* (46004a).[7] The mold was grown in 900 ml. of base medium[8] to which was added 54 mg. of L-arginine and 5 mg. of L-citrulline-carbamyl-C^{14}. After growth for four days at room temperature, the washed mycelium was extracted with cold trichloroacetic acid, lipid solvents, and hot sodium chloride. The nucleate precipitated from the latter extract with alcohol was grossly contaminated with polysaccharide, and could not be completely purified by reprecipitation with alcohol or by precipitation as the lanthanum salt.[9] A quantity of this material containing 14 mg. of nucleic acid was hydrolyzed with alkali[10] at room temperature, and

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[1] Supported by Contract Number AT(30-1)-1351 with the U. S. Atomic Energy Commission.

[2] M. R. Heinrich and D. W. Wilson, *J. Biol. Chem.*, **186**, 447 (1950).

[3] S. Ratner and A. Pappas, *ibid.*, **179**, 1183 (1949).

[4] S. Ratner, B. Petracek and O. Rochovansky, *ibid.*, **204**, 95 (1953).

[5] U. Lagerkvist, P. Reichard and G. Ehrensvard, *Acta Chem. Scand.*, **5**, 1212 (1951).

[6] A. C. Kurtz, *J. Biol. Chem.*, **122**, 477 (1938). Urea-C^{14} was purchased from Tracerlab, Inc., on authorization of the U. S. Atomic Energy Commission.

[7] Kindly supplied by Dr. N. H. Horowitz.

[8] G. W. Beadle, *J. Biol. Chem.*, **156**, 683 (1944). Sucrose was re~~placed by 15 g./l. of glucose.~~

[9] J. N. Davidson and C. Waymouth, *Biochem. J.*, **38**, 39 (1944).

[10] G. Schmidt and S. J. Thannhauser, *J. Biol. Chem.*, **161**, 83 (1945).

ribonucleotides were separated by ion-exchange chromatography.[11] 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,[12] 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 [2] The results shown below indicate incorporation of the carbamyl carbon of citrulline into carbon 2 of pyrimidines.[13]

		Counts/min./mg. C[a]
Citrulline-carbamyl-C^{14}		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$_2$[b]	2
	Oxalate	0
	Urea (carbon 2)	185

[a] $BaCO_3$ plates, counted in a gas-flow counter, and corrected to infinite thickness. [b] Uracil degradation products, not corrected for approximately 20-fold dilution.

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(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,[1] 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 coördination of three ions[2] of dimethylglyoxime about a cobalt atom, has never been described. Thus it has been a definite opinion that dimethylglyoxime cannot fill more than four coördination positions even when introduced into the six-coördinate complex.[3,4,5] 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 $[Co(DMG)_3]\cdot 2.5H_2O$: Co, 13.12; C, 32.08; H, 5.83; N, 18.71; H_2O, 10.02. Found: Co, 12.90; C, 32.51; H, 5.98; N, 18.80; H_2O, 9.75.

Furthermore, it will also be concluded that three ions of dimethylglyoxime coördinate 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.[6] From the results of this experiment a poor but definite optical activity was confirmed, supporting the above conclusion.

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(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) = $CH_3C(NO)C(NOH)$-CH_3.

(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).

(6) R. Tsuchida, M. Kobayashi and A. Nakamura, *J. Chem. Soc. Japan*, **56**, 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.[1] 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

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