

Figure 1. The structure of $\text{Co}(\text{CH}_3\text{S}(\text{CH}_2)_2\text{SCH}_3)_2(\text{ClO}_4)_2$ projected on the (010) crystal plane (bond distances in Å. and interbond angles in degrees are shown).

NO_3^- and ClO_4^- . For the nitrate ion, the weight of evidence from both chemical¹⁻³ and structural³⁻⁶ investigations has shown that, in fact, this is not a particularly poor ligand after all. While it still seems reasonable to consider the perchlorate ion a weak ligand, it is not clear⁷⁻⁹ that it has at least some ability to function as such, and several recent chemical and infrared studies have led to the postulation of "coordinated perchlorate ions." However, direct evidence (*i.e.*, from diffraction studies) has not, to our knowledge, ever been presented for such a claim, and surely some doubt could be said to remain regarding the nature of such compounds. We describe here the characterization, by single crystal X-ray diffraction, of an authentic perchlorate complex, bis(2,5-dithiahexane)cobalt(II) perchlorate.¹⁰

The crystallographic study gave the following results: habit, red parallelipipedon; monoclinic, $a = 8.25 \pm 0.01$, $b = 10.27 \pm 0.01$, $c = 12.11 \pm 0.01$ Å., $\beta = 115.6 \pm 0.2^\circ$, $V = 925.5$ Å.³; space group, $P2_1/c$ from systematic absences; $Z = 2$; X-ray density, 1.87 g. cm.⁻³, compared to density measured by flotation, 1.8 ± 0.1 g. cm.⁻³. A total of 650 reflections were measured, of which 125 were observed as zero, using the equi-inclination Weissenberg technique and visual compari-

- (1) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).
- (2) C. C. Addison and B. J. Hathaway, *ibid.*, 3099 (1958).
- (3) C. C. Addison, C. D. Gardner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 367 (1964).
- (4) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 85, 2402 (1963).
- (5) F. A. Cotton and J. G. Bergman, *ibid.*, 86, 2941 (1964).
- (6) S. C. Wallwork and W. E. Addison, *J. Chem. Soc.*, 2925 (1965).
- (7) B. J. Hathaway and A. E. Underhill, *ibid.*, 3091 (1961).
- (8) B. J. Hathaway, D. G. Holah, and M. Hudson, *ibid.*, 4586 (1963).
- (9) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 4, 404 (1965).
- (10) A compound to which this composition was assigned was earlier reported by Carlin and Weissberger,¹¹ but it was obtained in an impure form with a reported effective magnetic moment far different from that which we find. The compound is not very stable and purification presents some difficulties, so that in all probability the substance described by Carlin and Weissberger was an impure specimen of the compound we have studied.
- (11) R. E. Carlin and E. Weissberger, *Inorg. Chem.*, 3, 611 (1964).

son with a set of timed exposures of one reflection. The crystal used was small and absorption corrections were neglected. The structure was solved from Patterson syntheses, refined by Fourier and least-squares methods. At present, using anisotropic temperature factors for all atoms, the discrepancy index is 13.5%.

The Co atoms lie at crystallographic centers of inversion. Figure 1 shows the structure of one formula unit and gives its principal dimensions. The most important feature for present purposes is the location of the perchlorate ions relative to the cobalt atom. The Co-O distance of 2.34 Å. indicates a well-defined bonding interaction, but since it is perhaps 0.1–0.3 Å. longer than Co-O bonds in various other Co(II) complexes, it also suggests that the perchlorate ion is a relatively weak ligand.

The infrared spectrum of the compound is in excellent agreement with the structure, along the lines previously suggested⁷⁻⁹ for a C_{3v} perturbation of the ClO_4^- ion. There are bands (cm.⁻¹) at 1115 (s, b), 1047 (s), ~925 (m, b), and ~625 (m, doublet) which can be readily assigned⁷ to the perchlorate ion coordinated as it is in this complex.

Various other features of this complex, particularly its magnetic behavior and electronic spectrum, have also been studied and a complete report is in preparation.

F. A. Cotton, D. L. Weaver

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 30, 1965

Strained Systems.

IV.¹ The Tricyclo[1.1.0.0^{2,4}]butane System

Sir:

Current interest in strained systems is evident from numerous recent publications concerning syntheses and properties of these molecules.² Tricyclo[1.1.0.0^{2,4}]butane³ (tetrahedrane) is one of the most highly condensed compounds composed of carbon-carbon single bonds. The recent success⁴ in the photochemical synthesis of the tricyclo[1.1.1.0^{4,6}] system has led us to apply a similar method to the synthesis of diphenyl-tetrahedrane. We now wish to report the synthesis of this intriguing molecule.

