and Foltz[11] for the preparation of III are unnecessary. Salicylaldehyde (7 g.) was added to a boiling solution of IV (6.0 g.) in ethanol (30 ml.). The bright yellow bis-salicylal derivative soon crystallized out, and after 10 minutes was collected, recrystallized from ethanol, and thus obtained in yellow needles, m.p. 230°. Carlin and Foltz give the m.p. as 234–235°.

Anal. Calcd. for $C_{28}H_{24}N_2O_2$: C, 80.0; H, 5.7. Found: C, 79.7; H, 5.8.

***dl*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenylcopper(II) (V).**—A solution of copper(II) acetate monohydrate (0.5 g.) in methanol (40 ml.) was added to a boiling solution of III (1 g.) in ethyl acetate (15 ml.). The solution became deep olive-brown in color. Chloroform (100 ml.) was added. Then methanol and water-soluble salts were washed out by several treatments with water. Eventually the chloroform solution was dried (anhydrous sodium sulfate) and the solvent removed. The residual green-brown solid was recrystallized from ethanol and obtained in green-brown needles, m.p. 303°, moderately soluble in ethanol, benzene, ethyl acetate or acetone but insoluble in petroleum ether, methanol or water.

Anal. Calcd. for $C_{28}H_{22}N_2O_2Cu$: C, 69.7; H, 4.6; N, 5.8; Cu, 13.2; mol. wt., 482. Found: C, 69.2; H, 4.9; N, 5.4; Cu, 12.9; mol. wt. (Rast in camphor), 450–490.

This copper(II) complex was found to be paramagnetic with a magnetic moment of 1.95 Bohr magnetons.

***l*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl.**—The *dl*-base IV was resolved with the help of *d*-tartaric acid according to the method of Meisenheimer and Horing.[7] The pure *l*-base formed colorless plates, m.p. 155–156° (from ethanol) with $[M]^{20}_{\mathrm{D}}$ −73.8° (in 0.3 *N* hydrochloric acid solution). Meisenheimer and Horing give m.p. 156° and $[M]^{20}_{\mathrm{D}}$ −74°. An ethanol solution of the pure *l*-base (0.6 g.) and salicylaldehyde (0.7 g.) was boiled for 5 minutes. After several recrystallizations from ethanol, the yellow solid Schiff base was obtained in needles m.p. 164°.

Anal. Found: C, 80.0; H, 5.8.

The specific rotation in ethyl acetate solution was $[\alpha]^{24}_{\mathrm{D}}$ −593° and $[\alpha]^{24}_{5461}$ −830°, equivalent to $[M]^{24}_{\mathrm{D}}$ −2490° and $[M]^{24}_{5461}$ −3445°.

***l*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenylcopper(II)** was prepared similarly to the *dl*-complex. It crystallized from benzene–petroleum ether in brown needles, m.p. 274°.

Anal. Found: C, 69.2; H, 4.9; N, 5.6; Cu, 13.0.

The specific rotation in ethanol $[\alpha]^{24}_{\mathrm{D}}$ was +75°, $[\alpha]^{24}_{5461}$ −100°, whence $[M]^{24}_{\mathrm{D}}$ +3600° and $[M]^{24}_{5461}$ −4800°.

***d*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenyl.**—Dextrorotatory 2,2′-diamino-6,6′-dimethyldiphenyl, m.p. 157°, was prepared according to Dethloff and Mix.[9] Its solution in 0.3 *N* hydrochloric acid gave $[M]^{20}_{\mathrm{D}}$ +73.8°. The bis-salicylidene derivative formed yellow needles, m.p. 165°. A 50–50 mixture of the *d*- and *l*-Schiff bases had m.p. 228°.

Anal. Found: C, 79.8; H, 5.8.

The specific rotation in ethyl acetate solution was $[\alpha]^{24}_{\mathrm{D}}$ +582° and $[\alpha]^{24}_{5461}$ + 830° whence $[M]^{24}_{\mathrm{D}}$ +2445° and $[M]^{24}_{5461}$ +3445°.

***d*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenylcopper(II)** crystallized from benzene–petroleum ether in brown needles, m.p. 274°.

Anal. Found: C, 69.4; H, 4.7; N, 5.6; Cu, 12.9.

The specific rotation (ethanol) was $[\alpha]^{24}_{\mathrm{D}}$ −75° and $[\alpha]^{24}_{5461}$ +100°, whence $[M]^{24}_{\mathrm{D}}$ −3600° and $[M]^{24}_{5461}$ +4800°.

2,2′-Bis-(salicylideneamino)-diphenyl-copper(II).—A solution of salicylaldehyde (1.3 g.) and 2,2′-diaminodiphenyl (1 g.) in ethanol (10 ml.) was gently boiled for 5 minutes. After recrystallization the orange Schiff base formed prisms, m.p. 154°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2$: C, 79.6; H, 5.1. Found: C, 79.4; H, 5.2.

A hot solution of copper(II) acetate monohydrate (1 g.) in methanol (40 ml.) was added to a hot solution of this Schiff base (0.5 g.) in ethyl acetate (20 ml.). The solution became deep olive green. On cooling, the copper(II) complex crystallized. Recrystallized from ethanol, it was obtained in olive needles, m.p. 301°.

