The most significant contribution to report in this communication is that we have synthesized cobalt(III) complexes containing the ligand ethylenediamine-N,N,N'-triacetic acid (ED3A). The uniqueness of this pentadentate ligand renders it essential to cobalt(III) chemistry. First, it completes the series of cobalt(III) complexes of N-substituted ethylenediaminepolycarboxylic acids from ethylenediaminetetraacetic acid (EDTA) to ethylenediaminediacetic acid (EDDA). Secondly, the cobalt(III) complexes of ED3A act as models for the other cobalt(III) complexes containing EDTA-type pentadentate ligands.

The method used to prepare the acid, ED3A, was similar to that of Dwyer and Garvan[4] in their preparation of 1,2-propylenediaminetetraacetic acid.

When ethylenediamine is allowed to react with monochloroacetic acid, in a 1:3 mole ratio in basic solution at 10° for 24 hr, a solution results which is thought to contain a mixture of EDTA, ED3A, and EDDA.

The acid ED3A was separated from the other acid products of the reaction in complexed form with cobalt(III). The desired product, $Co(ED3A)(H_2O)$, was isolated from the other cobalt(III) species by passing the solution containing the cobalt(III) complexes through Dowex 1-X8 and Dowex 50W-X8 ion-exchange resins in the Cl^- and K^+ forms, respectively. Only the zero charged $Co(ED3A)(H_2O)$ species passed through both columns. The complex was collected and purified: yield, before final purification, 36% based on cobalt(II) added. *Anal.* Calcd for $[Co(ED3A)(H_2O)] \cdot 1.5H_2O$: C, 28.67; H, 4.81; N, 8.37. Found: C, 28.61; H, 4.70; N, 8.64.

The aquo complex was used to prepare $K[Co(ED3A)X]$ where X^- is Cl^-, NO_2^-, or ONO^-. The nitro and nitrito species were prepared by the addition of $NaNO_2$ to a solution of the aquo complex. The nitro and nitrito complexes were easily separated and purified by ion-exchange chromatography. Analysis of the two compounds proved to be nearly identical. *Anal.* Calcd for $K[Co(ED3A)X] \cdot H_2O$ where X is NO_2 or ONO: C, 24.43; H, 3.33; N, 10.68; K, 9.94. Found: C, 24.48; H, 3.35; N, 10.57; K, 9.94.

The chloro complex was prepared by dissolving the aquo complex in a saturated NaCl solution, acidifying with HCl, and evaporating to dryness on a steam bath. The blue complex that resulted was also purified by ion-exchange chromatography. *Anal.* Calcd for $K[Co(ED3A)Cl] \cdot 0.5H_2O$: C, 23.69; H, 2.98; N, 6.91; K, 9.64; Cl, 8.74. Found: C, 23.66; H, 3.15; N, 6.98; K, 10.04; Cl, 8.92

The colors of the complex salts in this study were found to be identical with those of the related series[5,6] of cobalt(III) complexes containing similar pentadentate ligands. The nitrito complex was found to be bluish purple in color. This color slowly changed to the brick red color of the nitro species when allowed to remain on the resin for several days. This observation reflects the possibility of linkage isomerization of the $-NO_2$ ligand.

The infrared absorption bands for the compounds under current investigation are in accord with those reported previously for similar compounds.[6,7]

The absence of the three absorptions typically associated with an uncoordinated carboxylic acid group, namely the absorptions at 2600–2800, 1700–1750, and 1228 cm^{-1}, rules out the possibility of an uncoordinated carboxylic acid group in the ED3A complexes. An absorption at 1648–1658 cm^{-1} arising from the complexed carboxyl group appears throughout the series of cobalt(III) complexes of ED3A. The nitro complexes show the characteristic bands associated with the coordinated nitro ligand, namely 1408, 1342, and 830 cm^{-1}. The nitrito complex gives two additional absorptions occurring at 1460 and 1065 cm^{-1} which have been assigned to the two ONO stretching vibrations.[8] The hydrogen, bound to the nitrogen atom of the ED3A ligand, gives rise to a N–H stretching frequency at 3150 cm^{-1}. This absorption was observed in all of the ED3A complexes. The occurrence of this absorption substantiates the existence of the ED3A ligand.

