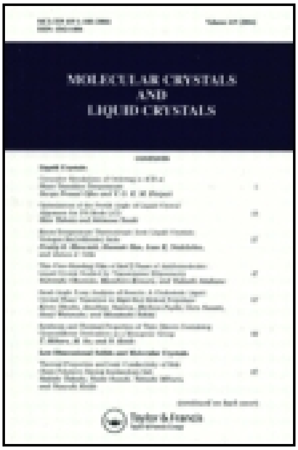

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Magnetic Properties of Complexes of TCNQ with Arenchromium Compounds

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Abstract—The magnetic susceptibility and proton magnetic resonance spectra of complexes with composition (dibenzenchromium)$^+$(TCNQ)$^{\overline{\cdot}}$(I), (ditoluenchromium)$^+$, TCNQ$^{\overline{\cdot}}$(II), (dibenzenchromium)$^+$(TCNQ)$^{\overline{\cdot}}{}_2$(III), and (ditoluenchromium)$^+$(TCNQ)$^{\overline{\cdot}}{}_2$(IV) have been measured in the temperature range from 1.5 to 300 °K. The magnetic susceptibility of complexes I and II at room temperature corresponds to the presence of one electron with $S = \frac{1}{2}$ on a molecule of complex. The lack of the paramagnetic shifts of those nmr-lines which are due to the protons of TCNQ indicates that the paramagnetism of these complexes is connected solely with the unpaired spins of arenchromium cations. In complex I, the existence of two inequivalent groups of cations has been discovered, whereas in complex II, all cations are presumably equivalent.

The temperature dependence of susceptibility of complexes III and IV testifies to the presence of small nearly temperature-independent contribution, typical for all highly conducting complexes of TCNQ and connected with the TCNQ-chains. The constants of hyperfine interaction between the unpaired electron and protons of arenchromium cations have been determined by combining the data on the temperature dependence of susceptibilities with the data on the paramagnetic shifts of nmr-lines.

1. Introduction

In the previous paper,$^{(1)}$ the preparation and some properties of new complexes of TCNQ with arenchromium compounds were briefly reported. Formally, in these complexes there are two unpaired spins on a molecule, one on the anion-radical TCNQ$^{\overline{\cdot}}$ and the other on the paramagnetic arenchromium cation, in distinction to the most TCNQ-complexes known which contain a diamagnetic cation. The presence of two unpaired spins on a molecule of complexes is confirmed by the existence of two epr-lines in a solution of acetonitrile. One of these lines with $g = 2.002 \pm 0.003$ is due to the spins of TCNQ, and one other with $g = 1.987 \pm 0.003$ is connected with the spins of cations. The existence of second unpaired spin in these complexes gives an additional possibility for investigation of their physical properties.

Two types of complexes were prepared: the simple salts with composition $D^+(TCNQ^{\cdot})$, and complex salts with composition $D^+(TCNQ)^{\cdot}_2$, where D^+ is the paramagnetic cation-radical of aren-chromium. At room temperature, the conductivity of complex salts is by 6–7 orders higher than the conductivity of simple salts.(1) In this paper the results of detailed investigations of (dibenzenchromium)$^+$TCNQ$^{\cdot}$(I), (ditoluenchromium)$^+$TCNQ$^{\cdot}$(II), (dibenzenchromium)$^+$(TCNQ)$^{\cdot}_2$(III) and (ditoluenchromium)$^+$(TCNQ)$^{\cdot}_2$(IV) are reported.

The magnetic susceptibility was measured on a Faraday-type microbalance(2) in the temperature range from 1.6 °K to 300 °K. The susceptibility of each specimen was determined in three different fields: 1.7, 4.26 and 8.1 kOe. The diamagnetic susceptibility of the lattice was calculated from Pascal's constants. The spectra of proton magnetic resonance were studied in the temperature range from 1.5 to 300 °K employing a Pound-Knight type spectrometer with operating frequency of 31 Mc/sec.

2. Simple Salts

As has been mentioned, each molecule of the complexes should contain two unpaired spins. However, the molar paramagnetic susceptibility of both simple salts is $12.6 \cdot 10^{-4}$ cgsm/mole, which corresponds exactly to the presence of one spin on a molecule. The temperature dependence of susceptibility is shown in Fig. 1 (upper solid line) and Fig. 2 for complexes I and II, respectively. At high temperatures (up to 100 °K) the susceptibility follows the Curie-law; below this temperature it begins to deviate from the Curie-law and passes through a maximum at 2.4 °K for complex II.

