

TABLE I
CHARACTERISTIC BANDS OF COÖRDINATED WATER IN Ni²⁺,
Cu²⁺ AND Cr³⁺ AQUO COMPLEXES

Metal	Compound	$\nu_{\text{H}_2\text{O}}$ (cm. ⁻¹)	M-OH ₂ (A.)	OH-O (A.)	Temp. for dehydration, °C.
Ni ²⁺	Ni(glycine) ₂ ·2H ₂ O	795	2.12	2.72	135 ~ 140
Cu ²⁺	CuSO ₄ ·5H ₂ O	875	1.98	2.75	220
Cr ³⁺	[Cr(ox) ₂ (H ₂ O) ₂]K·3	965	2.02	2.66	High
	H ₂ O	1012		2.72	

increases in the same order. As is shown by the M-OH₂ and O-H---O distances, the effects of coordination and hydrogen bonding are also increasing in the same order. Therefore we conclude that

a cooperative effect of coordination and hydrogen bonding is responsible for the shift of the band and the rise of temperature of dehydration.

Although the vibrational mode of the band is not yet determined, it is attributable to either one of the modes among wagging, twisting and rocking vibrations. A detailed study of the nature of this band is now in progress and will be reported later together with the measurements in the KBr region.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Platinum Olefin Coördination Compounds. I. The Structure of Dicyclopentadienedichloroplatinum(II)

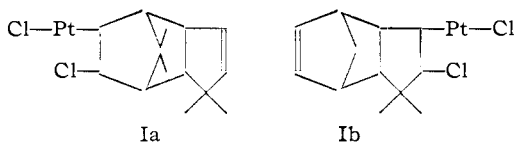
BY JOHN R. DOYLE¹ AND HANS B. JONASSEN

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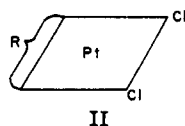
The previously proposed structure of dicyclopentadiene platinumous chloride has been re-examined and shown to be inconsistent with newly determined data. A new structure is proposed in which the dicyclopentadiene acts as a bidentate ligand with both double bonds coordinated to the platinum in the *cis*-positions of the coordination sphere.

Introduction

Recent interest in the olefin coordination compounds of platinum has prompted a re-examination of the structure of the compound formed by the reaction of dicyclopentadiene and potassium chloroplatinite as reported by Hofmann and Narbutt.² They believed that platinumous chloride added across one of the double bonds of dicyclopentadiene in a manner similar to the reaction of mercuric chloride and olefins. This type of addition would yield compounds having a structure similar to the possibilities shown in Ia or Ib.

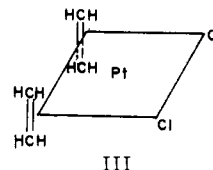


Jensen^{3,4} has prepared a series of compounds in which cyclooctatetraene and 1,6-hexadiene act as bidentate ligands. The double bonds of the diolefin occupy adjacent positions in the coordination sphere of the platinum, giving a *cis*-configuration to the molecules as shown in II.

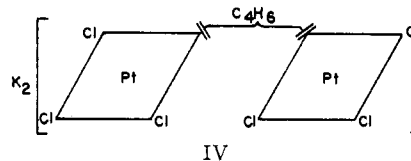


Chatt⁵ has recently reported a rather unstable bis-ethylene platinumous chloride, III, in which he pro-

poses that the molecules of ethylene occupy *cis*-positions



Chatt and Duncanson have reported the preparation of a platinum-olefin compound containing 1,4-butadiene in which this diolefin acts as the bridging group as in IV.



In determining the structure of dicyclopentadiene-dichloroplatinum(II) all of the various types discussed above have been considered and in addition the possibility of a bis-cyclopentadienyl derivative of platinum was examined.

