

and totally protonated acid $\text{Cs}(\text{H}_2\text{C}_2\text{O}_4)(\text{HC}_2\text{O}_4)(\text{H}_2\text{O})_2$ [4]. We focus here on the structural reinvestigation of a caesium oxalate at 100 K. The structure is resolved in the space group $P2_1/c$, with the lattice parameters consistent with the data reported in [3], ($a=10.3677(10)\text{\AA}$, $b=6.7050(15)\text{\AA}$, $c=6.5849(8)\text{\AA}$, $\alpha=93.552(4)^\circ$). However, the new XRD structural study shows that instead of the chemical formula suggested in [3], the compound contains both the acid and the dianion: $\text{Cs}_2(\text{H}_2\text{C}_2\text{O}_4)(\text{C}_2\text{O}_4)$.

The asymmetric unit contains one Cs atom, one half oxalate dianion (C(1)O(1)O(2)) and one half oxalic acid molecule [C(2)O(3)O(4)H]. The nine-coordinated caesium atom is surrounded by four centrosymmetrical $\text{H}_2\text{C}_2\text{O}_4$ molecules, acting in unidentate fashion, and four oxalato ligands. The dianion is involved in a chelation by one function and in unidentate mode by the second function. The 2D structure consists of double files of CsO_6 polyhedra, running along [001] and [010] directions. In the two kinds of files, each polyhedron is sharing one edge with its nearest neighbours forming layers of double files. Within the layers, the deprotonated ligands link the files, while the other ligands connect the double file layers.

The single H atom has been localized in the difference Fourier map. In this structure, it is noteworthy to point out that, in each kind of ligand, it occurs a distance C-OH longer than the others C-O distances, implying a vicinity of the proton near the O1 or O4 atom. Strong H-bonds involving O4 and/or O1, occur between acid molecules and oxalate anions, leading to files extending along [100] direction. Further studies should concern the H motion, eventually by H RMN and electrical conductivity.

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Key-words: oxalate, polymeric structure, static disordered H atoms

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Carbon nanotubes as nucleation agents in polypyrrole-carbon nanotube nanocomposites

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A nanocomposite has been synthesized by *in-situ* chemical polymerization using pyrrole (Py) as a monomer and single wall carbon nanotube (SWNT) as an additive component. Experiments show that PPy growth on the surface of SWNTs in the spherical and cylindrical core-shell structures. As a result of strong bonds with carbon nanotubes (CNTs) [1, 2], the radical monomers and oligomers forming during the polymerization are adsorbed and anchored on amorphous carbon and SWNT surfaces which act as preferable sites for nucleation and growth of PPy. Depending on the anchoring sites the growth modes give rise to different morphologies. Wide-angle X-ray diffraction patterns indicate a change in the crystallinity of PPy in the composite.

The FTIR and Raman spectra of PPy/SWNTs composites consist of a broad adsorption band in the special domain between 4000 and 2500 cm^{-1} , which is commonly assigned for the adsorption band of O-H, C-H, N-H groups. However, due to the intensity of this adsorption band relatively increases with the laser excitation intensity, a portion of the 3000-3500 cm^{-1} band is speculated as the photoluminescence arising from transitions between valence band to polaron or to bipolaron levels [3]. Charge transfer interaction between composite components likely brings

more new polaron and bipolaron levels into the band gap of PPy.

The Raman spectra of the composite show the change in 1590, 1280 cm^{-1} and 940 cm^{-1} peaks. The band located at about 940 cm^{-1} is assigned to the ring deformation associated with radical cation (polaron state) while the band around 1590 cm^{-1} is the tangential mode (G-band) associated with sp^2 -hybridized carbon atoms (C=C bond) of SWNTs and PPy. The 1280 cm^{-1} band in PPy/SWNTs is assumed to be the superposition of both 1310 and 1253 cm^{-1} bands which stand for the bipolaron state of PPy [4, 5]. The decline of 940 cm^{-1} band and the emergence of 1280 cm^{-1} band in Raman spectra then indicate the transition from polaron to bipolaron state, i.e., indicate an increase in conductivity of PPy.

