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PHYSICAL CHEMISTRY

1965

SovietRxiv

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Abstract

Full Text

UDC 541.49+541.50

PHYSICAL CHEMISTRY

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X-RAY SPECTRAL DETERMINATION OF ATOMIC CHARGES IN NICKELOCENE AND NICKELOCINIUM

(Presented by Academician V. V. Voevodskii, 29 IV 1965)

A special type of chemical bond, manifested in π-complexes of group 8 metals, has for a number of years attracted the close attention of theoretical chemists and experimentalists. Thus, Shustorovich and Dyatkina ([1,2]) successfully applied to these objects the molecular-orbital (m.o.) method, and Batsanov ([3]) the electronegativity (e.n.) method. The results of these methods in known cases coincided with experimental data from the X-ray spectral determination of atomic charges in π-complexes, carried out by Barinskii ([4]).

However, in the case of cobalticinium and nickelocinium the m.o. and e.n. methods led to fundamentally different results: the charges on the metal atoms in the first method are respectively -0.12 and $-0.60e$, and in the second $+0.94$ and $+0.76e$. Taking into account the accuracy of the calculations by the m.o. method (see ([5])), a significant contradiction can be established precisely in the case of nickelocinium. An experimental determination of the atomic charges in nickelocinium has still not been carried out, which does not make it possible to form a correct picture of the nature of the chemical bond in this ion. The aim of the present work was to eliminate this gap.

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curves are corrected for instrumental distortions ($\Gamma = 1$ eV). Below are indicated the positions of the centers of gravity of the bands and components into which each level is split. In brackets the corresponding component is indicated. At left is shown the construction of the first absorption band.

The experimental study of nickelocene is also of interest, since in the previously published works on its X-ray spectral investigation ([6,7]), owing to the great thickness of the absorber, it was not possible to reveal the fine structure of the K-edge absorption. The results of work ([8]) on determining the effective charge of the nickel atom in nickelocene also require clarification (see ([9])).

Nickelocene was provided to us by Yu. N. Ustynyuk, to whom the authors express their gratitude, and nickelocinium was prepared as the triphenylborate salt in our laboratory. The physicochemical characteristics of both products corresponded to the literature standards.

The nickel K-absorption spectrum in both compounds was obtained on an RSDI spectrometer with ionization recording in the first order of reflection from the $13\bar{4}0$ planes of quartz. The resolving power was equal to 7000.

The density of the absorber was 2 mg/cm^2 in terms of nickel. The spectra were recorded several times from freshly prepared samples. The nickel K-absorption edges thus obtained, corrected for instrumental distortions, are shown in Fig. 1.

The calculation of the effective charge of nickel in nickelocene and nickelocinium was carried out taking into account the splitting of the p-levels of the excited electron in the electric field of the ligands [10]. Since the point group of symmetry for the molecules studied is D_{5d}, it follows from group theory that the p-levels must split into two components—the nondegenerate A_{2u} and the doubly degenerate E_{1u}. The magnitude of the splitting was calculated in first-order perturbation theory.

The values of the effective charges in nickelocene and nickelocinium, found from the calculation of the series of absorption lines and the curve of the continuous spectrum, proved to be, respectively, $\eta = 2.2$ and 2.15. For the effective quantum numbers, the values $n^* = 2.4$ and 2.4 were obtained. Consequently, the effective charges of the nickel atoms in these two molecules, due to redistribution of the valence electrons of nickel upon its entry into a chemical bond, are $+1.2$ for nickelocene and $+1.15$ for nickelocinium.

At these values of the charge η and quantum number n^*, the splitting of the first absorption line in the spectrum of nickelocene is 1.5 eV. The splitting of the second line is 0.6 eV. However, with such splitting values the approximation of the experimental curve proves to be insufficiently satisfactory. To achieve better agreement of the calculated curve with experiment, it is necessary to remove completely the degeneracy of the first p-level. This means that the Stark effect in nickelocene is caused by the influence not only of the nearest environment (which has D_{5d} symmetry), but also of the following coordination spheres. This can occur only if the symmetry of the whole crystal is lower than D_{5d}. A similar effect was observed earlier [4] in the K-spectrum of iron in ferrocene when comparing absorption edges in the gas and in the crystal.

Since an exact calculation of the influence of the crystal field is impossible because the coordinates of the atoms are unknown, the magnitude of the splitting was chosen so as to obtain the best agreement with experiment. Removal of the degeneracy from the E_{1u} components for the second and subsequent absorption lines may be disregarded, since the splitting itself is much smaller for them. For all lines, the width of the individual components was 2.3 eV, which is close to the width of the K-state of nickel. The width of the arctangent is the same.

Figure 1 shows the decomposition of the nickel absorption spectrum in nickelocene into absorption bands whose centers of gravity form a Rydberg series. The dashed curve is the sum of all absorption lines, of the continuous spectrum, and of the band in the long-wavelength part, singled out and caused by the transition of the photoelectron to molecular levels (hatched).

The decomposition of the nickel spectrum in nickelocinium was carried out in an analogous manner.

As follows from the study performed, the experimental values of the effective charges on nickel atoms agree better with the data of the electronegativity method.

The authors express their gratitude to R. L. Barinskii for valuable consultations and assistance in calculating the spectra.

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Received
23 IV 1965

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