The proton magnetic resonance spectra at $T = 4.2$ °K for both simple salts are given in Fig. 3. Each spectrum consists of three lines. For complex I, the position of the narrow line corresponds to the resonance field of protons in a diamagnetic compound (H_0). Two others are shifted towards lower fields. The displacement of

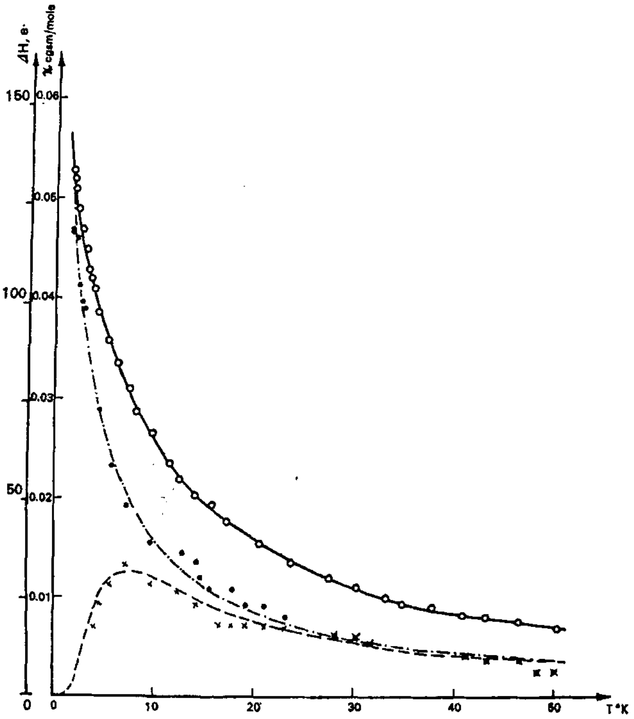

Figure 1. Temperature dependence of susceptibility of dibenzenchromium (TCNQ). O—susceptibility of dibenzenchromium (TCNQ) measured on microbalance; X and ●—paramagnetic shifts of the centres of gravity of two shifted lines of PMR of the same compound. Dashed lines are drawn according to Eqs. (4) and (5). Solid curve represents their sum. The scale of the ordinate axis is chosen to fit best to the solid curve with the measured susceptibility.

the centre of gravity of the absorption line is determined by the isotropic coupling constant a and the magnetic susceptibility χ:

$$H_0 - H_c = a\chi H_0/hN, \qquad (1)$$

where N is Avogadro's number, and h is Planck's constant.

The form of the most shifted line is typical for a polycristalline for the case where there is an axial-symmetric hyperfine interaction. The anisotropic coupling constant b determines here how the resonance fields are shifted relative to the centre of gravity with parallel and perpendicular orientations of the axes of symmetry

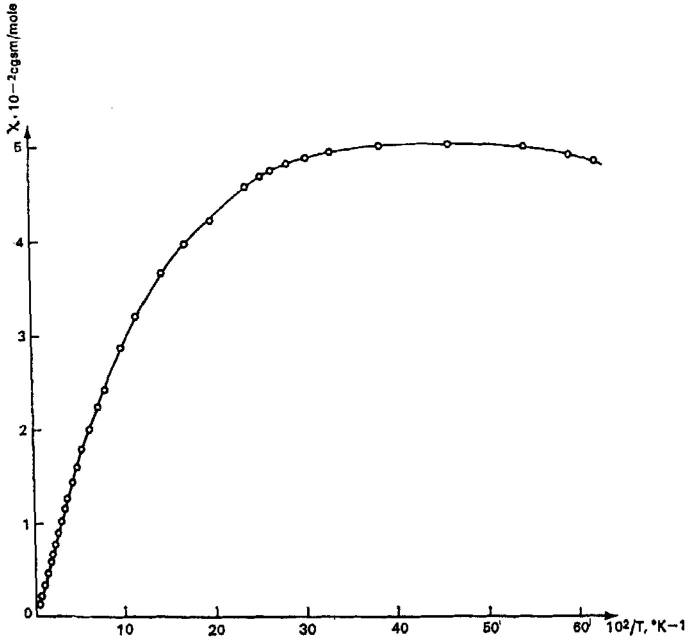

Figure 2. Temperature dependence of the susceptibility of ditoluenchromium (TCNQ).