The visible spectra of the cobalt(III) complexes of ED3A are very similar to the related complexes reported previously.[5,9,10] The absorption curve for the nitrito species has two low-energy maxima of nearly equal intensity occurring at 17,800 and 21,000 cm^{-1}. Upon rearrangement of the nitrito species the spectrum of the nitro complex is obtained which has a maximum absorption at 20,300 cm^{-1} and a shoulder at 17,100 cm^{-1}.

The absorption curves for the nitro and chloro complexes of cobalt(III) EDTA, HEDTA, and MEDTA[5] are all seen to be very similar to that of their model $Co(ED3A)NO_2^-$ and $Co(ED3A)Cl^-$.

Previous studies[5,9] as well as this investigation have shown no evidence for geometrical isomerism with respect to the ligand even though the possibility of such isomerism exists.

---

(4) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

(5) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).

(6) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

(7) K. Nakamoto, J. Fujita, and H. Murata, *ibid.*, **80**, 4817 (1958).

(8) R. B. Penland, T. J. Lane, and J. V. Quagliano, *ibid.*, **78**, 887 (1956).

(9) R. A. Haines and B. E. Douglas, *Inorg. Chem.*, **4**, 452 (1965).

(10) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *ibid.*, **2**, 1194 (1963).

Gary L. Blackmer, Randall E. Hamm
Department of Chemistry, Washington State University
Pullman, Washington 99163

Received February 3, 1969

A Contribution to the Chemistry of Stannane

Sir:

We wish to report the results of recent work in our laboratory which considerably expands the chemistry of stannane, SnH_4. The development of the chemistry of stannane[1] has been hampered by its instability which complicates the experimental situation and leads at best to low yields of products. The only reactions of stannane, besides its decomposition, which have been described are its conversion into the highly unstable compound SnH_3Cl[2] and some of its monoalkali metal derivatives.[3]

---

(1) For a review of stannane chemistry, see F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., New York, N. Y., 1962, p 79.

(2) E. Amberger, *Angew. Chem.*, 72, 78 (1960).

Stannane was prepared according to the method of Emeléus and Kettle.[4] The melting point was determined to be −146° and the boiling point −52.5° (lit.[5] mp −150°; bp −51.8°). The solubility of stannane at ~78° (Dry Ice–acetone) was found to be 1.4 g/100 ml in ethyl ether, 1.8 g/100 ml in hexane, 2.4 g/100 ml in tetrahydrofuran, and 7.7 g/100 ml in carbon disulfide.

When stannane was added to a suspension of lithium hydride in dioxane or sodium hydride in mineral oil at liquid nitrogen temperature and allowed to come to room temperature, no reaction could be detected. In both cases over 95% of the stannane was recovered so that it is clear that stannane did not form a complex hydride.

A survey of the reactivity of stannane with a selection of organic functional groups was conducted. Stannane was condensed into a tube containing the substrate at liquid nitrogen temperature, and the mixture was brought over a period of several hours to room temperature by sequential transfer through a series of freezing mixtures of increasing temperature. Stannane did not react with aniline, triethylamine, dimethylacetamide, ethylacetamide, or ethyl acetate. Nitrobenzene was reduced to aniline in 94% yield (all identity and yield data by vpc). Benzaldehyde was reduced quantitatively to benzyl alcohol while acetone was reduced to isopropyl alcohol in a 71% yield. The reaction with benzyl chloride was complex, but a 10% yield of toluene was detected.

In contrast to the clean reduction of nitrobenzene, only a 29% yield of isopropylamine was obtained in the reduction of 2-nitropropane, and the reduction was accompanied by extensive decomposition of stannane. This difference is understandable in light of the demonstration that isopropylamine was found to catalyze the decomposition while aniline was without effect. Attempts to form a complex with the ligand N,N,N′,N′-tetramethylethylenediamine in tetrahydrofuran yielded only the decomposition products of stannane. When the aliphatic chelating agent was replaced with 1,10-phenanthroline or 2,2′-bipyridine, no reaction could be demonstrated and stannane was recovered in high yield.

Stannane reacted with boron trifluoride etherate to give quantitative yields of stannic fluoride and presumably diborane. With glacial acetic acid the major product was tin metal, but about 4% of the tin was found as a complex tin(IV) acetate. We have confirmed literature reports[1] that stannane is unaffected by dilute aqueous acid and alkali. However, stannane was decomposed by 2.5 *N* NaOH to give tin metal as the main product. About 8% of the tin was found in solution as stannate ion. With concentrated hydrochloric acid an initial precipitate of tin was observed; then the metal dissolved and the major product isolated was stannous chloride.

