Journal of Molecular Structure xxx (2014) xxx-xxx



Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstruc

Cation–anion interactions via hydrogen bonding; synthesis, characterization and single crystal X-ray structure of $[Cu(phen)_3](1,3-benzenedisulphonate).7H_2O$

R.P. Sharma^{a,*}, S. Kumar^a, A. Saini^a, P. Venugopalan^a, A. Rodríguez-Diéguez^b, J.M. Salas^{b,*}

^a Department of Chemistry, Panjab University, Chandigarh, India ^b Departmento de Quimica Inorganica, Universidad de Granada, Campus Fuenteneva, s/n, E-18071, Granada, Spain

HIGHLIGHTS

- Synthesis of a new copper(II) complex, [Cu(phen)₃](1,3-C₆H₄(SO₃)₂)·7H₂O.
- Complex has been characterized by X-ray crystallography and spectroscopic techniques.
- Non-covalent interactions like hydrogen bonding, π–π, anion–π, etc. stabilize the crystal lattice of this inorganic salt.

G R A P H I C A L A B S T R A C T

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 xxxx

Keywords: Phenanthroline Non-covalent interactions Spectroscopic techniques Single crystal X-ray

ABSTRACT

A new copper(II) complex, $[Cu(phen)_3](1,3-benzenedisulphonate) \cdot 7H_2O$, 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.

© 2014 Elsevier B.V. All rights reserved.

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

* Corresponding authors. Tel.: +91 0172 2534433; fax: +91 0172 2545074. E-mail addresses: rpsharma@pu.ac.in (R.P. Sharma), jsalas@ugr.es (J.M. Salas).

http://dx.doi.org/10.1016/j.molstruc.2014.04.046 0022-2860/© 2014 Elsevier B.V. All rights reserved. activation, oxygen transport and catalysis [1–6]. Non-covalent interactions involving π -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.

In addition, a number of other supramolecular interactions involving aromatic moieties i.e. $C-H...\pi$, $\pi-\pi$ (stacking), cation- π , anion- π and lone pair- π [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 organosulphates 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. $[Cu(phen)_3]^{2+}$ or $[Cu(phen)_2(H_2O)_2]^{2+}$ (analogus to $[Cu(en)_2(H_2O)_2]^{2+}$ [22]) in continuation of our research interest in metal-*phen* based supramolecular assemblies [23–28]. Complex cation $[Cu(phen)_3]^{2+}$ 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, $[Cu(phen)_3](1,3-benzenedisulphonate)\cdot7H_2O$ is reported. To the best of our knowledge, this is first crystal structure of a compound containing $[Cu(phen)_3]^{2+}$ 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⁻¹ 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 [Cu(phen)₃](1,3-benzenedisulphonate 2).7H₂O; 1

1.71 g (0.01 mol) CuCl₂.2H₂O 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 α radiation (λ = 0.71073 Å) by applying the ω -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 leastsquares 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 disodium1,3-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	C42H42N6O13S2Cu
M/g mol ⁻¹	966.48
T (K)	100
λ (Å)	0.71073
Cryst. system	Monoclinic
Space group	P2 ₁ /n
a/Å	12.930(2)
b/Å	16.057(3)
c/Å	20.483(3)
β (deg)	90.224(2)
V (Å ³)	4252.3(12)
Ζ	4
ho (g cm ⁻³)	1.510
μ (mm ⁻¹)	0.686
Unique reflections	26,337
R (int)	0.038
GOF on F ²	1.033
$^{a}R1 [I > 2\sigma(I)]$	0.056
^b wR2 [$I > 2\sigma(I)$]	0.140

 $R(F) = \Sigma ||F_0| - |F_c||\Sigma||F_0|.$

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

R.P. Sharma et al./Journal of Molecular Structure xxx (2014) xxx-xxx



where as C12H8N2 = phen

Scheme 1. Schematic representation of the synthetic procedure.

refluxing, a light green precipitate was settled at the bottom of the round bottom flask.

The precipitated product so obtained was filtered and the resulting clear filtrate was allowed to stand at room temperature. After two days, a mixture of bluish-green crystals (**B**) and light green microcrystalline (**A**) product was formed. The product mixture was filtered and dried in air. Bluish-green crystals (**Fig. S1**) were manually separated from the mixture of products obtained. Repeated attempts to grow single crystals of light green precipitated product (**A**) were not successful. Elemental analysis of bluish-green crystals indicated the formation of $[Cu(phen)_3](1, 3-benzenedisulphonate) ·7H_2O$ which was further fully characterized by spectroscopic and single crystal X-ray structure determination as reported below.