relative to the external field:

$$H_{\parallel} - H_c = -2b\chi H_0/hN \tag{2}$$

$$H_{\perp} - H_c = b\chi H_0/hN \tag{3}$$

The ratio of the intensities of nmr-line is 2:3:3 for complex 1. The unshifted line, with the intensity 2, does not change when the temperature increases, whereas the shift and the width of two others depends on the temperature (Fig. 4). At low temperatures, these lines are well resolved, while at high temperatures they merge into one line. As can be seen in Fig. 1, the shifts of the centre of gravity of these lines do not follow the temperature variation of susceptibility.

For complex II, a line shifted towards lower fields is observed as well. Its shape is typical for the axial-symmetric hyperfine interaction. The shift of the centre of gravity and the width of this line are proportional to the susceptibility, in accordance with Eqs. (1–3). In this case, the unshifted line and the one shifted towards higher fields

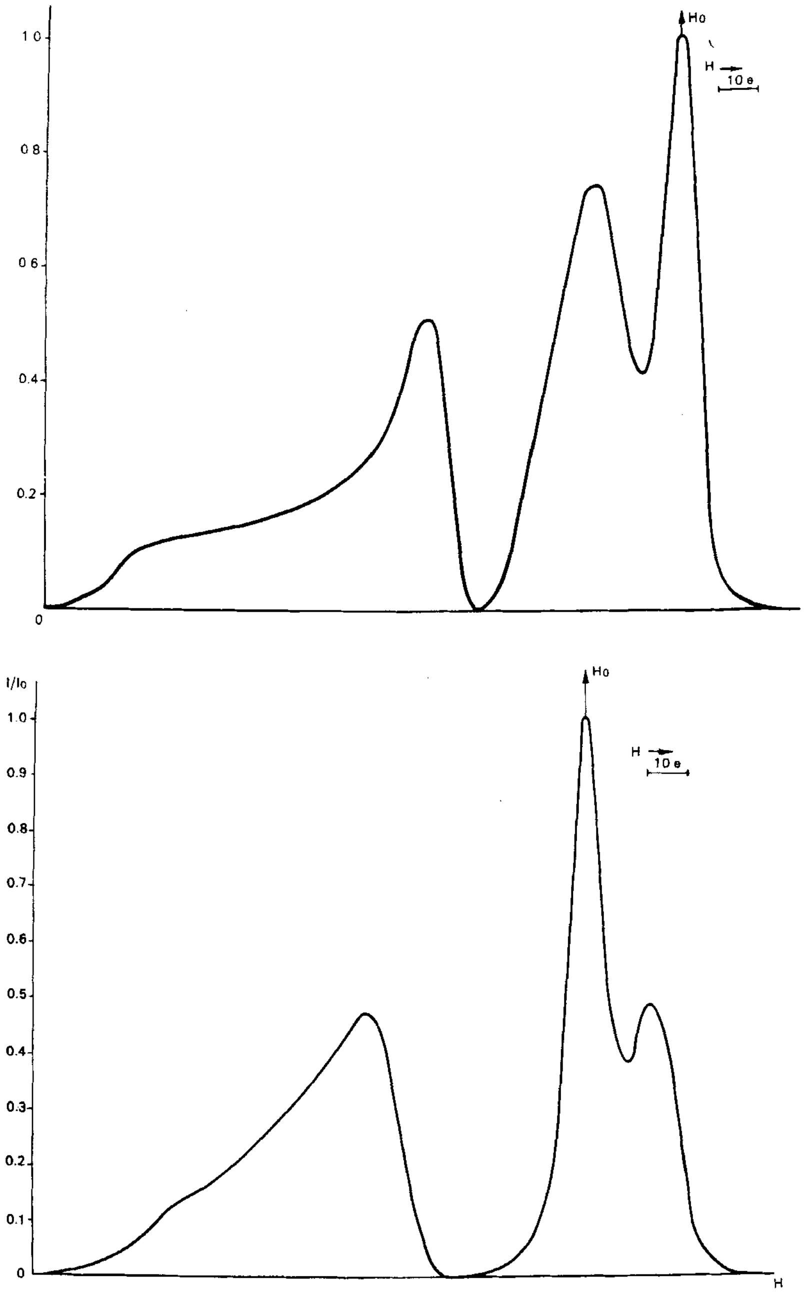

Figure 3. (a) Proton absorption spectra of dibenzenchromium (TCNQ), (b) Proton absorption spectra of ditoluenchromium (TCNQ).