The UV-Vis spectra of PPy and PPy/SWNTs show two major peaks centering around 340 nm and 460 nm. The 340 nm adsorption band stands for $\pi^*-\pi$ transition while the 460 nm adsorption band represents the bipolaronic transition in PPy relating to the oxidized levels. The 340 nm band is intensified and undergoes a redshift while the 460 nm band exhibits a blueshift when SWNTs are doped. The change in the intensity and position of these adsorption bands indicates a strong modification in electronic structure and polaron levels in PPy bandgap.

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Keywords: PPy, SWNTs, nanocomposite

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Molecular structure of binuclear Ag (I) complex of phenyl bis(2-pyridyl)phosphine

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The design of silver (I) complexes has attracted particular attention due to their interesting structures, photoluminescent, biological and pharmacological activities, such as anticancer and antifungal properties [1] we describe synthesis, spectroscopic studies and crystal structure of Ag(I) complex of phenyl bis(2-pyridyl)phosphine. This complex was synthesized by reacting 2-lithiopyridine and dichlorophenyl phosphine in Et_2O [2] ($\text{PhP}(2\text{-py})_2$) followed by treating with AgNO_3 in water. Single-crystal X-ray analysis reveals that mentioned complex crystallizes in monoclinic system, with $P2_1/n$ space group. The structure of this complex consists of two silver atoms, two molecules of ligand that act as tridentate beside two nitrate ions. The $\text{Ag}\cdots\text{Ag}$ distances is 3.216 (9) \AA , which is shorter than the sum of the van der Waals radii of two silver atoms (3.44 \AA), suggesting the existence of metal-metal interaction between the silver atoms. The free oxygen atoms of nitrate ligands interact with hydrogen atoms of the pyridyl groups to form hydrogen bonding. The separations for C(2) \cdots O(3), C(3) \cdots O(2), C(8) \cdots O(1) and C(10) \cdots O(3) (symmetry code: 1/2+x, 3/2-y, 1/2+z, 5/2-x, -1/2+y, 3/2-z and -1+x,y,z) are 3.369(8), 3.355(8), 3.313(8) 3.332(8) \AA .

In order to verify presence of silver-silver intra-molecular bonding the electron density of the synthesized complex was studied in the context of Quantum Theory of Atoms in Molecules, QTAIM[3]. The electron density of the complex was obtained from a single point energy calculation on the X-ray resolved crystal structure by Win-GAMESS.08 suite of programs at the B3LYP combined with three different basis sets for different elements; 6-31G for carbon and hydrogen atoms, 6-31+G(d) for nitrogen, oxygen and phosphorus and DZVP (DFT orbitals)

for silver atoms. Accuracy of QTAIM analysis was checked by keeping the integral of Laplacian for each atomic basin below 10^{-4} au that demonstrates a weak bond connects two silver nuclei which is in the normal range of metal-metal bonds in binuclear complexes.

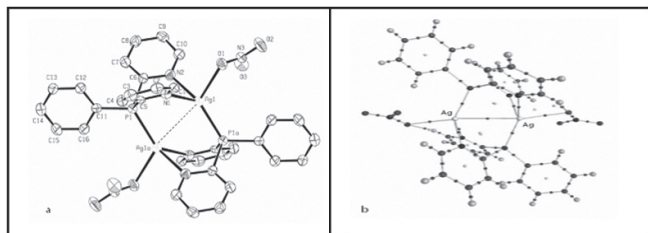


Figure 1. a) ORTEP view b) Molecular graph of synthesized complex

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Keywords: binuclear Ag (I) complex, metal-metal interaction, QTAIM analysis

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Structures, thermal behaviors and magnetic properties of two fumarato-bridged lanthanides

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$\{[\text{Ln}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}\}_n$ with $\text{Ln}=\text{Ho}^{3+}$; Gd^{3+} , are two isostructural coordination polymers belonging to $\text{P2}_1/\text{n}$ space group, which have been prepared via two different synthetic routes, and structurally studied at room temperature^[1] and 100 K, respectively. Single crystal structures reveal that the materials are 3D frameworks built up from corrugated layers containing noncentrosymmetric double oxo-bridged binuclear entities. In the extended network, the basic building block corresponds to the bi-polyhedra sharing one edge $\text{Ln}_2\text{O}_{12}(\text{H}_2\text{O})_4$. Each metal is nine-coordinate and surrounded by the same number of ligands. Two independent ligands are pentadentate, in a *syn-anti* conformation, acting as bridging-chelating, and moreover, one is carboxylato-bridging and the other a chelate. The third ligand is tetradentate, in a *syn-syn* conformation, and involves its two terminal groups respectively in a chelate and a conventional carboxylate-bridge.

