

## Electroconductivity of anion-radical TCNQ salts containing cations $[M(\text{bipy})_3]^{2+}$ (M — Fe, Ni or Zn)

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Electrical resistance temperature dependence of three TCNQ anion-radical salts of complex composition containing cations  $[M^{\text{II}}(\text{bipy})_3]^{2+}$  (M — Fe, Ni or Zn, bipy — 2,2'-dipyridil) have been studied. Measurements have been performed in the range 180–300 K on tableted samples. The compound exhibit semiconducting properties and undergo the Peierls transition. Specific resistance at room temperature is of 7.7  $\Omega\cdot\text{cm}$  for Fe containing salt and  $2.3\cdot 10^{-2}$   $\Omega\cdot\text{cm}$  and  $2.5\cdot 10^{-2}$   $\Omega\cdot\text{cm}$  for salts containing Ni and Zn, respectively.

**Keywords:** tetracyanoquinodimethane, electrical resistance, semiconductor, Peierls transition.

Исследована температурная зависимость электрического сопротивления трех анион-радикальных солей TCNQ сложного состава с комплексными катионами  $[M^{\text{II}}(\text{bipy})_3]^{2+}$  (M — Fe, Ni или Zn, bipy — 2,2'-дипиридил). Измерения проведены в интервале 180–300 K на таблетированных образцах. Соединения проявляют полупроводниковый характер проводимости и неустойчивы к переходу Пайерлса. Удельное сопротивление при комнатной температуре составляет 7,7 Ом·см для Fe содержащей соли и  $2,3\cdot 10^{-2}$  Ом·см и  $2,5\cdot 10^{-2}$  Ом·см для солей, содержащих Ni и Zn, соответственно.

**Електропровідність аніон-радикальних солей TCNQ, що містять катіони  $[M(\text{bipy})_3]^{2+}$ , де (M — Fe, Ni або Zn). Г.Ю.Василець, А.В.Хоткевич, О.С.Букриньов, О.С.Красний, В.О.Стародуб, О.А.Кравченко, В.В.Медведєв.**

Досліджено температурну залежність електричного опору трьох складних аніон-радикальних солей TCNQ з комплексними катіонами  $[M^{\text{II}}(\text{bipy})_3]^{2+}$  (M — Fe, Ni або Zn, bipy — 2,2'-дипіридил). Вимірювання проведено в інтервалі 180–300 K на таблетованих зразках. Сполуки проявляють напівпровідниковий характер провідності та нестійкі до переходу Пайерлса. Питомий опір при кімнатній температурі складає 7,7 Ом·см для Fe вмісної соли та  $2,3\cdot 10^{-2}$  Ом·см і  $2,5\cdot 10^{-2}$  Ом·см для солей, що містять Ni і Zn, відповідно.

## 1. Introduction

Organic metals and semiconductors based on anion-radical salts (ARS) of 7,7',8,8'-tetratyanohinodiethane (TCNQ) are perspective materials for microelectronics [1–3]. Its uniqueness is in combination of electroconductivity and ability to form magnetically ordered structures. Many of them have already found applications in gas sensors, electric capacitors, light emitting diodes etc. [4–7]. The attractive feature of the ARS is its high anisotropy of physical properties. Moreover, by varying composition and size of cation one can significantly alter the physical properties of resulting ARS. Electroconductivity of the ARS containing formally uncharged TCNQ molecules have been studied in wide temperature range.

## 2. Experimental

All of the investigated anion-radical salts  $[\text{Fe}(\text{bipy})_3](\text{TCNQ})_4 \cdot (\text{CH}_3)_2\text{CO}$  (**1**),  $[\text{Ni}(\text{bipy})_3](\text{TCNQ})_4 \cdot (\text{CH}_3)_2\text{CO}$  (**2**) and  $[\text{Zn}(\text{bipy})_3](\text{TCNQ})_4 \cdot \text{H}_2\text{O}$  (**3**) (where bipy is 2,2'-bipyridil) were obtained using procedure described in [8, 9]. All of the compounds are isostructural (see Table 1). Crystal and molecular structure of the ARS is described in [8–10] in details.