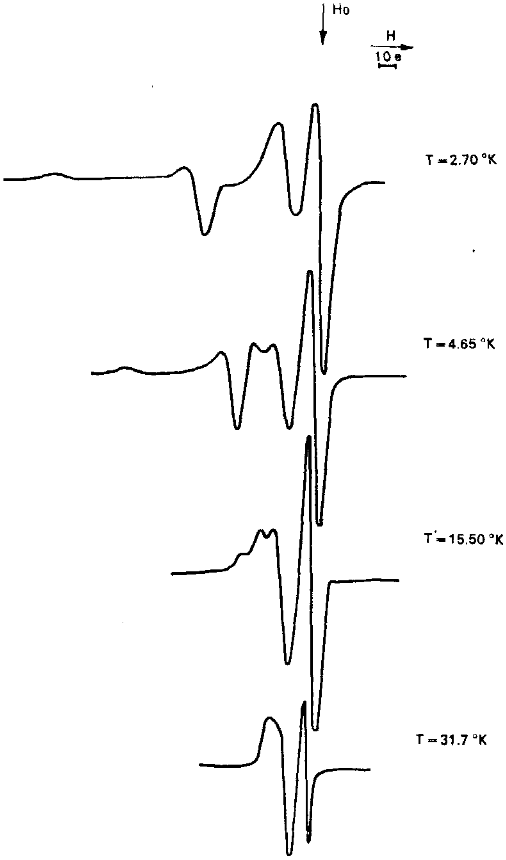

Figure 4. Records of PMR spectra's derivatives of dibenzenchromium (TCNQ) at different temperature.

are resolved rather poorly which makes impossible the determination of their form and relative intensities.

One can explain the above results by assuming that the spins of anion-radicals are coupled by a strong interaction, which gives rise to the complete pairing of them. Thus, the paramagnetism of the simple salts is connected solely with the unpaired spins of arenchromium cations.

The unshifted line observed in the nmr-spectra is due to the protons of TCNQ, and the lack of the shift from the resonance field H_0 points to the absence of the spin density on the TCNQ-anions.

Besides the unshifted line, there are two others in the nmr-spectra of complex I. Since all 12 protons of dibenzenchromium are equivalent, and the shifts of each line do not follow the paramagnetic susceptibility of the complex, it should be assumed that there are two non-equivalent groups of cations with different temperature dependence of the susceptibility. From the data on the temperature dependence of paramagnetic shifts, one can ascertain that the susceptibility of one half of cations varies with the temperature following the Curie-Weiss law:

$$\chi_1 = Ng^2\beta^2/8k(T - \theta) \tag{4}$$

with $\theta = -0.5\,°\mathrm{K}$

The susceptibility of the other part of cations can be fitted to the law of pair coupling:

$$\chi_2 = Ng^2\beta^2/2kT(1 + 3\exp I/kT)$$

with $I/k = 11.9\,°\mathrm{K}$ (5)

The dashed lines in Fig. 1 are the plots of χ_1 and χ_2 vs temperature. As can be seen, the summary susceptibility (solid line) is in good agreement with the data obtained from the microbalance measurements. Using the obtained values of χ_1 and χ_2, the Eqs. (1–3) allow the determination of the coupling constants between the unpaired electron and the protons. For the cations of both types, this gives: $a = 3.1 \pm 0.2$ Oe, $b = 1.1 \pm 0.1$ Oe, which agrees well with the constants reported early for dibenzenchromium iodide.$^{(3)}$ It should be noted that the existence of two non-equivalent cations in the unit cell of the complex I has also been shown by direct X-ray analysis.$^{(4)}$

In complex II, all cations are, presumably, equivalent. The nmr-line shifted towards lower fields is due to the protons of benzene rings. The coupling constants between these protons and the unpaired electron are $a = 3.1 \pm 0.2$ Oe, $b = 1.1 \pm 0.1$ Oe. The line shifted towards higher fields is due to the protons of CH_3-groups. It is impossible to determine the coupling constants for these protons in view of the poor resolution of lines.