Infrared spectroscopy

Infrared spectrum of the newly synthesized complex has been recorded in the region of 4000–400 cm⁻¹. Tentative assignments have been made on the basis of earlier reports in literature [36,37]. The broad band at 3381 cm^{-1} was assigned to O–H stretching frequency of water molecule. The stretching band at 3068 cm^{-1} corresponds to aromatic H–C=C group stretch. The peaks at 721 cm⁻¹; δ(C–H) out of plane, 846 cm⁻¹; δ(C=C), 1623, 1652 cm⁻¹(C=C/C=N stretch) were characteristics of *phen*. In the aromatic compounds containing sulphonate groups, the antisymmetric stretching vibrations of the -SO₃ groups were expected in the region $1202 \pm 40 \text{ cm}^{-1}$ and symmetric $-SO_3$ group were expected in the region $1112 \pm 40 \text{ cm}^{-1}$ [38]. The v_{as} (-SO₃) and v_s (-SO₃) bands for **1** appeared at 1190 cm⁻¹ and 1089 cm⁻¹ respectively. The peaks in the region 1000–1100 cm⁻¹ appeared due to internal vibrations in 1,3-benzenedisulphonate. A weak band at 694 cm^{-1} was assigned to $\nu_{(\text{C}-\text{S})}$ stretching. The peak due to $v_{(Cu=0)}$ was absent in the region 500–540 cm⁻¹ indicating that there is no direct Cu—O bond [39]. This means that *phen* forms an octahedral type arrangement around copper atom and 1,3-benzenedisulphonate links to primary coordination sphere via weak hydrogen bonding. FT-IR spectrum of **1** is shown in supplementary material (Fig. S2).

Electronic spectroscopy

An octahedral copper(II) complex is expected to show one broad absorption band in the electronic spectrum due to d-d (t_{2g} to e_g) transition in visible region [40]. The electronic spectrum of **1** recorded in methanol showed an absorption band at 679 nm ($\varepsilon_{max} = 42.80 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) corresponding to d–d transition [41]. The visible spectrum of **1** is shown in Fig. S3. The other absorption bands at 267 nm ($\varepsilon_{max} = 34522 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) correspond to $\pi - \pi^*$ transitions which are characteristic of *phen* moiety as reported in the literature [42].

EPR spectroscopy

The X-band EPR spectra for **1** exhibit near axial symmetry for the g tensor in the DM_s = ±1 region, but an appreciable extent of rhombicity can be detected operating at Q-band (Fig. 1). The main components of the g tensors obtained from the fit of the experimental room temperature spectrum are: g_1 = 2.261, g_2 = 2.091 and g_3 = 2.075. These values are typical of Cu(II) ions in distorted octahedral environments which is in good agreement with the structural characteristics of the CuN₆ chromophore [43,44]. Moreover, the lowest g deviates appreciably from the free electron value (g_0 = 2.0023) indicating a $dX^2 - y^2$ ground state, that corresponds to an axially elongated octahedral environment for Cu(II) ions.

The absence of well resolved hyperfine lines contrast with the structurally monomeric nature of the compound. The collapse of the hyperfine structure usually indicates the presence of long

3

R.P. Sharma et al./Journal of Molecular Structure xxx (2014) xxx-xxx



Fig. 1. Q-band EPR powder spectrum of **1** registered at room temperature. Dotted line is the best fit; see text for the fitting parameters.

range exchange coupling. In this sense, the calculated G parameter is 3.1 [44,45], which indicates that the g values obtained from experiment are not equal to the molecular ones. This fact implies the averaging by exchange coupling of the signal corresponding to magnetically non-equivalent copper sites. Moreover, when the temperature is lowered down to 5 K, a weak displacement of the perpendicular component was observed on the X-band spectra simultaneously to the expected signal narrowing (Fig. 2). This behavior can be attributed to a small change in the magnitude of the superexchange coupling because of the thermal expansion of the crystal structure [46]. Thus, in spite of the large distances between copper atoms (shorter distance, 10.762) and the absence of a covalent skeleton connecting them, it can be concluded that weak magnetic interactions are operative in this compound. The hydrogen bonding and/or the π -stacking of the *phen* rings can provide the necessary exchange pathway (vide infra).

Thermogravimetric analysis (TGA)

Thermal studies of **1** were performed under nitrogen atmosphere to study the stability of the complex at elevated temperature. Complex salt when heated from 33 °C to 1000 °C (Fig. 3), showed that it is stable only up to 70 °C. The first weight loss from 70 °C to 120 °C corresponds to the loss of seven water molecules (calcd. = 13.04, found = 12.94%). The resulted anhydrous salt at 130 °C was stable up to 230 °C. The second weight loss (calcd. = 20.52, found = 18.92%) step from 245 °C to 325 °C was due to loss of one *phen* moiety. The third weight loss step (calcd. = 49.06, found = 48.92%) from 325 °C to 575 °C in **1** corresponds to the formation of copper sulphate (loss of two *phen*, one benzene and one sulfur dioxide moieties). The final weight loss







from 575 °C to 1000 °C (calcd. = 10.83, found = 9.20%) corresponds to formation of CuO.

Single crystal X-ray structure determination

The compound crystallizes in the P2₁/n space group pertaining to monoclinic crystal system. The asymmetric unit is formed by one tris(phen)copper(II) cation, one 1,3-benzenedisulphonate anion and seven water molecules of crystallization (Fig. 4).

