



# Influence of metal ions on the structure and spectral properties of TCNQ salts with tris(phenanthroline) cations



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## ABSTRACT

New anion-radical TCNQ salts containing *o*-phenanthroline complex cations with metal ions and appropriate solvent molecules were structurally and spectrally investigated. Contrary to the majority of TCNQ salts the structure of the investigated salts do not contain anion-radical stacks. It was stated that anisotropy of Raman spectra is negligible whereas the form of IR absorption spectra suggests very weak electron–molecular vibrations couplings. On the other hand the IR spectra of the cations are dominated mainly by the vibrations of the phenanthroline ligands. The Raman spectra of the investigated salts are differentiated and are altogether unlike each other. Some bands of complex cations located between 1100 and 1650 cm<sup>-1</sup> show particular character and can characterize metal–phenanthroline cation.

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## 1. Introduction

In the past few decades molecular low-dimensional conducting materials have attracted much interest owing to their physical properties, in particular, electrical, magnetic and spectral [1–4]. Over their classical inorganic counterparts, their basic structural units are molecules or clusters containing light atoms above all. These building blocks can be designed, synthesized and intentionally modified according to our needs.

Anion-radical salts (ARS) of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) containing transition metals complex cations are interesting objects due to their ability of forming magnetically ordered electro-conductive materials [5–10]. These ARS capable to self-ordering on account of coordination of cyano-group nitrogen atoms with transition metal cation. As a result, dimension of electronic system increase and there are appear additional possibilities of magnetic ordering. On the other hand, specific structure of ARS formed with low-dimensional stacks or sheets and favorable conditions for various interactions and couplings, e.g. electron–molecular vibration coupling, lead to characteristic spectral properties. In particular, the electron–molecular vibration coupling provokes unusual enhancements and shifts of totally

symmetric intramolecular vibrational bands of TCNQ anions in the IR spectra [11–13].

In this paper we present synthesis, crystal structure and vibrational properties of three novel ARS containing *o*-phenanthroline (phen) complex cations with metal ions and appropriate solvent molecules. The general chemical formulae of the salts is [M(phen)<sub>3</sub>](TCNQ)<sub>2</sub> solvent, where M is Mn(II), Fe(II) or Co(II) central ion but solvent is H<sub>2</sub>O or CH<sub>3</sub>OH. The aim of the paper is to investigate an influence of the central metal ion and solvent on the crystal structure and vibrational properties in the infrared absorption and Raman scattering. Experimental data have been discussed using the density functional theory (DFT) and appropriate functionals.

## 2. Experimental

Monocrystalline samples of the ARS were obtained by slow (dropwise) adding of the LiTCNQ solution in methanol to the water–methanol (1:3) solution of [M(phen)<sub>3</sub>]<sub>2</sub> (in case of iron compound complex salt [Fe(phen)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> was used). After 15–20 days dark crystals of ARS were isolated, washed with methanol and dried in vacuum. Yield about 55–60%.

Salts composition was determined by elemental analysis. For [Mn(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·H<sub>2</sub>O (**1**) calculated (%): C – 70.51, N – 19.19, H – 3.16; found (%): C – 69.69, N – 19.02, H – 3.21. For [Fe(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·2CH<sub>3</sub>OH (**2**) calculated (%): C – 69.66,

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N – 18.35, H – 3.77; found (%): C – 69.17, N – 18.17, H – 3.84. For [Co(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·H<sub>2</sub>O (**3**) calculated (%): C – 70.23, N – 19.12, H – 3.35; found (%): C – 69.69, N – 18.86, H – 3.25.

The crystal structure was determined using an Oxford Diffraction Xcalibur2 diffractometer equipped with a Sapphire2 CCD detector. Crystalline CCD was used for data collection while crystalline RED was used for cell refinement, data reduction and absorption correction [15]. The structure was solved by the direct method with SHELXS97 and subsequent Fourier synthesis using SHELXL97 [16]. Anisotropic displacement parameters were refined for all non-H atoms. The H atoms of aromatic cycles were placed in calculated positions and refined riding on their parent C atoms with C–H distances of 0.93 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$ . An analysis of bond distances and angles was performed using SHELXL97, DIAMOND [17] was used for molecular graphics.

The infrared absorption spectra of the powdered [M(phen)<sub>3</sub>](TCNQ)<sub>2</sub> solvent samples were recorded in the frequency range from 400 to 7500 cm<sup>-1</sup>, at room temperature with FT-IR Bruker Equinox 55 spectrophotometer. The room temperature Raman spectra of the single crystals were collected with a Horiba Jobin Yvon LabRam HR800 spectrometer with excitation Ar laser beam at  $\lambda_{ex} = 488$  and 514 nm. The power of the laser beam at the sample was less than 1 mW to avoid damages of the sample.

The ab initio calculations of optimal geometry and normal modes frequencies of the three [M(phen)<sub>3</sub>]<sup>2+</sup> cations were performed using the Gaussian 03 program [14]. Calculations were carried out on an isolated cations using the density functional theory (DFT) with Becke's three parameter exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The 6-31G basis set was used for optimizations and all calculations. The experimental crystallographic data were used as an initial geometry of the cations. The modes description was made by visual inspection of the individual modes using the GaussView program. The normal modes assignment of [M(phen)<sub>3</sub>](TCNQ)<sub>2</sub> solvent was performed on the basis of experimental and theoretical data.