3. Complex Salts

The temperature dependences of the susceptibility of complexes

III and IV are shown in Figs. 5 and 6, respectively. At room temperature its values for both salts are smaller by a factor of approximately 1.5 than those obtained from the Curie-law. The extrapolation of the plots of χ vs $1/T$ on the χ-axis represented in Figs. 5 and 6 show that at high temperatures there is a paramagnetic contribution χ_∞, which is higher than diamagnetic susceptibility of the lattice. For the complex III, $\chi_\infty = 4.9 \cdot 10^{-4}$ cgsm/mole, and for the complex IV, $\chi_\infty = 4.2 \cdot 10^{-4}$ cgsm/mole. It should be noted that, for simple salts discussed in previous section there is no additional paramagnetic contribution of this kind, and the extrapolation of the plot of χ vs $1/T$ on the χ-axis yields just χ_{dia}.

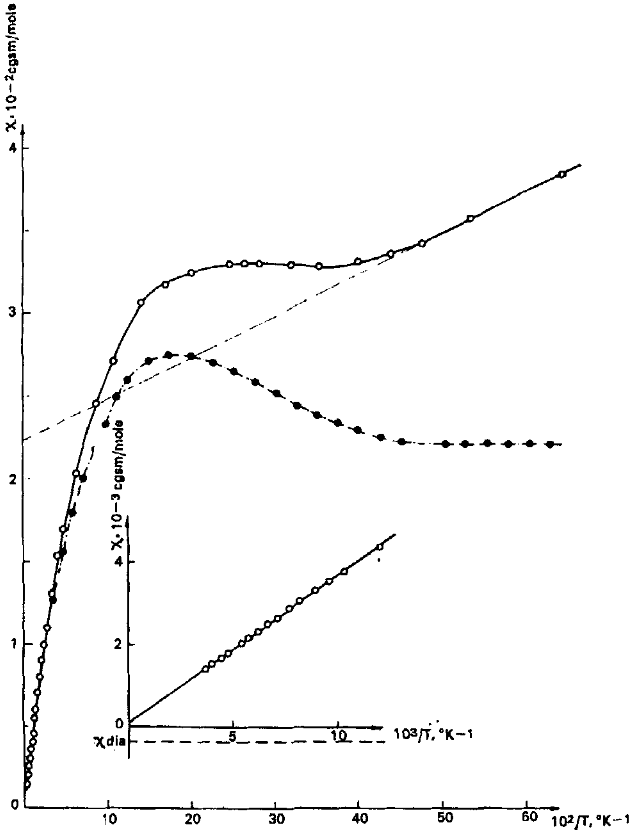

Figure 5. Temperature dependence of the susceptibility of dibenzenchromium $(TCNQ)_2$.

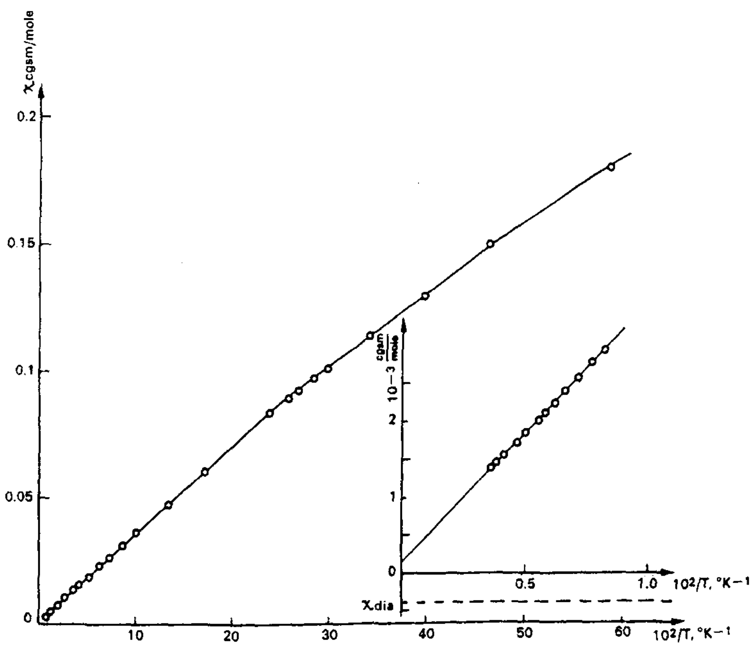

Figure 6. Temperature dependence of the susceptibility of ditoluenchromium $(TCNQ)_2$.