Anal. Calcd. for $C_{26}H_{18}N_2O_2Cu$: C, 68.8; H, 4.0; Cu, 14.0. Found: C, 68.4; H, 4.0; Cu, 13.8.

This complex was paramagnetic with a magnetic moment of 1.95 Bohr magnetons at 22°.

***dl*-2,2′-Bis-(salicylideneamino)-6,6′-dimethyldiphenylberyllium(II).**—Basic beryllium acetate (2 g.) and III (1 g.) were heated together in chloroform (50 ml.) solution under reflux for 2 hours. The chloroform was then distilled off and the residue recrystallized many times from ethanol. It eventually was obtained in golden micro-needles, m.p. 289°.

Anal. Calcd. for $C_{28}H_{22}N_2O_2Be$: C, 78.7; H, 5.2; N, 6.5; Be, 2.1. Found: C, 78.9; H, 5.5.; N, 6.2; Be, 1.9.

Acknowledgment.—The authors gratefully acknowledge their indebtedness to Miss B. Stevenson for the C, H and N microanalyses recorded in this paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Olefin Coördination Compounds. II. The Preparation and Infrared Spectral Properties of Olefin–Platinum(II) Chloride Complexes[1,2]

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The complex compounds $[PtCl_2 \cdot C_4H_8]_2$, $[PtCl_2 \cdot i\text{-}C_4H_8]_2$ and $[PtCl_2(C_4H_8)_2]$ have been prepared. The infrared spectra of 1,3-bis-(ethylene)-2,4-dichloro-μ-dichloroplatinum(II), 1,3-bis-(butene-1)-2,4-dichloro-μ-dichloroplatinum(II) and 1,3-bis-(isobutene)-2,4-dichloro-μ-dichloroplatinum(II) have been measured from 2 to 15 μ by the KBr disc method. Shifts in the C=C frequencies indicate a carbon-to-carbon bond order of one and two-thirds for the complexes.

Introduction

Platinum (II) complexes containing an olefin as a ligand have been known since 1827 when Zeise first prepared and characterized potassium ethylenetrichloroplatinum(II).[3] Since then, a large number of olefin complexes with platinum have been prepared,[4] but the nature of the platinum–olefin bond has remained somewhat of a mystery. The most recent suggestion by Chatt[5] involves an

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[1] Abstracted in part from M.S. Thesis of J. E. Field, Tulane University, June, 1955.

[2] Presented at the American Chemical Society Meeting, Dallas, April, 1956.

[3] W. C. Zeise, *Pogg. Ann.*, **9**, 623 (1827).

[4] J. Chatt, *Ann. Rpts.*, **43**, 120 (1946).

[5] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

interaction of the π-cloud of the olefin with a dsp^2 orbital of the platinum. In support of this proposal, Chatt notes a shift of the C=C frequency in the infrared spectra of the ethylene and propylene complexes as observed upon dispersion of the sample in a Nujol mull.

In general, spectra of mulls are not too satisfactory, so the spectra of these compounds were measured by the KBr disc technique.[6] The absorption frequencies observed were substantially the same as reported by Chatt, but a number of additional frequencies were apparent in the KBr determinations.

Experimental

A. **Preparations.** 1. **1,3-Bis-(ethylene)-2,4-dichloro-μ-dichloroplatinum(II).**—This compound I was prepared by Chatt's method.[7] Potassium chloroplatinite (20 g.) was mixed with 10 ml. of concd. HCl and 90 ml. of water. The mixture was shaken for 10 days under 1.5 atmospheres of ethylene pressure. The resultant solution was evaporated to dryness, then extracted with 200 ml. of absolute alcohol containing 8 ml. of concd. HCl. The solution was evaporated to dryness under reduced pressure in a flask fitted with a capillary ebulliator. A 90% yield of 13 to 13.5 g. was obtained. This product decomposes at 160–165° and is sufficiently pure for further preparative work.

2. **1,3-Bis-(butene-1)-2,4-dichloro-μ-dichloroplatinum (II).**—This complex compound II was prepared by an extension of Anderson's[8] method of displacement of ethylene from I. Butene-1 was passed into a test-tube immersed in a Dry Ice bath at −78°. Then 1,2-bis-(ethylene)-2,4-dichloro-μ-dichloroplatinum(II) was added to the liquid and the solution was permitted to warm to room temperature to boil off the excess butene-1. A canary yellow solid is first obtained, but this changes to a viscous orange oil in a few minutes at room temperature. Mechanical working of the oil causes eventual solidification to yield the desired product.

