

Pt 35.75. Calc. for  $[\text{PtI}_2\text{C}_8\text{H}_{10}]$  (547.2): C 13.17; H 1.84; Pt 35.67.

*Biallyl-dichloropalladium(II)*. Biallyl (0.17 ml) was added to a solution of the benzonitrile complex<sup>8</sup>  $[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$  (0.5 g) in benzene (10 ml). A brownishyellow, crystalline precipitate separated. The quantity was increased by addition of petroleum ether and cooling in ice (yield 0.30 g). Found: C 28.58; H 4.12. Calc. for  $[\text{PdCl}_2(\text{C}_8\text{H}_{10})]$ : C 27.74; H 3.88.

*Diallylether-dichloroplatinum(II)*. Diallylether (0.80 g) was added to a solution of  $\text{K}_2\text{PtCl}_4$  (2 g) in water (10 ml). An almost white precipitate soon began to separate. After 3 days the precipitate was filtered off (yield 1.00 g). The dry product was dissolved in warm chloroform (100 ml) and carbon tetrachloride (50 ml) added to until crystallization just started. As the solution cooled the compound separated as a fine, white crystalline powder, m.p.  $180^\circ$  (dec.). Found: C 20.05; H 2.94; Pt 53.71. Calc. for  $[\text{PtCl}_2(\text{C}_8\text{H}_{10}\text{O})]$  (364.3): C 19.78; H 2.77; Pt 53.57. Molecular weight (cryoscopically in bromoform): 344.

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1. Zeise, W. C. *De chlorido platinæ et alcohole vini sese invicem permutantibus nec non de novis substantiis inde oriundis*. Anniversary Volume of the University of Copenhagen, 1830. Complete German translations of this paper appeared in: *J. Physik und Chemie (Schweigger-Seidel)* **62** (1831) 393; **63** (1831) 121; *Ann. Physik und Chemie (Poggendorf)* **21** (1831) 497. A short summary of the last translation appeared in: *Magazin für Pharmazie* **35** (1831) 105. (In Keller's review this article is erroneously cited as Zeise's original paper).
2. Anderson, J. S. *J. Chem. Soc.* **1934** 971; **1936** 1042.
3. Keller, R. N. *Chem. Revs.* **28** (1941) 229.
4. Chatt, J., and Wilkins, R. G. *Nature* **165** (1950) 859.
5. Chatt, J., and Wilkins, R. G. *J. Chem. Soc.* **1952** 2622.
6. Gelman, A. *Compt. rend. acad. sci. U.R.S.S.* **23** (1939) 532.
7. Gelman, A. *Compt. rend. acad. sci. U.R.S.S.* **32** (1941) 347; *Chem. Abstracts* **37** (1943) 3364.
8. Kharash, M. S., Seyler, R. C., and Mayo P. R. *J. Am. Chem. Soc.* **60** (1938) 882.

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## Platinum Compounds of Cyclo-octatetraene \*

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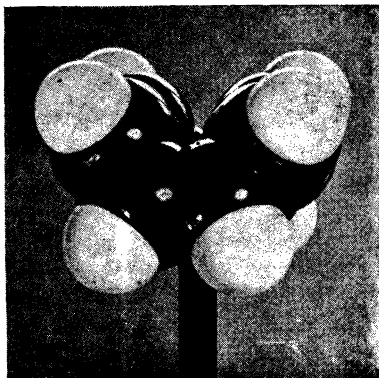
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In the preceding article platinous complexes of some alkadienes were described. I have prepared similar derivatives of cyclooctatetraene. A compound of composition close to  $\text{PtCl}_2 \cdot \text{C}_8\text{H}_8$  separates as an orange-yellow precipitate when cyclooctatetraene is added to an aqueous solution of  $\text{K}_2\text{PtCl}_4$ . It is insoluble in water and organic solvents and therefore could not be purified. However, the corresponding iodide could be recrystallised from chloroform and was obtained as a beautiful orange-red (dichromate-coloured) crystalline powder of the exact composition  $\text{PtI}_2 \cdot \text{C}_8\text{H}_8$ .