ATG/ATD analyses show that the dehydrated solids $[\text{Ln}_2(\text{C}_4\text{H}_2\text{O}_4)_3(\text{H}_2\text{O})_4]$ nor $[\text{Ln}_2(\text{C}_4\text{H}_2\text{O}_4)_3]$ cannot be obtained, all the water molecules being released at the same time. This behavior indicates the great effect of the lattice water upon the crystallinity, and the role of the strong H-bonds among the coordinated and uncoordinated water molecules, in coordination polymer's stability. After dehydration, the decomposition process involves intermediate compounds as Ho acrylate^[2] and complex Gd oxide respectively. Variable-temperature magnetic measurements in the range (0-300) K, obey the Curie-Weiss law, and reveal the occurrence of very weak antiferromagnetic coupling between the lanthanide ions. In the light of the XRD structures, the possible exchange pathways could be responsible for the magnetic coupling through $\mu-1,1$ and $\mu-1,3$ bridges within the binuclear entity, or

across the backbone of the ligand. However, the shorter Ln-Ln distances are observed through μ bridges (4.143(2) Å and 4.113(2) Å for Gd and Ho compound respectively). In the resulting modeling of the magnetic data, although J values are negative, they are very small if compared to other lanthanide coordination polymers containing binuclear entities.^[3] This might be due to the relatively great values^[4] of Ln-O-Ln angles (111.57(6)° and 110.24(6)° for Gd and Ho compound respectively).

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Key-words: binuclear entities, antiferromagnetic coupling, coordination polymers

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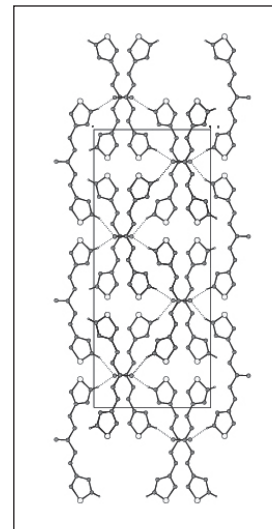
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Crystal structure and semi-empirical quantum chemical calculation of 1,5-Bis (3-thiophenyl)-1,4-pentadiene-3-one

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The chalcones are important chemical intermediates used in the synthesis of various organic compounds containing five and seven-membered heterocycles. The study of such compounds have attracted considerable interest as they possess wide spectrum of biological activities such as anti-oxidant, neuroprotective, anti-miotic and anti-malarial etc. Moreover, they have significant contribution in the production of photochemical materials through the solid-state photo cycloaddition process. In view of the importance of these factors, the title compound is synthesized and its crystal structure is studied. The compound crystallizes in orthorhombic space group Pbca with the crystal parameters as: $a=11.8908(3)\text{Å}$, $b=7.18070(10)\text{Å}$, $c=28.3004(6)\text{Å}$, $V=2416.41(9)\text{Å}^3$, $Z=8$ and $\mu=0.415\text{mm}^{-1}$. The structure is solved by direct method using SIR-97 program and refined by full matrix least square on F^2 using SHELXL-97 program to a final value 0.0443 for 3671 reflections with $I > 2\sigma(I)$. The crystal structure is stabilized by intra- and intermolecular C-H...O interactions, as well as weak C-H... π interactions. The thiophene rings are planar within themselves and are oriented at an angle of $5.60(15)^\circ$ and $14.26(15)^\circ$ with the mean plane passing through 1,4-pentadiene-3-one moiety.

Semi-empirical Quantum Chemical Calculations were performed on the refined parameters using MOPAC2009 program to optimize the structure with Parametrization Model 6 (PM6) approximation together with the



Molecular Packing viewed down the 'b' axis