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## Abstract

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# ON THE NATURE OF THE BOND BETWEEN THE CENTRAL ATOM AND CERTAIN UNSATURATED MOLECULES IN COMPLEX COMPOUNDS OF PLATINUM

*(Presented by Academician V. I. Spitsyn, 7 VII 1958)*

The question of the bond between a metal and an unsaturated molecule in complex compounds of platinum is of considerable interest in connection with the general investigation of the nature of the chemical bond. Numerous works devoted to this topic have been reviewed in the surveys by Keller and Chatt (^1). A. D. Gel' man (^2) proposed that, when a platinum atom forms a complex compound with an unsaturated molecule, it acts simultaneously as both an electron donor and an electron acceptor. As a result, a double covalent bond arises between the central atom and the olefin. Ya. K. Syrkin (^3) believed that the unsaturated hydrocarbons $C_2H_4$ and $C_3H_6$, etc., are to a considerable degree covalently bonded to platinum. Chatt and Duncanson (^4) propose their own scheme for the formation of the bond between an olefin molecule and platinum in a complex compound, which may be characterized as a $\pi$-electron interaction. The authors find the justification for their scheme in the infrared absorption spectra of a series of complex compounds of platinum with olefins. However, the interpretation of the observed spectra given by Chatt and Duncanson seems to us not very convincing.

Chatt and Duncanson observed very weak absorption bands in the spectral region above 3000 $\text{cm}^{-1}$. In individual olefin hydrocarbons these bands are due to the stretching vibrations of CH in the groups $= CH_2$ and always appear intense. One of the characteristic frequencies of an olefin molecule is the frequency of the stretching vibration of the double bond C=C, with wave number $\sim 1650$ $\text{cm}^{-1}$. In complex compounds of platinum with olefins this frequency is not observed. In the infrared spectra of platinum complexes with propylene and of dimeric platinum complexes with ethylene and propylene, the above-mentioned authors observed absorption bands whose maxima correspond to wave numbers 1504–1506 $\text{cm}^{-1}$. Chatt and Duncanson ascribe these absorption bands to the frequency of stretching vibrations of the double bond C=C, shifted from the value of the frequency in the corresponding isolated addend molecule. This assumed frequency shift (by $\sim 130$ cm$^{-1}$) is explained by the authors by the formation of a bond between the olefin and platinum. On the basis of the interpretation set forth of two spectral characteristics, Chatt and Duncanson come to the conclusion that the double bond of the olefin is preserved upon formation of the complex. This conclusion, without any attempt at analysis, is also accepted in the work of Jonassen and Field ($\hat{}5$). It seems to us, however, that there are insufficient grounds for this.

The authors of the present communication set themselves the task of carrying out a critical analysis of the infrared spectra of complex compounds of platinum with ethylene, propylene, and carbon monoxide. The infrared spectra of the first two compounds were reproduced, and the spectra of cis-

and trans-forms of $K[PtCONH_3Cl_2]$. A calculation of the skeletal vibrations of the $(CH_2)_2Pt$ system was carried out, and the secular equation for the trans-form of $[PtCONH_3Cl_2]$ was investigated.

The number and values of the frequencies of the infrared absorption bands of platinum with ethylene and propylene proved to be, in the main, in agreement with the works ($^{4-6}$).

Let us consider the general spectral characteristics of complex compounds of platinum with olefins.

1. In contrast to Chatt and Duncanson ($^{4}$), the presence of frequencies in the region above 3000 cm$^{-1}$ in the infrared spectrum of the complexes mentioned is taken to be a necessary, but still not sufficient, indication of the preservation of the double bond $C = C$ in the olefinic part of the complex. Absorption bands in this region of the spectrum occur in such molecules as ethylene oxide, ethylene sulfide, ethyleneimine, and cyclopropane. As has been shown in theoretical and computational studies ($^{7}$), this is due to the close similarity of the electronic configuration in the $CH_2$ group of the molecules ethylene, ethylene oxide, and cyclopropane. This similarity makes it possible to suggest that the olefin forms with platinum a compound of the type of a triangular cyclic structure.