3. **1,3-Bis-(butene-1)-dichloroplatinum(II).**—This compound III is obtained as one initial product in the preparation of 1,3-bis-(butene-1)-2,4-dichloro-μ-dichloroplatinum(II). In order to determine the nature of the yellow solid mentioned above, the reaction was run in a vacuum system using measured quantities of reactants. Thus, 3.36 mmoles of I was allowed to react with 16.87 mmoles of butene-1 at −78°. The excess gases were then removed and found to consist of 6.41 mmoles of butene-1 and 3.83 mmoles of ethylene. This seems to indicate that the course of the reaction is

$$\underset{\text{I}}{[PtCl_2\cdot C_2H_4]_2} + 3C_4H_8 \longrightarrow \underset{\text{IV}}{[PtCl_2(C_2H_4)(C_4H_8)]} + \underset{\text{V}}{[PtCl_2(C_4H_8)_2]} + C_2H_4$$

The two products are both unstable above 0° and attempts to separate them were unsuccessful.

4. **1,3-Bis-(isobutene)-2,4-dichloro-μ-dichloroplatinum-(II).**—This complex VI was prepared in a completely analogous fashion from I. Again there was a transformation from a yellow solid to an orange oil which solidified on stirring to give a granular solid.

B. **Infrared Spectra.**—Infrared spectra of I, II, III and K[$PtCl_3\cdot C_2H_4$] (VII) were recorded using the KBr disc method (Table I). The region of particular interest is that of the C=C bond absorption which appears at 1650 cm.$^{-1}$. In the case of ethylene no double bond absorption in the free gas occurs because of the symmetry of the molecule. As the bond between the carbons is altered in the formation of the complex, the symmetry of the molecule disappears and some evidence of a double bond stretching frequency is to be expected and it appears as a very weak absorption at 1527 cm.$^{-1}$ in VII and at 1511 cm.$^{-1}$ in I. In the case of butene-1, it is possible to make an unambiguous assignment of the C=C frequency in the gas at 1648 cm.$^{-1}$. This band occurs at 1501 cm.$^{-1}$ in II, a lowering of 147 cm.$^{-1}$.

To a first approximation the vibration frequency will be determined by the formula $\nu = 1307\sqrt{k/\mu}$ where k is the force constant and μ the reduced mass of the system. Using the 1511 frequency in this formula to calculate the force constant, a value of 8.03 is obtained, compared to $k = 9.6$ for a double bond and $k = 4.9$ for a single bond. This corresponds to a bond order of one and two-thirds for the carbon to carbon bond in the ethylene ligand. Calculations for the two butene complexes also show a bond order of one and two-thirds for the carbon to carbon "double" bond.

A mixed (propylene) (ethylene) dichloro platinum(II) monomer, [$PtCl_2(C_2H_4)(C_3H_6)$], recently has been suggested[9] as forming at low temperatures in a fashion similar to the 1,3-bis-(ethylene)-dichloroplatinum(II) compound [$PtCl_2(C_2H_4)_2$], reported by Chatt.[10] The discovery of a mixed butene-(ethylene)-dichloroplatinum(II) monomer IV, is therefore not surprising and, following Chatt's reasoning, should be the *trans* isomer. However, it should be mentioned that there is the alternate possibility of a clathrate type compound. If the arrangement of the ethylene group in the platinum complex is similar to that in the palladium complex,[11] the replacement of ethylene by butene in the crystal lattice would lead to an enlargement of the cell dimensions. This might allow some of the ethylene molecules to remain entrapped in a regular fashion in the crystal lattice in the manner of clathrate compounds.

TABLE I

INFRARED TRANSMISSION MINIMA OF OLEFIN COMPLEXES (IN WAVE NUMBER CM.$^{-1}$)[a]

[$PtCl_2\cdot C_2H_4$]$_2$	[$PtCl_2\cdot C_4H_8$]$_2$	[$PtCl_2\cdot i\text{-}C_4H_8$]$_2$	K[$PtCl_3\cdot C_2H_4$]
3413 (vw)	3425 (m)	3448 (m)	3413 (m)
2959 (vw)	3077 (vw)	3096 (vw)	3086 (w)
2041 (w)	2959 (m)	2924 (vw)	2353 (vw)
1616 (w)	2874 (m)	2336 (vw)	2053 (w)
1511 (w)	2833 (w)	2045 (w)	1626 (w)
1422 (s)	1639 (vw)	1623 (w)	1527 (vw)
1412 (s)	1501 (s)	1504 (vw)	1418 (vs)
1248 (vw)	1458 (s)	1425 (s)	1250 (w)
1232 (w)	1429 (m)	1416 (s)	1235 (w)
1215 (w)	1408 (w)	1372 (w)	1189 (w)
1174 (w)	1376 (s)	1359 (vw)	1030 (vs)
1020 (vs)	1302 (m)	1267 (w)	1022 (vs)
818 (w)	1256 (w)	1233 (m)	841 (w)
815 (w)	1248 (m)	1174 (m)	735 (m)
725 (m)	1206 (m)	1127 (vw)	
722 (m)	1199 (m)	1063 (w)	
	1182 (m)	1021 (s)	
	1171 (m)	977 (vw)	
	1068 (m)	956 (vw)	
	1038 (m)	884 (w)	
	1021 (m)	852 (w)	
	1014 (s)	820 (vw)	
	1000 (m)	814 (vw)	
	965 (w)	748 (w)	
	887 (w)	726 (m)	
	859 (s)		
	855 (s)		
	850 (m)		
	769 (s)		

[a] Abbreviations for intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

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