

# Cation–anion interactions via hydrogen bonding; synthesis, characterization and single crystal X-ray structure of $[\text{Cu}(\text{phen})_3](1,3\text{-benzenedisulphonate})\cdot 7\text{H}_2\text{O}$



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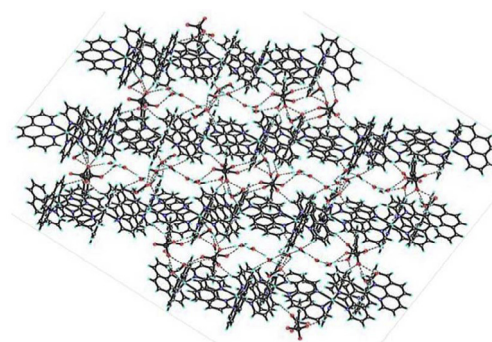
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## HIGHLIGHTS

- Synthesis of a new copper(II) complex,  $[\text{Cu}(\text{phen})_3](1,3\text{-C}_6\text{H}_4(\text{SO}_3)_2)\cdot 7\text{H}_2\text{O}$ .
- Complex has been characterized by X-ray crystallography and spectroscopic techniques.
- Non-covalent interactions like hydrogen bonding,  $\pi\text{-}\pi$ , anion– $\pi$ , etc. stabilize the crystal lattice of this inorganic salt.

## GRAPHICAL ABSTRACT

Cation–anion interactions via hydrogen bonding.



## ARTICLE INFO

### Article history:

Received 10 February 2014

Received in revised form 14 April 2014

Accepted 14 April 2014

Available online 24 April 2014

### Keywords:

Phenanthroline

Non-covalent interactions

Spectroscopic techniques

Single crystal X-ray

## ABSTRACT

A new copper(II) complex,  $[\text{Cu}(\text{phen})_3](1,3\text{-benzenedisulphonate})\cdot 7\text{H}_2\text{O}$ , has been synthesized by reacting hydrated cupric chloride with phenanthroline (*phen*) and disodium salt of 1,3-benzenedisulphonate in ethanol–water mixture. It has been characterized on the basis of elemental analysis, spectroscopic techniques (FT-IR, UV-visible, EPR), thermogravimetric analyses and single crystal X-ray structure determination. A detailed packing analysis has revealed the existence of non-covalent interactions which stabilize the crystal lattice.

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## Introduction

It is well recognized that non-covalent interactions play a very important role in our daily life through their involvement in interactions of metal complexes with DNA, chemical sensors, gene

activation, oxygen transport and catalysis [1–6]. Non-covalent interactions involving  $\pi$ -systems play crucial role in different areas of modern chemistry, from materials design to molecular biology [7]. Structural investigations, mostly fortuitously, can lead to unexpected supramolecular structures due to the cooperative effect of multiple non-covalent interactions, in addition to metal coordination.

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In addition, a number of other supramolecular interactions involving aromatic moieties i.e. C–H... $\pi$ ,  $\pi$ – $\pi$  (stacking), cation– $\pi$ , anion– $\pi$  and lone pair– $\pi$  [8–10] interactions can lead to strong cooperativity effects [11] to build solid state networks [12,13].

Great attention has been paid to organosulphonates as a consequence of their longstanding applications as surfactants, dyes, fuels, lubricant detergents, antioxidants, potential liquid crystalline and non-linear optical materials [14–17]. The activity of these organosulphonates is enhanced if we made coordination of these organosulphonates with metal centers. Such coordination can impart useful properties like optical, electrical, catalytic and second sphere interactions to the receptor molecule which are quite helpful in determining the receptor molecule–anion association [18–21]. In this work, we explored the supramolecular chemistry of copper *phen* based coordination complexes i.e.  $[\text{Cu}(\text{phen})_3]^{2+}$  or  $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$  (analogous to  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  [22]) in continuation of our research interest in metal–*phen* based supramolecular assemblies [23–28]. Complex cation  $[\text{Cu}(\text{phen})_3]^{2+}$  fulfills all the requirements to be a good binding agent [29] i.e. (i) it has doubly positive charged cation for electrostatic interactions, (ii) coordinated *phen* contains 8 C–H groups, that can act as hydrogen-bond donor groups, and (iii) it has a stable structural framework. All these donor groups (8 per ligand) can facilitate interactions with properly oriented negatively charged oxygen atoms of organosulphonate groups and hence can result in a donor–acceptor complex involving second sphere coordination via C–H...O hydrogen bonds [30]. Such structural studies can be very interesting in the context of their formation, thermodynamic stability, association patterns involving different coordination mode(s) and packing patterns that can result in the crystalline phase.

Thus in this paper, synthesis, characterization and single crystal X-ray structure of newly synthesized copper(II) complex,  $[\text{Cu}(\text{phen})_3](1,3\text{-benzenedisulphonate})\cdot 7\text{H}_2\text{O}$  is reported. To the best of our knowledge, this is first crystal structure of a compound containing  $[\text{Cu}(\text{phen})_3]^{2+}$  and arene-disulphonate anion.