The van der Pauw method was used to measure the temperature dependence of resistance in the range of 180–300 K [11]. Due to small sizes of single crystals of the ARS 1–3 samples their resistance was measured on tablets of 5 mm diameter obtained using hydraulic press (pressure is of 3 kbar). Slow (1 K/min) decrease of temperature of the sample was performed by

fractional addition of liquid nitrogen into nitrogen screen of cryostat. Temperature of the sample was measured by wide-range resistance temperature detector. To determine specific conductivity on direct current at room temperature and to measure electrical resistance of the sample a digital voltmeters B7-27 were used.

## 3. Results and discussion

The characteristic feature of composition of the investigated ARS is that one double charged cation  $[\text{M}(\text{bipy})_3]^{2+}$  requires four anion-radicals  $\text{TCNQ}^{\cdot-}$ . They are all crystallographically non-equivalent, therefore we may designate them as anion-radicals of A, B, C and D types. According to structural data the differences in bonds lengths of all TCNQ species are in the limit of X-ray experimental error. Therefore we assume that the average charge of the anion-radicals  $\text{TCNQ}^{\cdot-}$  is of  $-0.5\bar{e}$ .

Due to  $\pi$ - $\pi$  interaction the anion-radicals form two types of stacks along *a* axis. The first stack is formed by A and B molecules and contains tetraads AABB, the second one is formed by C and D molecules and contains CC and DD diades (Fig. 1). Interplane distances (see Table 2) in the stacks formed by C and D molecules and in AABB tetraads are less than the sum of the Van der Waals radii [12] of carbon atoms (3.42 Å).

Investigations of spectral properties of the ARS [8, 9] by methods of reflective IR and Raman spectroscopy show that the salts are high-conductive materials. Besides, maximal conductivity should be observed along *a* axis that is along the anion-radical stacks. Measurements of electrical resistance were performed on the tableted sam-

Table 1. Unit cell parameters of **1–3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{81}\text{H}_{46}\text{N}_{22}\text{OFe}$	$\text{C}_{81}\text{H}_{46}\text{N}_{22}\text{ONi}$	$\text{C}_{78}\text{H}_{42}\text{N}_{22}\text{OZn}$
Crystal system	triclinic	triclinic	triclinic
Space group	P-1 (2)	P-1	P-1
$a/\text{Å}, b/\text{Å}, c/\text{Å}$	13.720(4)	15.762(4)	16.424(4)
	13.6621(6)	15.8238(6)	16.4577(7)
	13.395(2)	15.881(3)	16.645(2)
$\alpha/^\circ, \beta/^\circ, \gamma/^\circ$	98.23(2)	97.969(3)	97.738(12)???
	97.969(3)	95.138(4)	95.104(3)???
	97.738(12)	94.923(11)	96.050(13)
Cell volume/ $\text{Å}^3$	3481.53(16)	3490.8(3)	3471.0(9)
<i>Z</i>	2	2	2

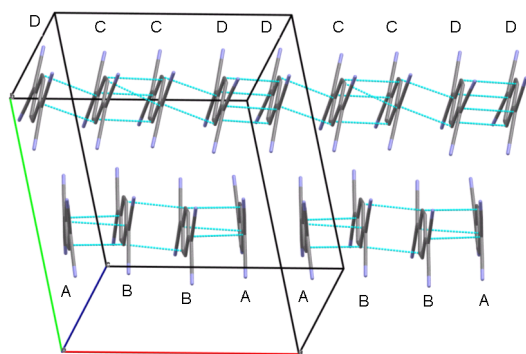


Fig. 1. Tetramerization and dimerization of TCNQ stacks in structures **1–3**.

Table 2. Interplane distances between anion-radicals in TCNQ stacks of **1–3**

Interplane distances, Å:	Compound		
	<b>1</b>	<b>2</b>	<b>3</b>
A...B	3.224	3.227	3.181
B...B	3.322	3.315	3.331
A...A	3.536	3.514	3.474
C...C	3.202	3.220	3.181
C...D	3.367	3.397	3.388
D...D	3.254	3.228	3.222

ples causing that values of resistivity are averaged on all directions of the crystallographic axes.