### 3. Results and discussion

The compounds **1** and **3** have similar crystal structure. Anion-radicals TCNQ<sup>•-</sup> in the lattice can be presented as those of two types: A and B. Anion-radicals of A type create dimers AA due to overlapping of  $\pi$ -systems of two parallel adjacent TCNQ molecules. These dimers create neither stacks nor short contacts one with another. TCNQ molecules of B type are isolated one from another and from AA dimers.

#### 3.1. [Mn(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·H<sub>2</sub>O (**1**)

The crystal structure of [Mn(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·H<sub>2</sub>O formed by tris(*o*-phenanthroline) manganese(II)-cation [Mn(phen)<sub>3</sub>]<sup>2+</sup> and two types of crystallographically independent anion-radicals TCNQ<sup>•-</sup> (labeled in the text below A and B). A and B anion-radical charge values –0.79e and –0.98e, respectively were estimated on the basis of C–C bond lengths in TCNQ molecule [18,19]. The main feature of the present structure is absence of TCNQ anion-radical stacks which are quite characteristic for most of its ARS.

Both A and B anion-radicals are located at obtuse angle relative to each other in the unit cell. Anion-radicals of A type form dimers: C–C shortest distances between two adjacent TCNQ molecules of A type are 3.174, 3.173 and 3.158 Å. Besides, neighboring AA dimers are isolated one from another; i.e. there are no short van der Waals contacts between them. In contrast of it anion-radicals of B type are connected in infinite length chains by hydrogen bond with water molecules. Alternating distances N–H in the chains are 2.606 and 2.575 Å. An interesting feature of these chains is that two such

neighboring chains oriented antiparallel and have no van der Waals contacts with each other. The AA dimers sequences are separated by these two chains.

It should be noted, that [Mn(phen)<sub>3</sub>]<sup>2+</sup> complex cations are not isolated one from another. Two neighboring cations are connected with short contacts trough nitrogen atom of A TCNQ<sup>•-</sup>. The carbon atom in 2nd position of *o*-phenanthroline molecule of the first cation interacts through TCNQ nitrogen atom (cyano-group in 7th position) with carbon atom in 3rd position of *o*-phenanthroline molecule of the second cation. Corresponding C–N distances are 3.163 and 3.166 Å respectively. In addition, complex cation has short contact C–N (3.157 Å) with B TCNQ<sup>•-</sup> (carbon atom in 9th position of said *o*-phenanthroline molecule interacts with nitrogen atom of TCNQ cyano-group that does not take part in hydrogen bonding with water molecule). This phenanthroline molecule has hydrogen bond (2.818 Å) between hydrogen atom located at carbon in 5th position and carbon atom of cyano-group of A TCNQ<sup>•-</sup> (cyano-group in 8th position). All of short contacts formed by complex cation are related to one *o*-phenanthroline molecule. Other two coordinated *o*-phenanthroline molecules take no part in any intermolecular van der Waals interactions.

As a result of described intermolecular interactions, AA dimers and . . . BBB. . . chains of anion radicals are connected one to another through complex cations. We observe the formation of infinite length chain, where a link of the chain consists of two B anion-radicals, one dimer AA and two complex cations.

#### 3.2. [Fe(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·2CH<sub>3</sub>OH (**2**)

The compound [Fe(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·2CH<sub>3</sub>OH was synthesized and structurally characterized before by Ballester et al. [20,21]. The crystal structure of the compound **2** is the same that reported in [20]. Small differences (which does not exceed the X-ray experiment precision) in bond lengths are observed only.

Iron(II) ion is surrounded by six nitrogen atoms of three *o*-phenanthroline molecules. The symmetry of crystal field is close to octahedral. Fe–N bond lengths are in the range 1.967–1.972 Å, therefore we consider Fe<sup>2+</sup> cation as being in low-spin state (in case of high-spin state values of Fe–N bond lengths should be nearly 2.16 Å).

Anion-radicals TCNQ<sup>•-</sup> form dimers, which distinctive feature is the formation of long C–C  $\sigma$ -bond (1.629 Å) between exocyclic carbons of neighboring TCNQ molecules. That is why (TCNQ)<sub>2</sub><sup>2-</sup> dimer, presumably, has zero spin. This is true only at liquid helium temperatures, since the electron spin resonance (ESR) spectrum of the compound at 300 K represented by a single ESR line (g-factor is nearly 2). The intensity of ESR signal increases with temperature. ESR spectra at 5 and 19 K show very weak broad line. Thus, we made a conclusion about spin unpairing in the dimers.

#### 3.3. [Co(phen)<sub>3</sub>](TCNQ)<sub>2</sub>·H<sub>2</sub>O (**3**)

The crystal structure of **3** formed by complex cations [Co(phen)<sub>3</sub>]<sup>2+</sup> and anion-radicals TCNQ<sup>•-</sup>. The crystal structure of **3** contains no stacks of anion-radicals, that is similar to **1** and **2**. Its structural motif has much in common to that for compound **1**.

It is possible also to distinguish two types of anion-radicals: A and B. Anion-radicals of A type form dimers AA due to overlapping of  $\pi$ -systems thereof, where the shortest C–C distances are 3.136, 3.146 and 3.161 Å. Cyano-group in 7th position of B anion-radical form hydrogen bond with water molecule (N–H distance is 2.631 Å). Instead of compound **1**, B anion-radical form only one hydrogen bond in the present ARS. And, like in crystal structure of **1**, two such neighboring sequences are oriented antiparallel.

Cobalt(II) cation is surrounded by six nitrogen atoms of three *o*-phenanthroline molecules. The symmetry of this is close to

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