

The structure of these complexes is under investigation. Tin-metal bonding has recently been proposed by Gorsich¹⁰ for the related compounds $\text{Mo}(\text{CO})_5\text{SnCl}_3$ and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnCl}_3$. The platinum-tin complexes may contain $(\text{SnCl}_3)^-$ ligands attached through platinum-tin bonds.

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(10) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

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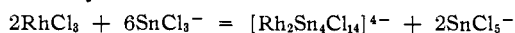
TIN(II) CHLORIDE COMPLEXES OF PLATINUM METALS

Sir:

It has been known for decades¹ that certain platinum metal halides or halide complex ions in aqueous solution or in solvents such as ethanol or ethyl acetate give colored species when treated with tin(II) chloride. The platinum chloride-tin(II) chloride system is also known to be a carbonylation and hydrogenation catalyst.²

Although Ayres³ considered the platinum species to be cationic, *viz.*, $[\text{PtSn}_4\text{Cl}_4]^{4+}$, Shukla¹ showed by electrophoresis measurements that the rhodium and platinum species are anionic in hydrochloric acid solution, an observation we have confirmed by ion exchange study. Recently⁴ a ruthenium complex (Ru:Sn ratio 1:4-5) was shown to be anionic and to be precipitated by large cations.

Our studies on the rhodium(III) chloride-tin(II) chloride system provided the first evidence for what we now consider to be the true nature of these tin-containing platinum metal complexes. Thus in ethanolic or in 3 *M* hydrochloric acid solution (main species SnCl_3^-) the Job method using the visible absorption spectrum showed that in both media the ratio Rh:Sn required for the formation of the red complex was 1:3. Addition of tetramethylammonium chloride to the solutions gave orange-yellow precipitates. The analysis corresponds to $[(\text{CH}_3)_4\text{N}]_4[\text{Rh}_2\text{Sn}_4\text{Cl}_{14}]$ [*Anal.* Calcd. C, 13.0; H, 3.2; Cl, 33.7; N, 3.8; Sn, 32.2. Found: C, 13.1; H, 2.9; Cl, 34.0; N, 3.7; Sn, 32.0] so that the interaction in 3 *M* acid may be written



We have prepared similar diamagnetic tetraalkylammonium salts (shown to be 2:1 electrolytes in dimethylformamide) of the ions $[\text{Ru}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$, $[\text{Ir}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ and $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$. While the latter ion can be obtained from PtCl_4^{2-} by chloride ion displacement, it is also formed by direct replacement by tin(II) chloride of the ligands in complexes such as $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$ and mesityloxyplatinum(II) chloride.⁵

(1) For references see S. K. Shukla, *Ann. Chim. (Paris)*, [13] **6**, 1383 (1961).

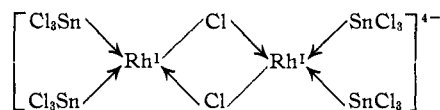
(2) E. L. Jenner and R. V. Lindsey, Jr., U.S. Pat. 2,876,254, March 3, 1959; R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(3) G. H. Ayres, B. L. Tuffy and J. S. Forester, *Anal. Chem.*, **27**, 1742 (1955); A. S. Meyer and G. H. Ayres, *J. Am. Chem. Soc.*, **77**, 2671 (1955).

(4) H. Okuno, H. Yamatera, T. Ishimori and K. Mizumachi, Abstract 4E3, 7th International Conference on Coordination Chemistry, 1962.

(5) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

Although numerous examples of transition metal to tin bonds are known from the work of Hieber and more recently Gorsich,⁶ these are best regarded as derivatives of tin(IV). However, we believe that the present complexes are best formulated as complexes of tin(II). Thus, for example, the rhodium and platinum species can be considered as square planar complexes of Rh^I and Pt^{II} , respectively, in which either SnCl_3^- (in the complex anions) or solvated tin(II) chloride (in neutral species) act as donor ligands using the lone-pairs known to be present.⁷ The ion $[\text{Rh}_2\text{Sn}_4\text{Cl}_{14}]^{4-}$ thus can be regarded as



and the other species can be similarly formulated. Support for this view is provided by the direct replacement, from the Ru, Rh, Ir and Pt complexes, of tin(II) chloride—which can be characterized by standard tests—by ligands such as pyridine, triphenylphosphine and carbon monoxide, in the latter case the rhodium complex giving $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. In these studies we have also isolated an orange complex which can be formulated $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2\text{SnCl}_3$ and there appear to be similar complexes of rhodium, iridium and ruthenium. It may be noted that Dwyer and Nyholm⁸ have reported compounds of rhodium containing methyl diphenylarsine and stannous chloride which they formulated as bridged species containing combinations of Sn-Cl-Rh, Sn-Cl-Sn and Rh-Cl-Rh bridges; we believe that Rh-Sn bonds probably are present here also.

(6) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962), and references therein.

(7) D. Grdenić and B. Kamenar, *Proc. Chem. Soc.*, 304 (1961); *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962).

(8) F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **76**, 129 (1942).

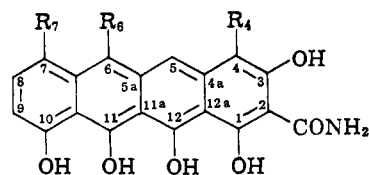
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BIOSYNTHESIS OF THE TETRACYCLINES. V.¹ NAPHTHACENIC PRECURSORS

Sir:

We wish to report the biological conversion of 1,3-, 10,11,12-pentahydroxynaphthacene-2-carboxamide² (2) and some related compounds to tetracycline antibiotics. These naphthacenic precursors, which can be represented by the general formula 1, were prepared by degradation of tetracycline antibiotics.³



- 1
2 $\text{R}_4, \text{R}_6, \text{R}_7 = \text{H}$
3 $\text{R}_4, \text{R}_7 = \text{H}; \text{R}_6 = \text{CH}_3$
4 $\text{R}_4 = \text{N}(\text{CH}_3)_2; \text{R}_6 = \text{CH}_3; \text{R}_7 = \text{H}$
5 $\text{R}_4 = \text{N}(\text{CH}_3)_2; \text{R}_6 = \text{H}; \text{R}_7 = \text{Cl}$

(1) Paper IV: J. R. D. McCormick, P. A. Miller, S. Johnson, N. Arnold and N. O. Sjolander, *J. Am. Chem. Soc.*, **84**, 3023 (1962).

(2) We propose the name "pretetramid" for this tetracyclic amide which is the parent of the family of precursors reported here.

(3) The preparation of compound 2 from 6-demethyltetracycline is described in the accompanying communication [J. R. D. McCormick, J. Reichenthal, S. Johnson and N. O. Sjolander, *J. Am. Chem. Soc.*, **85**, 1694 (1963)]. Compound 3 was prepared from tetracycline by the method of A.