The lines of proton magnetic resonance of complexes III and IV are drawn in Figs. 7a and 7b, respectively. The nmr-spectrum of the complex III consists of two lines. One of them, shifted towards lower fields relative to the field H_0, has the form which is typical for a polycrystalline specimen in the case when there is an axial-symmetric hyperfine interaction; this line is due to the protons of benzene ring of cations.(3) Another line whose position corresponds to the resonance field H_0 of protons in a diamagnetic substance is to be ascribed to the protons of TCNQ. The ratio of intensities of these lines is 3 : 2, as could be expected.

The spectrum of complex IV consists of three lines. Here, the unshifted symmetric line is again to be ascribed to the protons of TCNQ, while the others shifted towards lower and higher fields are due to the protons of benzene rings and to the protons of CH_3-group of cations, respectively [3]. The ratio of intensities of these lines, 5 : 3 : 4, confirms this conformity.

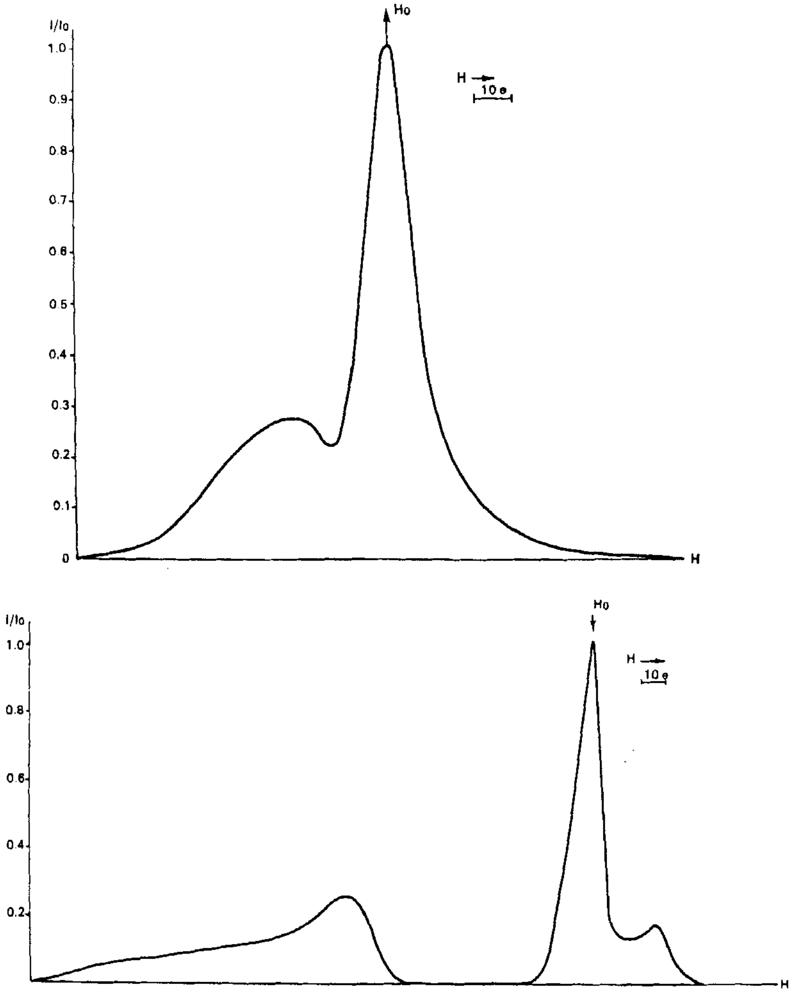

Figure 7. (a) Proton absorption spectra of dibenzenchromium $(TCNQ)_2$.
(b) Proton absorption spectra of ditoluenchromium $(TCNQ)_2$.