(Δ^2 -2,3-Diphenylcyclopropenyl)carbinol⁵ was oxidized with chromic anhydride in pyridine to afford in 90% yield the corresponding aldehyde (I), m.p. 103.5–104°. *Anal.* Found: C, 87.11; H, 5.50. Compound I was converted to its tosylhydrazone (II), m.p. 196–198°. *Anal.* Found: C, 71.27; H, 5.13; N, 7.42. A solution of II (500 mg.) in dry tetrahydrofuran (200 ml.) containing an equivalent amount of sodium methoxide was irradiated at -20° under an inert atmosphere with a Hanovia 450-w. mercury lamp using

- (1) Part III: S. Masamune, *Tetrahedron Letters*, 945 (1965).
- (2) For a review see D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, 4, 121 (1965).
- (3) Beesley and Thorpe's report on methyl tricyclobutanetricarboxylic acid, often quoted in the literature, was found to be in error: H. O. Larson and R. B. Woodward, *Chem. Ind. (London)*, 193 (1959).
- (4) S. Masamune, *J. Am. Chem. Soc.*, 86, 735 (1964).
- (5) R. Breslow, J. Lockhart, and A. Small, *ibid.*, 84, 2793 (1962).

data of III are compatible with structure VII. In view of the chemical shift (τ 7.01) reported for the C-4 hydrogen of 1,3-dimethyltricyclo[1.1.1.0^{4,5}]pentane,¹¹ the τ value 6.67 is in the region expected for the hydrogens directly attached to the tetrahedrane system. Since diphenyltricyclo[1.1.1.0^{4,5}]pentanol-2 showed a maximum at 269 $\mu\mu$ (ϵ 1.1×10^4)¹² the strong ultraviolet absorption of III, similar to that of diphenylacetylene but shifted toward shorter wave length, is reasonable. Thus, having eliminated all other possible structures, we must conclude that compound III possesses the tricyclo[1.1.0.0^{2,4}]butane system.

The thermal stability of the tetrahedrane is surprising. Although a crude sample decomposed readily, the analytically pure material has been stored under nitrogen without decomposition at least for a month. We plan to prepare a sufficient quantity of this compound for further investigation.

Acknowledgment. The authors are grateful to the National Research Council of Canada for financial support.

(11) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965). It appears that the chemical shift of the C-1 hydrogen of the bicyclobutane system is very sensitive to the angle between the C-H bond and the plane of the cyclopropane. The bridging of C-2 and C-4 by a carbon chain, thus further distorting the bicyclobutane system, tends to shift the signal downfield.

(12) S. Masamune, unpublished results.

(13) A University of Alberta postdoctoral Fellow.

Satoru Masamune, Masahiko Kato¹³

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received August 9, 1965

6-Hemi-L-selenocystine-oxytocin and 1-Deamino-6-hemi-L-selenocystine-oxytocin, Highly Potent Isologs of Oxytocin and 1-Deamino-oxytocin¹

Sir:

Considerable attention has been given to the study of selenium isologs of naturally occurring sulfur compounds. The present communication concerns the

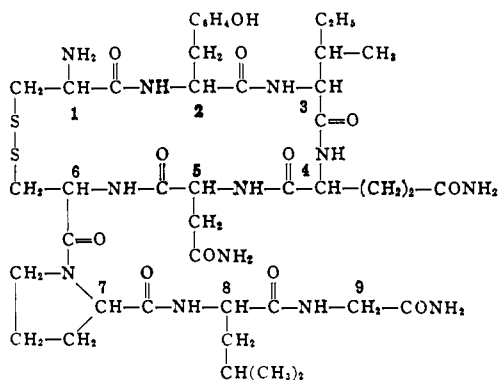


Figure 1. Structure of oxytocin.

syntheses of 6-hemi-L-selenocystine-oxytocin (6-seleno-oxytocin) and its deamino analog, two molecules which may be considered as being isosteric with oxytocin (Figure 1) and 1-deamino-oxytocin, respectively.

(1) This work was supported in part by Grant HE-01675 from the National Heart Institute, U. S. Public Health Service.

