Chemistry

Yu. D. Tsvetkov, V. V. Voevodskii, G. A. Razuvaev,

1957

SovietRxiv

Abstract

Full Text

Chemistry

Yu. D. Tsvetkov, V. V. Voevodskii, G. A. Razuvaev,
Yu. V. Sorokin, and G. A. Domrachev

ELECTRON PARAMAGNETIC RESONANCE IN SOME CHROMAROMATIC COMPOUNDS OF SANDWICH STRUCTURE

(Presented by Academician A. N. Nesmeyanov, April 19, 1957)

Recently there has been a sharp increase in interest in the study of compounds of sandwich structure—of the ferrocene type, $Fe(C_5H_5)_2$, the ferrocenium ion $[Fe(C_5H_5)_2]^+$, and molecules analogous to them with aromatic addends: $Cr(C_6H_6)_2J$, $[Cr(C_6H_6)_2]^+$, etc. Despite the large number of works devoted to this question, there is still no general theory explaining the available data on the "layered" structure of these molecules. The very fact of their formation and stability cannot be fully explained on the basis of generally accepted valence concepts. The data obtained to date indicate that, in most compounds of this type, the bond of the addends with the complex-forming atoms is covalent in character. This is indicated, in particular, by magnetic measurements, according to which these substances are either diamagnetic or possess a magnetic moment corresponding to one, two, or at most three unpaired electrons ([1]), whereas ionic salts of these same metals possess a considerably higher paramagnetism.

Until now, the literature has not described results on the investigation of such compounds by the method of electron paramagnetic resonance (EPR). At the same time, such measurements may prove very useful for elucidating certain details of the structure of molecules of sandwich structure*.

The present work was devoted to measuring the EPR spectrum of the following compounds: $Cr(C_6H_6)_2J$ (I), $Cr(C_6H_5—C_6H_5)_2J$ (II), $Cr(C_6H_5—C_6H_5)_2OC_6H_5$ (III) ([2,3]). The static magnetic susceptibility of these substances corresponds to one unpaired electron ([4]).

Our measurements were carried out on a superheterodyne EPR apparatus constructed at the Institute of Chemical Physics of the Academy of Sciences of the USSR, operating at a frequency of ~ 9000 MHz. The sensitivity of the circuit when observing signals on an oscilloscope corresponds to $5 \cdot 10^{14}$ particles of the reference radical diphenylpicrylhydrazyl (DPPH). The widths and g-factors

Fig. 1

Figure 1: Fig. 1

of the paramagnetic absorption lines were measured with the aid of a nuclear sensor. Photographs of the spectra of compounds I, II, and III in polycrystals are given in Fig. 1. The photographs also show the signals from the standard DPPH sample. The values of the g-factors for these substances, measured relative to DPPH ($g = 2.0036$) at the maximum of the absorption curve, as well as the corresponding line half-widths, proved to be as follows.

---

* In the work of Lutts ([8]), an attempt was made to find the EPR spectrum for biscyclopentadienyls of iron, chromium, nickel, and magnesium. However, no paramagnetic-resonance signals were detected at room temperature.

The absorption lines in Fig. 1 for substances I and II have a distinctly asymmetric character, which is associated with anisotropy of the g-factor. When J^- is replaced by

	I	II	III
g-factor	1.975 ± 0.001	1.987 ± 0.001	1.993 ± 0.007
$\Delta H_{1/2}$ (oerst.)	38 ± 2	28 ± 2	26 ± 2

$\{OC_6H_5\}^-$, this asymmetry practically disappears. It is also removed when these compounds are dissolved in organic solvents and in water.

Fig. 1. Spectra of paramagnetic resonance of chromoorganic compounds in polycrystals:
a–$Cr(C_6H_6)_2J$ (I),
b–$Cr(C_6H_5 - C_6H_5)_2J$ (II),
v–$Cr(C_6H_5 - C_6H_5)_2OC_6H_5$ (III).
At the left is the signal from the standard (DPPH).

In solutions of compounds I, II, and III the half-width of the absorption line is the same and amounts to 17 ± 2 oerst., while the g-factors of all the compounds coincide and are equal to 1.984 ± 0.001.