## Experimental

### Materials and physical measurements

Analytical grade reagents were used throughout this work without any further purification. Carbon, hydrogen and nitrogen were measured micro-analytically by an automatic Perkin Elmer 2400 CHN elemental analyzer and copper was determined gravimetrically [31]. FT-IR spectra were recorded as KBr pellets with PERKIN ELMERSPECTRUM RXFT-IR system. Electronic spectrum was recorded in water using a HITACHI 330 SPECTROPHOTOMETER. The thermogravimetric analysis (TGA) was conducted with a SDT Q600 instrument. The sample contained in alumina pan was heated from 33 to 1000 °C at a constant rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere with flow rate of 10 mL/min. X-band EPR measurements were carried out on a Bruker ELEXSYS 500 spectrometer with a maximum available microwave power of 200 mW and equipped with a super-high-Q resonator ER-4123-SHQ. For Q-band studies, EPR spectra were recorded on a Bruker EMX system equipped with an ER-510-QT resonator and a ER-4112-HV liquid helium cryostat. The magnetic field was calibrated by a NMR probe and the frequency inside the cavity was determined with a Hewlett-Packard 5352B microwave frequency counter. Computer simulation: WIN-EPR-Simfonia, version 1.5, Bruker Analytische Messtechnik GmbH).

### Synthesis of $[\text{Cu}(\text{phen})_3](1,3\text{-benzenedisulphonate})\cdot 7\text{H}_2\text{O}$ ; 1

1.71 g (0.01 mol)  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  was dissolved in 20 mL of ethanol taken in 100 mL round bottom flask. Added to it, a warm ethanolic

solution of *phen* 3.96 g (0.02 mol) with stirring. To the above warm solution, an aqueous solution of disodium salt of 1,3-benzenedisulphonic acid, 2.82 g (0.01 mol) was added. The resulting solution was refluxed for 30 min. After cooling the mixture to ambient temperature a light green product was obtained. It was filtered through a fine filter paper to obtain a bluish green clear filtrate and it was put aside at room temperature for evaporation. After two days we obtained mixture of bluish green crystals along with light green microcrystalline product. After drying in air, bluish green crystals (Fig. S1) were separated manually from the mixture of crystals. The newly synthesized **1** is freely soluble in methanol, partially soluble in water and decomposes at 303 °C. Anal. Calcd. (%): C, 52.17; H, 4.34; N, 8.69; S, 6.62; Cu, 6.57. Found (%): C, 52.37; H, 4.18; N, 8.92; S, 6.78; Cu, 6.66.

### Single crystal X-ray diffraction

A suitable single crystal of **1** was mounted on glass fiber and used for data collection. Data were collected with a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by applying the  $\omega$ -scan method. The data were processed with APEX2 [32] and corrected for absorption using SADABS [33]. The structure was solved by direct methods using SIR97 [34] revealing positions of all non-hydrogen atoms. These atoms were refined on  $F^2$  by a full matrix least-squares procedure using anisotropic displacement parameters [35], except for O7W and O8W for solvent disordered patterns. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.5 times those of the respective atom. Final  $R(F)$ ,  $wR(F^2)$  and goodness of fit agreement factors, details on the data collection and analysis can be found in Table 1.

## Results and discussion

### Synthesis

Complex **1** was obtained by refluxing (30 min) a mixture of ethanolic solution made out of cupric chloride dihydrate and *phen* with aqueous solution of disodium 1,3-benzenedisulphonate in appropriate stoichiometric ratio as shown in Scheme 1. When the solution reached to ambient temperature after stopping the

**Table 1**  
Crystal data, data collection and refinement details of **1**.

Chemical formula	$\text{C}_{42}\text{H}_{42}\text{N}_6\text{O}_{13}\text{S}_2\text{Cu}$
M/g mol <sup>-1</sup>	966.48
T (K)	100
$\lambda$ (Å)	0.71073
Cryst. system	Monoclinic
Space group	$\text{P2}_1/\text{n}$
$a/\text{Å}$	12.930(2)
$b/\text{Å}$	16.057(3)
$c/\text{Å}$	20.483(3)
$\beta$ (deg)	90.224(2)
$V$ (Å <sup>3</sup> )	4252.3(12)
Z	4
$\rho$ (g cm <sup>-3</sup> )	1.510
$\mu$ (mm <sup>-1</sup> )	0.686
Unique reflections	26,337
R (int)	0.038
GOF on $F^2$	1.033
<sup>a</sup> R1 [ $I > 2\sigma(I)$ ]	0.056
<sup>b</sup> wR2 [ $I > 2\sigma(I)$ ]	0.140

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR(F^2) = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum wF^4}]^{1/2}$$

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