The isologs have been synthesized by the stepwise *p*-nitrophenyl ester procedure earlier employed in this laboratory for the synthesis of oxytocin² and deamino-oxytocin.³ The tripeptide, L-prolyl-L-leucyl-glycinamide,⁴ was coupled with *p*-nitrophenyl N-carbobenzoxy-Se-benzyl-DL-selenocysteinate (m.p. 98–99°), prepared by condensation of *p*-nitrophenol with N-carbobenzoxy-Se-benzyl-DL-selenocysteine⁵ in the presence of dicyclohexylcarbodiimide. *Anal.* Calcd. for C₂₄H₂₂N₂O₆Se: C, 56.1; H, 4.32; N, 5.45. Found: C, 56.2; H, 4.38; N, 5.41.

The protected tetrapeptide, N-carbobenzoxy-Se-benzyl-L-selenocysteinyl-L-prolyl-L-leucylglycinamide,⁶ was separated from its diastereoisomer in 78% of the theoretical yield by crystallization from ethyl acetate followed by the slow addition of ethyl ether with the resulting ratio of 4:1.

After removal of the carbobenzoxy group by HBr-acetic acid the tetrapeptide was lengthened step by step as in the synthesis of oxytocin² and 1-deamino-oxytocin³ to give the protected intermediates, N-carbobenzoxy-S-benzyl-L-cysteinyl-L-tyrosyl-L-isoleucyl-L-glutaminyll-L-asparaginyl-Se-benzyl-L-selenocysteinyl-L-prolyl-L-leucylglycinamide and S-benzyl- β -mercaptopropionyl-L-tyrosyl-L-isoleucyl-L-glutaminyll-L-asparaginyl-Se-benzyl-L-selenocysteinyl-L-prolyl-L-leucylglycinamide.⁷ The isologs were obtained after the cleavage of the protecting groups from these intermediates by sodium in liquid ammonia, followed by ring closure through air oxidation in aqueous solution at pH 6.8 and by treatment with ferricyanide until the solutions gave negative reactions to Ellman's reagent.⁸ Subsequently, the ferrocyanide and ferricyanide ions were removed with the ion-exchange resin AG3X4 in the chloride form.

In the case of 6-seleno-oxytocin the solution containing the crude material was concentrated to a small volume and subjected to countercurrent distribution in the system 1-butanol-1-propanol-0.5% aqueous acetic acid containing 0.1% pyridine (4:1:5). The desired isolog was found to have an approximate *K* value of 0.52 as detected by determination of the Folin-Lowry color values,⁹ and the material representing this peak was isolated by lyophilization; $[\alpha]^{20.5D} -10.5^\circ$ (*c* 0.5, 1 *N* acetic acid). *Anal.* Calcd. for C₄₃H₆₆N₁₂O₁₂SSe: N, 15.9. Found: N, 15.6. The 6-seleno-oxytocin was indistinguishable from oxytocin upon thin-layer chromatography on silica gel G in the upper phase of the solvent system 1-butanol-acetic acid-water (4:1:5, ascending) and gel filtration (Sephadex G-25) in 0.2 *N* acetic acid.

The 1-deamino-6-hemi-L-selenocystine-oxytocin (deamino-6-seleno-oxytocin) was isolated by countercurrent distribution in a 1-butanol-benzene-0.05%

(2) M. Bodanszky and V. du Vigneaud, *J. Am. Chem. Soc.*, 81, 5688 (1959).

(3) V. du Vigneaud, G. Winestock, V. V. S. Murti, D. B. Hope, and R. D. Kimbrough, Jr., *J. Biol. Chem.*, 235, PC 64 (1960); D. B. Hope, V. V. S. Murti, and V. du Vigneaud, *ibid.*, 237, 1563 (1962).

(4) C. Ressler and V. du Vigneaud, *J. Am. Chem. Soc.*, 76, 3107 (1954).

(5) J. Janicki, J. Skupin, and B. Zagalak, *Roczniki Chem.*, 36, 353 (1962).

(6) W. Frank, *Hoppe-Seyler's Z. Physiol. Chem.*, 339, 222 (1964).

(7) All intermediate peptides showed correct C, H, and N analyses, which were carried out by Galbraith Laboratories, Knoxville, Tenn.

(8) G. L. Ellman, *Arch. Biochem. Biophys.*, 82, 70 (1959).

(9) O. H. Lowry, N. J. Rosebrough, A. L. Farr, and R. J. Randall, *J. Biol. Chem.*, 193, 265 (1951).