2. Similarly to the preceding point, the frequencies of the ethylene and propylene complexes with platinum observed in the region 1490—1510 cm$^{-1}$ should more correctly be assigned to the deformation vibration of $CH_2$ (as established by a rigorous calculation for cyclopropane and deuteriocyclopropane ($^{7a}$), and also by interpretation of the vibrational spectrum of ethylene oxide), and not to the frequency of stretching vibrations of the double bond $C = C$.

3. The frequency of the out-of-plane deformation vibrations of the CH group is characteristic ($^{8}$) of olefins. In the ethylene molecule it is equal to 949 cm$^{-1}$, and is very intense in the infrared spectrum. The absence of this frequency in the spectrum of $K[PtC_2H_4Cl_3] \cdot H_2O$ and the presence of

four additional intense vibrational frequencies in the region from 1300 to 700 $cm^{-1}$, in comparison with the spectra of the initial addends, indicate a significant rearrangement of the ethylene molecule. The latter can be associated only with transformation of the double bond $C = C$ into a single bond.

4. The considerations set forth are in agreement with data on the structure of $K[PtC_2H_4Cl_3] \cdot H_2O$, obtained by G. B. Bokii and G. A. Kukina ($^9$), according to which the ethylene molecule is situated perpendicular to the plane of $PtCl_3$ and almost symmetrically with respect to it. The distance between the carbon atoms was found to be 1.50 Å, i.e., it has a value characteristic of a single bond between these atoms. The use of the structural parameters of this compound made it possible to calculate the vibrational frequencies and force constants of the triangular three-mass model $(CH_2)_2Pt$ of the complex. For simplicity, the influence of vibrations of the chlorine atoms was not taken into account, since it is known that the interaction transmitted through a heavy atom is usually small. The $CH_2$ group was taken as one atom. It was also assumed that, in the case under consideration, the central-force model is valid. The calculations showed that the frequencies 1188, 500, and 632 $cm^{-1}$ pertain to the vibration of the "ring," and that the force constant between the carbon atoms is $a_{C-C} = 4.7 \cdot 10^5$ dyn/cm, and between the platinum atom and the carbon atom $a_{Pt-C} = 3.2 \cdot 10^5$ dyn/cm.
5. The analysis performed of the infrared spectrum of the complex compound $K[PtC_2H_4Cl_3]H_2O$ shows that the double bond $C = C$ in ethylene, upon entering the inner sphere of the platinum atom, is transformed into a single bond, while the strength of the bond between platinum and the carbon atoms is, in order of magnitude, equal to the strength of an ordinary covalent bond.
6. The propositions set forth in points 1-3 apply equally to the complex compound $K[PtC_3H_6Cl_3] \cdot H_2O$. On this basis the authors consider that its structure and the nature of the formation of the bond of propylene with the central atom are analogous to the structure and nature of the bond of ethylene with platinum in their complex compound.
7. The infrared spectra of the complex compounds of the cis- and trans-forms of $K[PtCoNH_3Cl_2] \cdot H_2O$ were investigated. For the trans-compound, a

the secular equation, whose investigation showed that, in the matrix of force coefficients, the group of atoms O—C—Pt may be regarded as an isolated triatomic molecule. The observed spectrum can be explained by adopting the assumption of linear addition of the ethylene oxide molecule to platinum. The force constant of the Pt—C bond proved to be $3.38 \cdot 10^5$ dyn/cm, and the force constant of the deformation vibration associated with the change in the O—C—Pt angle is $0.5 \cdot 10^5$ dyn/cm.

The force constants calculated both for the complex compound of platinum with ethylene and for the compound of platinum with carbon monoxide are in agreement with the literature data (10).

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*Note: Figure translations are in progress. See original paper for figures.*