The above described results can be interpreted as follows. It is known that at suffciently high temperatures (say, > 50 °K) the susceptibility of the highly-conducting complexes of TCNQ depends rather slightly on the temperature.(5,6) Such a behavior of the susceptibility reveals a strong interaction between spins of TCNQ-molecules, and is related, presumably, to the high conductivity of these complexes. Therefore, it can be naturally suggested that the paramagnetic contribution χ_∞ has in our case the same origin and is connected with the system of TCNQ-spins. Its value, as well as that for other highly-conducting complexes of TCNQ,(5,6) is smaller by a factor of 2.5 to 3 than the room-temperature susceptibility calculated from the Curie law.

If one subtracts this temperature-independent susceptibility (at very low temperatures, it can vary of course, but here its contribution to the total susceptibility is small) from the total susceptibility, the value $\chi_{\text{para}} = \chi - \chi_\infty$ is obtained which, for both complexes in the wide range of temperatures, is described rather well by the Curie-Weiss law $\chi_{\text{para}} = C/(T+\theta)$ with constant C which corresponds to one spin on a molecule of the complex and with $\theta = 1$ °K and 0.5 °K for complexes III and IV, respectively. It is natural to ascribe this contribution to the total susceptibility to the spins of arenchromium cations.

For complex IV, the above Curie-Weiss law holds true for the whole temperature range, revealing the weakness of the interaction between the spins of ditoluenchromium cations. Using these values of susceptibility, one can determine the constants of hyperfine interaction for the protons of the benzene rings: $a = 3.4 \pm 0.3$ Oe, $b = 1.0 \pm 0.1$ Oe. They agree well with the values obtained for simple salts. We cannot determine the hyperfine coupling constants for the protons of CH_3-groups because of the poor resolution of the corresponding lines.

For complex III, the considerable deviations of χ_{para} from the above Curie-Weiss law begin at temperatures below 20 °K. As can be seen in Fig. 5, the susceptibility achieves the maximum value at 5 °K, and then passes through a slight minimum at 2.9 °K. At much lower temperatures, the susceptibility again increases approximately following the Curie-law.

The increase of the susceptibility at the lowest temperatures is also typical for other highly-conducting complexes of TCNQ, and is connected, presumably, with the presence of small amount (of order of few percent) of localized spins in the specimens. If one subtracts this susceptibility connected with localized spins from the measured susceptibility, then a plot is obtained which corresponds to the susceptibility of linear chain of spins with exchange integral

$I/k = (8 \pm 1)$ °K. The displacement of centre of gravity of shifted line in the nmr-spectrum agrees well with the obtained values of susceptibility up to 5 °K. At lower temperatures, this line exhibits strong broadening, and the determination of position of its centre of gravity becomes very difficult. However, such broadening is again characteristic of the behavior of the linear chain of spins.

The constants of hyperfine interaction between the unpaired electron and the protons of benzene rings calculated by using the values of susceptibility obtained in this way, are $a = 3.0 \pm 0.3$ Oe, $b = 1.1 \pm 0.1$ Oe.

Note in conclusion that the lack of the observable shifts for the nmr-lines connected with the spin-system of TCNQ testifies to the very small interaction between this spin-system and the spins of arenchromium cations.

REFERENCES

1. Yagubsky, E. B., Khidekel, M. L., Shchegolev, I. F., Buravov, L. I., Gribov, V. G. and Makova, M. K., *Izv. Acad. nauk, ser. chim.* **9,** 2124 (1968).
2. Ljubovsky, R. B. and Shchegolev, I. F., *Prib. Techn. Exp.* **5,** (1968).
3. Karimov, Yu. S., Chibrikin, V. M. and Shchegolev, I. F., *J. Phys. Chem. Solids* **24,** 1683 (1963).
4. Shibaeva, R. P., Atovmjan, L. O. and Rosenberg, L. P., *Chem. Communications*, 649 (1969).
5. Kepler, R. G., *J. Chem. Phys.* **39,** 3528 (1963).
6. Shchegolev, I. F., Buravov, L. I., Zvarykina, A. V. and Ljubovsky, R. B., *JETP, Pisma* **8,** 353 (1968).