Experimental

Dicyclopentadiene-dichloroplatinum(II).—Five grams of potassium chloroplatinite was dissolved in a mixture of 60 ml. of water and 15 ml. of *n*-propyl alcohol. Eight ml. of dicyclopentadiene dissolved in 25 ml. of ethyl ether was added to this clear red solution. The solutions were mixed in a 250-ml. flask and allowed to react at room temperature for three days. The dark brown precipitate which formed was removed by filtering and washed with two 10-ml. portions of ethyl ether. The crude product was redissolved in hot chloroform, clarified with decolorizing carbon and the solution evaporated to 25 ml. Ethyl alcohol was then added to the hot chloroform solution until the mixture began to cloud, and upon cooling to room temperature small needle shaped ivory colored crystals separated. The crystals

(1) Abstracted in part from the doctoral dissertation presented to the Graduate School of Tulane University, 1955.

(2) K. A. Hofmann and J. V. Narbutt, *Ber.*, **41**, 1625 (1908).

(3) K. A. Jensen, *Acta Chim. Scand.*, **7**, 866 (1953).

(4) K. A. Jensen, *ibid.*, **7**, 868 (1953).

(5) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

were filtered off and washed with 5 ml. of a 1:1 mixture of ethanol and chloroform. The yield was 2.2 g. (45% yield based on the potassium chloroplatinite). A recrystallized sample melted with decomposition at 218–220°. It sublimed at 215–217° (10⁻⁴ mm.) with extensive decomposition.

Anal. Calcd. for C₁₀H₁₂PtCl₂: C, 30.15; H, 3.04; Pt, 49.26; Cl, 17.80. Found: C, 30.68; H, 3.29; Pt, 49.41; Cl, 18.20.

Dicyclopentadienediiodoplatinum(II).—A 3.75-g. sample of dicyclopentadiene platinous chloride was suspended in 250 ml. of acetone and the mixture was heated until the solid had completely dissolved. A solution of 4 g. of sodium iodide in 50 ml. of acetone was added to this solution causing the immediate precipitation of sodium chloride and the formation of a deep yellow solution of dicyclopentadiene platinous iodide. The mixture was cooled and filtered and the filtrate poured into 2 liters of water. A fine yellow precipitate formed which after settling overnight was removed by filtration. The product was recrystallized by dissolution in acetone and concentration to the point of crystallization. The yield was 3.45 g. (63.1% of the theoretical based on the dicyclopentadiene platinous chloride) of orange-colored platelets which darkened at 175° and melted with decomposition at 209–211°.

Anal. Calcd. for C₁₀H₁₂PtI₂: C, 20.66; H, 2.08; Pt, 33.59; I, 43.67. Found: C, 20.88; H, 2.20; Pt, 34.08; I, 43.14.

Dicyclopentadienemethoxychloroplatinum(II).—A mixture of 4 g. of potassium chloroplatinite, 50 ml. of water, 100 ml. of methanol and 5 ml. of dicyclopentadiene was allowed to reflux at 50° for 12 hours.

A white residue formed and was removed by filtering and washed with ethyl ether. The product was recrystallized from a chloroform-methanol mixture. The yield was 1.3 g. (34% of the theoretical based on potassium chloroplatinite) of fine white crystalline material.

Anal. Calcd. for C₁₁H₁₆OClPt: C, 33.54; H, 3.84; Pt, 49.56; Cl, 9.00. Found: C, 33.56; H, 3.80; Cl, 8.97; ash, 49.44.

Molecular Weights.—The molecular weight of dicyclopentadienedichloroplatinum(II) was determined ebullioscopically using chloroform as a solvent and naphthalene as a standard.

Anal. Calcd. for C₁₀H₁₂PtCl₂: mol. wt., 398.35. Found: mol. wt., 332.3, 379.4, 335.5 (av., 349.1).

Dipole Moments.—The dipole moments were determined by the heterodyne-beat method with chloroform as a solvent. On the basis of a molecular weight of 398.35 a value of 13 Debye units was calculated from the data. If the material was considered to be dimeric with a molecular weight of 796.68 the calculated value is 18 Debye units. Because of the high dipole of the solvent and the low solubility of dicyclopentadienedichloroplatinum(II) in chloroform the values obtained in this determination only indicate the order of magnitude of the dipole moment.

