



# An unusual $\mu_{-1,2,3}$ -squarato-bridged two dimensional coordination polymer: Crystal structure, thermal, photoluminescence and magnetic studies



Somen Goswami<sup>a</sup>, Rajat Saha<sup>a</sup>, Ian M. Steele<sup>b</sup>, Papri Dasgupta<sup>c</sup>, Asok Poddar<sup>c</sup>, Sanjay Kumar<sup>a,\*</sup>

<sup>a</sup> Department of Physics, Jadavpur University, Jadavpur, Kolkata 700032, India

<sup>b</sup> Department of the Geophysical Sciences, The University of Chicago, USA

<sup>c</sup> Experimental Condensed Matter Physics Division, Saha Institute of Nuclear Physics, Kolkata 700064, India

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## ABSTRACT

A new 2D coordination polymer,  $\{[\text{Ni}^{\text{II}}(\text{squarate})(2,2'\text{-bipy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ , [squarate = 3,4-dihydroxycyclobut-3-ene-1,2-dionate, 2,2'-bipy = 2,2'-bipyridine], has been synthesized by using multi-oxygen donor squaric acid ligand and characterized by single crystal X-ray crystallographic and various spectroscopic studies. The structural analysis has revealed that the complex crystallizes in orthorhombic  $P_{bca}$  space group and it has 3D supramolecular structure. Within the complex, the squarato-dianion exhibits unusual  $\mu_{-1,2,3}$  bridging mode with Ni(II) ions and 2D coordination sheets are formed through bridging the metal ions by squarato-anions. The 2D coordination sheets are packed along crystallographic  $b$ -axis and the 2,2'-bipyridyl (blocking ligand) moieties are hanging in the interlamellar spaces between the 2D coordination sheets. These 2D coordination sheets are further bridged by supramolecular  $\pi \cdots \pi$  interactions using 2,2'-bipyridyl ligands leading to the formation of 3D supramolecular framework which acts as a metal-organic supramolecular host (MOSH). During formation of 3D supramolecular structure, 1D supramolecular channels are formed along the crystallographic  $c$ -axis. The guest water molecules get stability within such supramolecular channels through hydrogen bonding interactions with free oxygen atoms of bridging squarate ions. The thermal study indicates that the complex decomposes in three steps. The variable temperature magnetic measurements suggest that the complex is antiferromagnetic in nature. The complex exhibits solid-state photoluminescence spectra at room temperature due to  $\pi\text{-}\pi^*/n\text{-}\pi^*$  transition of the squarate and 2,2'-bipyridine ligands. The present study points to the squarato-bridged metal complexes as unique model system to carry out the study on different bridging modes exhibited by the ligand.

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## 1. Introduction

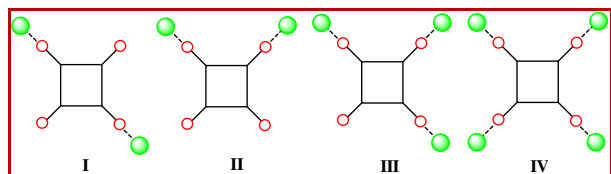
In the recent past, the rational design and synthesis of coordination polymers have received paramount attention not only due to their aesthetical beautiful architectures and topologies but also for their several potential functional properties such as gas and solvent adsorption, catalysis, magnetism, ferroelectricity, nonlinear optical activity, optical sensing etc. [1–15]. The structural topology of coordination polymers can be tuned by judicious selection of parameters like stereo-electronic preferences of the metal ions, spatial disposition of binding sites within the ligands and reaction conditions. Moreover, several weak interactions such as directional hydrogen bonds,  $\pi \cdots \pi$  interactions etc. may also play important role in determining the resultant architecture [16–18].

The ordered arrangement of paramagnetic metal centers within such coordination network allows us to design and synthesize novel magnetic materials such as ferromagnetic, ferrimagnetic, antiferromagnetic, canted-antiferromagnetic and spin glass systems [19–30]. It is well established that the propagation of magnetic exchange interaction within coordination polymers is greatly influenced by the nature of binding sites of ligands attached with metal centers and obviously on the coordination mode of the bridging ligands [31,32]. The oxygen donor based ligands such as carboxylates have widely used to design several types of magnetic materials. Besides, the multi oxygen donor ligands like rhodizionate, croconate and squarate are highly attractive for designing the metal clusters and coordination polymers [33–36]. These ligands have multi-oxygen donor sites around a planar-aromatic motif and thus they can exhibit different binding aptitudes with metal ions.

Here, we have used squaric acid as the bridging ligand. Due to its good donor ability offered by its four oxygen atoms, presence of extensive delocalized  $\pi$ -electrons, highly symmetrical, cyclic

\* Corresponding author. Tel.: +91 9831115427; fax: +91 33 2414 6584.

E-mail address: [kumars@phys.jdvu.ac.in](mailto:kumars@phys.jdvu.ac.in) (S. Kumar).



**Scheme 1.** Different bridging mode of squarate dianion.

shape and the stable aromatic character it has been attracted to several research groups. And, thus in last few years, a large number of discrete poly-nuclear and coordination polymers with diverse structural motifs have been synthesized using Squaric acid [37–46]. The different bridging modes exhibited by the squarate (Scheme 1) are: bridging *bis*- ( $\mu_{-1,2}$  and  $\mu_{-1,3}$ ), *tris*- ( $\mu_{-1,2,3}$ ) and *tetra-kis-monodentate* ( $\mu_{-1,2,3,4}$ ) that leads to the formation of bridged metal complexes with different extents of nuclearity and dimensionality. It is noteworthy that the binding modes of squarate dianion in the metal complexes are mainly governed by the structure and geometry of the blocking ligands coordinated to the central metal ions as well as the reaction conditions.