Stannane added to the double bond of acrylonitrile even though no reaction could be detected with methyl acrylate. When stannane (2.8 g, 0.023 mole) and inhibitor-free acrylonitrile (10 g, 0.20 mole) were condensed into a trap held at liquid nitrogen temperature (−195°) and the temperature was allowed to rise to room temperature, 2.6 g (34%, 0.008 mole) of tetrakis(2-cyanothyl)tin[6] was isolated from the residue by distillation of the excess acrylonitrile.

Simple, unactivated olefins would not add stannane across the double bond in the absence of catalyst. We found, however, that cobalt naphthenate di-*t*-butyl peroxide (or *t*-butyl hydroperoxide), palladium (10% on charcoal), or hexachloroplatinic acid were effective in catalyzing the addition of stannane to a number of terminal olefins and at least one internal olefin. This addition was remarkably clean in that no alkyltin hydrides could be detected. In every case only the tetraalkyltin was found.

In a typical example, a trap held at liquid nitrogen temperature was charged with 60 mg of di-*t*-butyl peroxide, 150 mg of a 6% solution of cobalt naphthenate in mineral spirits, and butene-1 (6.0 g, 0.11 mole). Stannane (2.6 g, 0.021 mole) was then condensed in the trap, and the whole was allowed to come up to room temperature. The liquid residue weighed 2.4 g (34%, 0.07 mole). Vpc analysis showed it to be 99% tetrabutyltin and its infrared spectrum was free of any bands attributable to Sn–H bonds. Under the same conditions the following additional olefins reacted (the figure in parentheses is the per cent conversion of stannane to tetraalkyltin as determined by vpc): ethylene (34), propylene (20), isobutylene (14), octene-1 (6), and cyclohexene (20).

Acknowledgment. We thank Mr. John Saraka, Jr., for his technical assistance in these investigations and Messrs. I. L. Simmons and P. D. Brannigan and their colleagues for their analytical support.

---

[3] E. Amberger, R. Roemer, and A. Layer, *J. Organometal. Chem.*, **12**, 417 (1968).

[4] H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958).

[5] F. Paneth, W. Haken, and E. Rabinowitsch, *Ber.*, **57B**, 1898 (1924).

[6] A. P. Tomilov and L. V. Kaabak, *Zh. Prikl. Khim.*, **32**, 2600 (1959); *Chem. Abstr.*, **54**, 7374 (1960).

[7] Geigy Chemical Corp., Ardsley, N. Y. 10502.

G. H. Reifenberg, W, J. Considine[7]
Corporate Research Department, M&T Chemicals Inc.
Rahway, New Jersey 07065

Received December 13, 1969

On the Mechanism of the Kolbe Electrosynthesis. A Comment on a Paper by Reichenbacher, Liu, and Skell

Sir:

Some years ago[1] it was proposed that the Kolbe electrosynthesis might occur *via* a concerted electron transfer and loss of CO_2 rather than the commonly

$$\mathrm{RCOO^-} \rightarrow [\mathrm{R}\cdots\cdots\mathrm{CO_2}\cdots\cdots\mathrm{e^-(anode)}]^{\ddagger} \rightarrow \mathrm{R}\cdot + \mathrm{CO_2} + \mathrm{e^-} \quad (1)$$

assumed rate-determining step,[2] discharge of $RCOO^-$ to form RCOO· with subsequent decarboxylation of this species. Reichenbacher, Liu, and Skell[3] have recently determined "relative rate constants," k/k',[4]

---

[1] L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

[2] For a discussion, see A. K. Vijh and B. E. Conway, *Chem. Rev.*, **67**, 623 (1967); L. Eberson in "Chemistry of the Carboxyl Group," S. Patai, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969, Chapter 6.

[3] P. H. Reichenbacher, M. Y. Liu, and P. S. Skell, *J. Am. Chem. Soc.*, **90**, 1816 (1968).

[4] Defined as $(\log [\mathrm{RCOO^-}]_{\mathrm{final}} - \log [\mathrm{RCOO^-}]_{\mathrm{initial}})/(\log [\mathrm{R'COO^-}]_{\mathrm{final}} - \log [\mathrm{R'COO^-}]_{\mathrm{initial}})$, potassium pentanoate being the reference compound.