Infrared Measurements.—The spectra were determined as noted, with a Perkin-Elmer double beam instrument (Model 21), with sodium chloride optics.⁶

Discussion

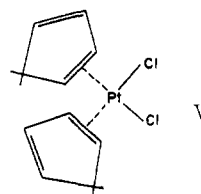
The elementary analysis confirms the work of Hofmann and Narbutt and indicates the presence of one dicyclopentadiene molecule and two chlorine atoms for each platinum.

The absence of an absorption band in the infrared region of the spectrum at 6.25 μ shows that both double bonds of the dicyclopentadiene have been coordinated with the platinum. The small absorption band at 6.25 μ when the sample was incorporated in a potassium bromide wafer is due to water absorption usually present in such spectra.

(6) The spectra have been deposited as Document number 4841 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

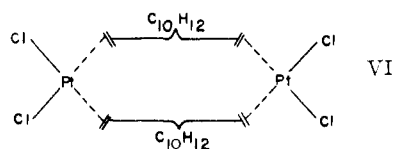
This was confirmed by obtaining a spectra of the sample in a Nujol mull in which media the 6.25 μ band was absent. As a further confirmation a comparison of the intensities of the band at 6.25 μ and the water band at 2.96 were found to be directly proportional to each other in several spectra while no such correlation could be obtained between the carbon-hydrogen stretching frequency and the 6.25 μ band. If the addition of platinum and chlorine had taken place in the manner proposed by Hofmann and Narbutt, an absorption frequency characteristic of the carbon to carbon double bond should have been observed, as only one of the double bonds of the dicyclopentadiene would be involved in such a reaction.

The lack of a characteristic double bond frequency also precludes any structure in which an uncoordinated double bond would occur, such as shown in V.



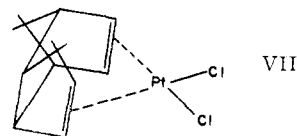
It is not possible to distinguish accurately between a bis-cyclopentadienyl and a dicyclopentadiene configuration by an elementary analysis. However, the bis-cyclopentadienyl derivatives have a single, strong, characteristic absorption band in the infrared region at 3.25 due to the carbon-hydrogen stretching vibration. The compound of platinum and dicyclopentadiene has three distinct absorption bands in this region of the infrared spectrum; this coupled with the large dipole moment measured for this molecule led to elimination of a bis-cyclopentadienyl configuration.

A structure in which the dicyclopentadiene acts as a bridging group would have both double bonds coordinated as shown in VI.



Such a configuration would be consistent with the chemical properties of the compound; however, it would have a molecular weight twice the observed value and from the symmetry of the molecule one would expect a low dipole moment.

The properties of dicyclopentadienedichloroplatinum(II) can best be explained by a three-dimensional structure in which both double bonds are coordinated to a single platinum atom. A possible diagram of such a structure is



This formulation for the structure would explain the lack of an observable double bond absorption band in the infrared region. The chloride groups in such a molecule would be very labile, due to the *trans*-platinum-olefin bond, and this explains the ease of formation of the di-iodo derivative. The observed molecular weights and dipole moments are of the expected order of magnitudes for such a configuration. The inability to form a di-alkoxy derivative is apparently due to the size of such groups. It has been found that a mono-methoxy or mono-ethoxy derivative can be formed readily; however, it has not been possible to isolate a mono-propoxy derivative or any dialkoxy derivatives.

The ability of certain diolefins to chelate with platinum seems to depend on the distance between the double bonds and the ability of the molecule to assume a configuration in which the axes of the double bonds are in the same plane and approximately parallel to each other.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Gluconate Complexes. III. The Lead Gluconate System¹

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The lead gluconate system has been investigated under widely varying conditions of basic strength and gluconate concentration. A technique involving optical rotation measurements has supplied useful information for determining the structures of the species present in the *pH* range 1 to 12. A 1:1 species, PbGH_4^+ , present in the *pH* range 1 to 6, is at maximum concentration at *pH* 3.7. The *pK* for this species is 2.6 ± 0.1 (determined polarographically). In the *pH* range 6 to 10 a solid or mixture of solid lead gluconate complexes is formed. In the *pH* range 10.5 to 12.5 a levorotatory, negatively charged, 3:2 lead gluconate species exists which reaches maximum concentration at *pH* 11.5. In the presence of excess lead a 3:1 lead gluconate solid also forms at this *pH*. In strongly basic media the predominant species is a 1:1 chelate. The dissociation constant of this species has been determined polarographically for ionic strengths varying from 3 to 0.1.