For understanding the structure of the molecules of chromoorganic compounds, what appears most essential to us is the presence of hyperfine structure of the absorption line in solutions of substances II and III. We did not detect hyperfine structure of the line for substance I. The absorption spectrum for substance III in aqueous solution is shown in Fig. 2. The concentration corresponded to $10^{-2}\,M$. The spectrum consists of at least 7 components of hyperfine structure, with a spacing between the components of 3.5 ± 0.2 oerst. Analogous hyperfine

Fig. 2. Hyperfine structure of the paramagnetic-resonance spectrum of a 0.01 M solution of substance III

Figure 2: Fig. 2. Hyperfine structure of the paramagnetic-resonance spectrum of a 0.01 M solution of substance III

structure was also observed by us for compound II. A spectrum of this type arises through interaction of the unpaired electron of the molecule with the magnetic nuclear moments of several hydrogen atoms that are part of the molecule. Since in compounds II and III the hydrogen atoms occur only in the aromatic rings, the presence of hyperfine structure means that the unpaired electron has a nonzero density on the aromatic addends of the complex. We assumed that the total width of the absorption line in a solution of substance I is also determined by components of hyperfine structure. In this case, when H is replaced by D in the aromatic rings of substance I, a decrease in the width of the absorption line should be observed ([5]). This was verified by special experiments*.

* The experiments were carried out in our laboratory by V. M. Chibrikin.

The existence of hydrogen hyperfine structure in the EPR spectrum can be explained in two ways.

1. The unpaired electron and the positive charge of the complex are localized on the chromium atom. An approximate calculation carried out under this assumption shows that the density of the unpaired $3d$-electron at the positions of the hydrogen atoms of the aromatic rings is sufficient to cause hyperfine splitting of the EPR spectrum.

2. The unpaired electron and the positive charge are localized on the aromatic addends of the complex. In this case the hyperfine structure is due to the interaction of the unpaired π-electron of the aromatic ring with the hydrogen atoms of this ring. The magnitude of the splitting, the number of components, and the ratio of their intensities in this case depend on the distribution of electron density over the addend molecule ([6]).

Fig. 2. Hyperfine structure of the paramagnetic-resonance spectrum of a 0.01 M solution of substance III

The following facts speak in favor of the first assumption: a) the presence of anisotropy of the g-factor in substances I and II; b) the value of the g-factor is smaller than the g-factor of the free electron (2.0023) ([7]). However, on the basis of this assumption it is impossible to explain the absence of hyperfine structure in dibenzolchromium ion. Considerable difficulties also arise in this case in interpreting the number of components of the hyperfine structure and the ratios of their intensities.

If one assumes localization of the unpaired electron on the aromatic addends of the complex, then the number of components and the intensity ratio can be satisfactorily explained for bis-diphenylchromium. The calculation was carried

out under the assumption that the electron density at the H atoms in the para position in bisdiphenylchromium is twice as large as at the H atoms in the ortho position, and that the hydrogens located in the meta positions do not participate in the splitting of the levels. The absence of hyperfine structure on going to dibenzolchromium in this case is explained by an increase in the number of hyperfine-structure components and, apparently, by a decrease in the distance between the components. These causes did not permit, at the given homogeneity of the constant magnetic field, resolution of the hyperfine-structure components in dibenzolchromium.

The true picture of the distribution of the density of the unpaired electron in the compounds studied is apparently a superposition of the two limiting cases considered above. To solve the question of the exact distribution of the density of the unpaired electron, a quantitative interpretation of the data on the anisotropy of the g-factor in these compounds is necessary.

However, the X-ray structural data necessary for this are not yet available. This question can also be approached by studying the hyperfine structure of the EPR spectrum for substances of types I and II with different numbers of various substituents in the rings, as well as of analogous compounds with the isotope Cr^{53}, which possesses its own nuclear moment capable, if the first scheme is valid, of sharply changing the hyperfine structure of the spectrum.

In conclusion, the authors express their deep gratitude to Prof. L. A. Blumenfeld for his help in discussing the results. The authors are also very grateful to Prof. B. K. Shembel, V. M. Chibrikin, and Yu. N. Molin for valuable advice and assistance in carrying out the work.

Institute of Chemical Physics
Academy of Sciences of the USSR
Gorky State University

Received
13 IV 1957

CITED LITERATURE

1. E. O. Fischer, *Angew. Chem.*, **67**, No. 17–18, 475 (1955).

2. G. A. Razuvaev, Yu. A. Sorokin, G. A. Domrachev, DAN, **111**, 1264 (1956).

3. G. A. Razuvaev, Yu. A. Sorokin et al., DAN, **113**, No. 6 (1957).

4. W. Klemm, A. Neuber, *Zs. Anorg. Allgem. Chem.*, **227**, 261 (1936).

5. B. Venkataraman, G. Fraenkel, *J. Chem. Phys.*, **24**, 737 (1956).

6. H. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

7. J. Owen, *Disc. Farad. Soc.*, No. 19, 127 (1955).

8. E. Lutze, *Zs. Phys. Chem.*, **8**, 32 (1956).

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