Temperature dependence of the specific resistance of the investigated ARS can be approximated precisely by the simple activation model for semiconductors:

$$R(T) = R_{RT} \cdot \frac{e^{E_a}}{2RT},$$

where  $R_{RT}$  — specific electrical resistance at room temperature,  $E_a$  — activation energy of conductivity. The results of the experiment are presented in Table 3, where one can see that conductivity is quite sensible to small changes in the conductive

Table 3. Specific resistance at room temperature and activation energy of conductivity of **1–3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
$R_{RT}$ , $\Omega \cdot \text{cm}^{-1}$	7.7	$2.3 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$
$E_a$ , eV	0.16	0.102	0.38

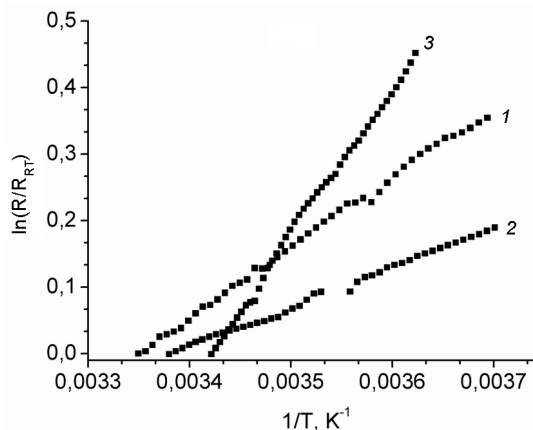


Fig. 2. Relative resistance of tableted samples **1–3**.

stacks despite of identity of the crystal structure of **1–3**.

The semiconductive character of conductivity of the investigated ARS is consistent with the result of magnetic measurements performed for compound **1** in [10]. ARS **1** undergo transition from diamagnetic state to paramagnetic along with the temperature increasing. These are attributes of the Peierls instability, i.e. transition when the conductive paramagnetic anion-radical stack turn to n-merized diamagnetic one [13, 14].

According to the structural data, the stacks containing tetrades AABB should be diamagnetic and possess the low conductivity due to localized electronic states. On the contrary, the stacks containing CC and DD dimers should have spin moment and high electroconductivity.

#### 4. Conclusions

The investigation of TCNQ anion-radical salts containing complex cations of general formula  $[\text{M}(\text{bipy})_3]^{2+}$  (where M — Fe, Ni or Zn) in wide temperature range show them to be semiconductors due to charge transfer along the anion-radical stacks. Additionally they are unstable to the Peierls transition.

The difference in conductivity among the anion-radical salts can be caused by small differences in interplane distances between the TCNQ molecules in the stacks.

#### References

1. Yonghua Chen, Dongge Ma, *J. Mater. Chem.*, **22**, 18718 (2012).
2. Yufeng Liab, Fangfang Jian, *J. Mater. Chem. C*, **2**, 1413 (2014).
3. V.A.Starodub, T.N.Starodub, *Russ. Chem. Review*, **83**, 391 (2014).

4. O.Pyshkin, G.Kamarchuk, A.Yeremenko et al., *J. Breath Res.*, **5**, 016005 (2011).
5. U.S. Patent 20050179399 A1 (2005).
6. U.S. Patent EP 2179458 A1 (2010).
7. U.S. Patent 7994708 B2 (2011).
8. K.Lewandowska, B.Barszcz, G.Vasylets et al., *Synth. Metals*, **162**, 1577 (2012).
9. G.Vasylets, V.A.Starodub, B.Barszcz et al., *Synth. Metals*, **191**, 89 (2014).
10. G.Vasylets, V.A.Starodub, A.Feher et al., *Synth. Metals*, **194**, 7 (2014).
11. Van der Pauw L.J. *Philips Res. Reports*, **13**, 1 (1958).
12. Yu.V.Zefirov, P.M.Zorkiy, *Usp.Khim.*, **58**, 713 (1989).
13. S.A.Bewick, Z.G.Soos, *J. Phys.Chem.B*, **110**, 18748 (2006).
14. D.Jerome, H.J.Schulz, *Adv. Phys.*, **51**, 293 (2002).