Preliminary experiments with the gluconate chelates of a large number of transition metals indicated the excellent chelating ability of gluconic acid in strongly basic media. The present study is a continuation of the investigation of the structures and stabilities of the various species present under widely varying conditions of basic strength and gluconate concentration. The procedures used are, in general, similar to those described in the previous papers of this series on the glucono-copper^{2a} and the glucono-ferric iron systems.^{2b} A method involving optical rotation measurements has been useful in determining the structures of the species present in the *pH* range 1 to 12.

Pepinsky³ has measured the space group and lead positions in the simple salt, lead gluconate, $\text{Pb}(\text{C}_6\text{H}_{11}\text{O}_7)_2$, by X-ray measurements, but no attempt has been made to determine the structures of the species which exist in solution. Schmidt⁴ has reviewed the history of the use of lead in cancer studies. A number of complex lead salts for use in animal tumor experiments were prepared, among which was calcium lead gluconate (*ca.* 17% Pb). However, the solid reported may have been a mixture of compounds since the percentage of lead is far smaller than would be expected for any likely compound. No previous study has been reported

for the various lead gluconate species present in solution.

Experimental

Apparatus and Technique.—Polarograms were recorded according to usual technique⁵ with a calibrated Sargent Model XXI Recording Polarograph. Corrections for *IR* drop through the cell were made where necessary, and corrections were made for residual currents in determining all diffusion current data. The rate of flow, *m*, was 1.452 mg. sec.⁻¹, and the drop time was 5.41 sec. at -1.0 v. *vs.* S.C.E. at which most measurements of the diffusion current were made. Temperatures were maintained at 25.0° . The three-compartment polarographic cell previously described⁶ was used since the strongly basic solutions present in several experiments attacked the agar plug in cells of conventional design and would eventually have contaminated the reference electrode.

Optical rotation experiments were carried out with a Hilger Standard Polarimeter at room temperature ($25 \pm 2^\circ$) using a 4-dm. cell. Each rotation reported is the average of at least eight observations. The average deviation of the readings is $\pm 0.01^\circ$. A sodium vapor lamp was used for all measurements. For solutions in which a precipitate was formed, the precipitate was removed by centrifugation before measurements were made.

All *pH* measurements were made with a Beckman Model H-2 *pH* meter. A type-E glass electrode was used for *pH* values greater than 10. Special precautions were necessary when measuring *pH* values in concentrated perchlorate solutions to prevent apparent drift in *pH* caused by precipitation of potassium perchlorate at the tip of the calomel electrode. A saturated sodium chloride calomel reference electrode (made simply by exchanging the saturated potassium chloride in a Beckman calomel electrode with sodium chloride saturated with mercurous chloride) was used for measuring *pH* in solutions containing large concentrations

(1) Taken in part from a thesis submitted by R. S. Juvet, Jr., to the faculty of the University of California, Los Angeles, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) R. L. Pecsok and R. S. Juvet, Jr., *THIS JOURNAL*, **77**, 202 (1955); (b) R. L. Pecsok and J. Sandera, *ibid.*, **77**, 1489 (1955).

(3) R. Pepinsky, *Phys. Rev.*, **61**, 726 (1942).

(4) H. Schmidt, *Med. u. Chem. Abhandl. med.-chem. Forschungsstätten I. G. Farbenind.*, **3**, 418 (1936); *C.A.* **31**, 5861 (1937).

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York N. Y., 1952.

(6) R. L. Pecsok and R. S. Juvet, Jr., *Anal. Chem.*, **27**, 165 (1955).