The platinum atom in these compounds is certainly co-ordinated to one or more double bonds. The unlikely possibility that the platinum atom be bound to all 4 double bonds is definitely ruled out because compounds of the type  $[\text{Pt}_4]\text{Cl}_2$  are generally colourless, easily soluble in water, and contain ionised chlorine. This is not the case with the cyclooctatetraene compound. Neither can the platinum atom be bound to only one double bond because the compound would then be dimeric, as is generally true of platinum compounds of the type  $\text{PtCl}_2\text{a}$  (a = amine, phosphine, alkyl sulphide, etc.). A cryoscopic determination of the molecular weight in bromoform solution shows that  $\text{PtI}_2 \cdot \text{C}_8\text{H}_8$  is monomeric; thus it seems that cyclooctatetraene occupies two co-ordination places, in the same way as biallyl. According to the preceding paper a certain distance between the double bonds is necessary for the formation of chelate compounds by

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diolefins, thus if the platinum atom is bound to two of the double bonds in *cyclo-octatetraene* these cannot be neighbouring double bonds. Actually a very plausible formula for the complex can be constructed if it is supposed that  $\text{PtCl}_2$  or  $\text{PtI}_2$  is bound to two double bonds in the tub form of *cyclooctatetraene* (see the figure); a platinum atom with radius *ca.* 1.3 Å can form two bonds with valence angle  $90^\circ$  perpendicular to two of the double bonds. Most investigations of the molecular structure of *cyclooctatetraene* have been inconclusive, but a recent electron diffraction investigation<sup>1</sup> is strongly in favour of the tub configuration ( $D_{2d}$ ).



The structure proposed for the platinum compounds is corroborated by the dipole moment of the iodide, which shows the compound to have the *cis*-configuration.

*Cyclooctatetraene* is easily transformed into other compounds and can, for instance, be isomerised to form styrene. The platinumous compounds prepared from *cyclo-octatetraene* are, however, quite different from the platinumous compounds of styrene, prepared by Anderson<sup>2</sup>. Furthermore, *cyclooctatetraene* — easily recognised by its odour — is liberated by boiling a suspension of the platinum compounds in water to which some pyridine or potassium cyanide has been added. When pyridine is added to a chloroform solution of  $[\text{PtI}_2(\text{C}_8\text{H}_8)]$  *cyclooctatetraene* is liberated and a yellow crystalline precipitate of  $[\text{PtI}_2\text{py}_2]$  is formed (no compound containing both *cyclooctatetraene* and pyridine could be prepared).

The filtrate from  $[\text{PtCl}_2(\text{C}_8\text{H}_8)]$  still contains platinum and was tested to see whether it contained a soluble *cyclooctatetraene* platinumous complex, *e.g.* corresponding to Zeise's acid or the bialllyl complex described in the preceding paper. The warm ( $50^\circ$ ) filtrate, by addition of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ , yielded a pink precipitate; at room temperature a silver-grey precipitate was obtained and from the icecold

filtrate a green precipitate. Although the grey and pink precipitates are formed at higher temperature than the green one they are both transformed into the latter by boiling with water. These precipitates contained only traces of C and H and had compositions close to that of Magnus' green salt,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ , which is known to exist also in a red form<sup>3</sup>; the silvery precipitate is a mixture of both forms. The tendency to yield the red form appears to be rather greater than usual, and it may be that the dimensions of the unit cell are modified by the presence of a small amount of a compound  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_3\text{C}_8\text{H}_8\text{PtCl}_3]$ .

#### EXPERIMENTAL.

*Cyclo-octatetraene-dichloroplatinum (II).* *Cyclooctatetraene* (1 g) was added to a solution of  $\text{K}_2\text{PtCl}_4$  (2 g) in water at  $60^\circ$  (10 ml) and the solution shaken vigorously. An orange-coloured precipitate soon began to separate and, after the mixture had stood overnight, the precipitate was filtered off and washed with water. Found: C 26.18; H 2.07; Pt 52.21. Calc. for  $[\text{PtCl}_2 \cdot \text{C}_8\text{H}_8]$ , (370.2): C 25.95; H 2.18; Pt 52.72.