According to literature survey, the  $\mu_{-1,2}$  and  $\mu_{-1,3}$  bridging modes are most common [37–43], only in few cases  $\mu_{-1,2,3,4}$  bridging mode have been found [13,24,31,44,52]. The sole example of  $\mu_{-1,2,3}$  bridging pattern of squarate-dianion in a tri-nuclear Cu(II) complex has been reported by Vicente et al. [46]. In this endeavor, we are going to report a new 2D coordination polymer formed by using unusual  $\mu_{-1,2,3}$  bridging mode of squarate-dianion with Ni(II) and the blocking 2,2'-bipyridyl ligand. The structural analysis reveals that the blocking 2,2'-bipyridyl moieties are hanging in the interlamellar space between 2D coordination sheets. The thermal and photoluminescence properties of the complex have been studied. The variable temperature magnetic measurements indicate that the complex is antiferromagnetic in nature.

## 2. Experimental

### 2.1. Materials and methods

Nickel(II) nitrate, hexahydrate; 2,2'-bipyridine; 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) and sodium carbonate were purchased from Merck chemical company. All other chemicals were AR grade and used without further purification. The elemental analysis (C, H, N) was carried out using a Perkin-Elmer 240C elemental analyzer. The thermal analysis was carried out using a Mettler Toledo TGA-DTA 85 thermal analyzer under a flow of dinitrogen ( $30 \text{ ml min}^{-1}$ ). The sample was heated at a rate of  $5 \text{ }^\circ\text{C min}^{-1}$  with inert alumina as a reference. The IR spectra of the sample were recorded on Nicolet Impact 410 spectrometer between 400 and  $4000 \text{ cm}^{-1}$ , using the KBr pellet method. The photoluminescence spectra were recorded by Shimadzu RF-5301PC spectrophotometer. The magnetization measurements were performed using a superconducting quantum interference device vibrating sample magnetometer (Quantum Design SVSM, USA) over a wide temperature range of 3–300 K. The experimental susceptibility data were corrected for underlying diamagnetism by use of tabulated Pascal's constants.

### 2.2. Synthesis of the complex

0.5 mmol squaric acid (0.05703 g) was dissolved in 10 ml distilled water and neutralized by aqueous solution of sodium carbonate to adjust the pH at 8.0. The nickel(II) nitrate,

hexahydrate (0.2908 g, 1.0 mmol) was dissolved in 5 ml distilled water and added to the previous solution. The resultant mixture was stirred at room temperature for 15 min. Then, 10 ml methanolic solution of 2,2'-bipyridine (0.156 g, 1.0 mmol) was added to the previous solution and stirred for another 1 h. The whole mixture was then refluxed for 2 h at  $90 \text{ }^\circ\text{C}$ . It was then allowed to cool to room temperature, the blue precipitate was filtered off and light blue colored filtrate was kept in undisturbed condition. After few days, the block shaped greenish blue colored crystals suitable for single crystal X-ray structural study were obtained and these were separated and dried. Yield 72%. *Anal. Calc.* for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{NiO}_6$ : C, 46.2; H, 2.5; N, 7.7. *Found:* C, 46.5; H, 2.4; and N, 7.5%. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu$  (O–H) stretching  $3445 \text{ (m)}$ ;  $\nu$  (CO)  $1506 \text{ (m)}$ ,  $1524 \text{ (s)}$ ,  $1483 \text{ (s)}$  and  $1445 \text{ (w)}$ .

### 2.3. Crystallographic data collection and refinement

Suitable single crystal of the complex was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The structure was solved by Patterson method using SHELXS-97. The subsequent difference Fourier synthesis and least square refinement revealed the positions of the non-hydrogen atoms. The non-hydrogen atoms were refined with independent anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atoms. The successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations have been carried out using SHELXS-97 [47], SHELXL-97 [48], PLATON-99 [49], ORTEP-32 [50] and WINGX system Ver-1.64 [51]. The data collection and structure refinement parameters and crystallographic data for the complex are given in Table 1. Some selected bond lengths, bond angles and non-covalent interaction parameters are presented in Table 2.

**Table 1**  
Crystallographic data and refinement parameters of complex.

Crystal data	
Formula	$\text{C}_{14}\text{H}_9\text{N}_2\text{NiO}_5, \text{H}_2\text{O}$
Formula weight	362.97
Crystal system	orthorhombic
Space group	$P_{bca}$ (No. 61)
$a$ (Å)	12.774(5)
$b$ (Å)	16.818(6)
$c$ (Å)	12.140(5)
$V$ (Å <sup>3</sup> )	2608.1(17)
$Z$	8
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.833
$\mu$ (Mo $K\alpha$ ) (mm)	1.525
$F(000)$	1464
Crystal size (mm)	$0.08 \times 0.08 \times 0.40$
Data collection	
$T$ (K)	100
$\lambda$ (Å)	Mo $K\alpha$ 0.71073
$\theta$ min–max (°)	2.4–25.3
Dataset	–15;12; –19;20; –14;13
Total	12353
Unique data	2363
$R_{\text{int}}$	0.194
Observed data [ $I > 2.0\sigma(I)$ ]	1088
Refinement	
Parameters refined	209
$R$	0.0726
$wR_2$	0.1516
$S$	0.80
Minimum and maximum resd. density [ $\text{e}/\text{\AA}^3$ ]	–0.75, 1.40

$$w = 1/[s^2(\text{Fo}^2) + (0.0949P)^2] \text{ where } P = (\text{Fo}^2 + 2\text{Fc}^2)/3.$$

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