*Cyclooctatetraene-di-iodoplatinum (II).*  $\text{K}_2\text{PtCl}_4$  (2 g) was dissolved in water (10 ml) at  $60^\circ$ , KI (3 g) was added and the solution filtered and cooled. *Cyclooctatetraene*

(1 g) was then added with vigorous shaking. A precipitate immediately separated. After standing for 24 hours, the yellow precipitate was filtered off, washed and dried. Yield: 2.6 g (calc. 2.8 g). The compound was dissolved in 100 ml boiling chloroform, the solution filtered and cooled in ice. Orange-red (dichromate-coloured) crystals separated. The compound was recrystallised once more from chloroform. It does not melt on heating, but gradually turns black without change of the crystal form. Found: C 17.59; H 1.59; Pt 34.97. Calc. for  $[\text{PtI}_2(\text{C}_8\text{H}_8)]$ , (553.2): C 17.37; H 1.46; Pt 35.38.

Molecular weight (cryoscopically in bromoform solution): 492, 610. Dipole moment:

$c = 0.00198$  molar,  $\Delta\epsilon = 0.0130$ ,  $\mu = 7.3\text{D}$ ;  
 $c = 0.00406$  molar,  $\Delta\epsilon = 0.0240$ ,  $\mu = 7.0\text{D}$ .

1. Karle, I. L. *J. Chem. Phys.* **20** (1952) 65.
2. Anderson, J. S. *J. Chem. Soc.* 1936 1042.
3. Jørgensen, S. M., and Sørensen, S. P. L. *Z. anorg. Ch.* **48** (1906) 441.

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### Release of Hydantoins from Proteins \*

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In a note by the author <sup>1</sup>, the procedure of Fraenkel-Conrat and Fraenkel-Conrat <sup>2</sup> for the release of hydantoins from proteins was erroneously quoted, the temperature for the reaction being given at 75° C instead of 36° C (cf. Fraenkel-Conrat and Fraenkel-Conrat <sup>3</sup>).

1. Christensen, H. N. *Acta Chem. Scand.* **6** (1952) 1555.
2. Fraenkel-Conrat, H., and Fraenkel-Conrat, J. *Acta Chem. Scand.* **5** (1951) 1409.
3. Fraenkel-Conrat, H., and Fraenkel-Conrat, J. *Federation Proc.* **11** (1952) 214.

\* Correction to Attempted Successive Applications of the Edman Degradation to Insulin <sup>1</sup>.

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### The Occurrence in Lichens of the Folic Acid-, Folinic Acid-, and Vitamin B<sub>12</sub>-Group of Factors

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In connection with investigations on the folic acid-, folinic acid-, and vitamin B<sub>12</sub>-group of factors in algae it was considered of interest to study the occurrence of these factors in some lichens, a group of plants known to represent a symbiosis between fungi and algae. The following lichens have been studied using microbiological and bioautographic methods: *Cladonia silvatica*, *Umbilicaria pustulata*, *Parmelia physodes*, *Parmelia furfuracea*, *Cetraria islandica*, *Evernia prunastri*, *Alectoria jubata*, and *Usnea comosa*. The lichens were collected at Grönvik, Nämndö.

*Escherichia coli* 113-3<sup>1</sup> served as a test organism for the vitamin B<sub>12</sub>-factors, *Leuconostoc citrovorum* ATCC 8081<sup>2</sup> for the folinic acid and *Streptococcus faecalis* ATCC 8043 for the folic acid tests. The organisms were utilized in the agar cup plate method. For *Streptococcus faecalis* the Difco folic acid assay medium with 1.6 % Bacto agar was used <sup>3</sup>. The solvent for the chromatographic separation was sec. butanol saturated with water, and containing 3 % acetic acid and 25 mg KCN/l.

The lichens were carefully cleaned and dried at room temperature. Two grammes of finely ground material were suspended in 25 ml of water or buffer solution. Three different methods of freeing the active substances were tried, namely, extraction with water at 37° C for 24 hrs, autoclaving for 20 min. at 120° C in water containing small amounts of KCN, and enzymatic treatment with a chicken pancreas homogenate at 37° C for 24 hrs at pH 7.5. Autoclaving gave the highest

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