The coordination geometry around central copper(II) ion is slightly distorted from octahedron because of the geometrical restrictions imposed by the *phen*. The Cu—N bond distances are in agreement with those found in similar compounds of known structures, which are in the range 2.032(3)–2.349(3) Å. The copper atom shows Jahn-Teller distortion, due to this, there are two longer distances in apical positions, 2.313(3) and 2.349(3) Å (see Table 3). All bond lengths of Cu—N(cis) and Cu—N(trans) in the title complex salt fall within the range reported in literature (see Table 2). The bite angle of *phen* ligands i.e. <N—Cu—N in complex salt **1** approx. 76.8° is also closer to that reported in similar compounds (see Table 2 and Table 3).

The structural parameters of sulphonate group (S–O, C–S, <C–S, –O) in **1**, amongst other disulphonate salts also do not show any significant variation (see Table 2).

In crystal lattice, 1,3-benzenedisulphonate and phen groups are held together by a complex three-dimensional network of hydrogen bonds (O–H···O, C–H···O) and π – π stacking interactions as shown in Fig. 5 (hydrogen bonding parameters are given in Table 4). Indeed, the packing pattern can be conceived as a complex network of counter ions interspersed by water molecules and for convenience, it can be described by two types of sheets in which the first cationic one is made of the mononuclear copper(II) entities united by $\pi - \pi$ stacking interactions of 3.385 Å (phen...phen), 3.380 Å (phen...1,3-benzenedisulphonate) and the anionic sheet is constructed through hydrogen bonds involving the 1,3-benzenedisulphonate anions and the water molecules. It is noteworthy that all the seven water molecules of crystallization are extensively O-H...O hydrogen bonded and all of them get involved in multiple ways (two for each water molecules) as shown in Table 4 and Fig. 6.

The SO₃ groups of 1,3-benzenedisulphonate anion and water molecules are involved in a complex 2-dimensional hydrogen bonds network (Fig. 6). In this network, hydrogen bonds are in the range 2.437–2.931 Å. Along *b* axis, the structure can be described by supramolecular sheets generated by hydrogen bonds among 1,3-benzenedisulphonate anions and water molecules.

R.P. Sharma et al./Journal of Molecular Structure xxx (2014) xxx-xxx



Fig. 4. A Perspective view of 1. Thermal ellipsoids are drawn at the 50% probability level. Water molecules and hydrogen atoms are omitted for clarity.

Cation, $X = [Cu(phen)_3]$	Cu—N (axial)	Cu—N (eq.)	cis- <n—cu—n< th=""><th>Trans-<n—cu—n< th=""><th>Ref.</th></n—cu—n<></th></n—cu—n<>	Trans- <n—cu—n< th=""><th>Ref.</th></n—cu—n<>	Ref.
$X \cdot (S_4O_6)S_8$	2.31	2.06	93.8	164.1	[47a]
$X \cdot (BF_4)_2$	2.30	2.04	87.0	170.2	[47a]
$X \cdot Cl_2 \cdot CH_2 Cl_2 \cdot 9H_2 O$	2.26	2.11	77.8	167.2	[47b]
$X \cdot (ClO_4)_2$	2.32	2.03	96.3	169.1	[47c]
$X \cdot (PF_6)$	2.29	2.05	-	_	[47d]
$X \cdot (CF_3SO_3)_2 \cdot 2H_2O$	2.34	2.04	96.2	167.3	[47e]
$X \cdot (C(CN)_3)_2$	2.22	2.10	93.4	171.1	[47f]
$X \cdot (1,3C_6H_4(SO_3)_2 \cdot 7H_2O$	2.34	2.03	95.1	166.6	This work
Anion, Y = aromatic disulphonate	C—S	S-0	<c—s—0< td=""><td></td><td></td></c—s—0<>		
K ₂ ·Y	1.79	1.45	108.6		[48a]
[Pot·tetramethyl ammoniumsalt]·Y	1.79	1.42	104.2		[48a]
$[Zn(C_4H_{12}N_2)_2(H_2O_2)]\cdot Y$	1.77	1.44	105.7		[48b]
[Ag(4,4'-bipy)H ₂ O)]·Y	1.57	1.42	109.3		[48c]
$[Ag(NH_3)_2]_4 \cdot Y$	1.79	1.45	104.8		[48d]
$[Mg(H_2O)_6] \cdot Y$	1.77	1.46	106.3		[48e]
[Cu(phen) ₃]·Y	1.78	1.45	105.4		This work

Table 3

Table 2

Structural parameters in 1.

Bond lengths (Å) Cu1–N1C Cu1–N8A Cu1–N1A	2.032(3) 2.039(3) 2.047(3)	Cu1—N8B Cu1—N8C Cu1—N1B	2.052(3) 2.313(3) 2.349(3)
Bond angles (°) N1CCu1N8A N1CCu1N1A N8ACu1N8B N8ACu1N8B N1ACu1N8B N1CCu1N8C N8ACu1N8C	$\begin{array}{c} 167.39(10)\\ 94.09(11)\\ 81.38(11)\\ 92.79(10)\\ 95.13(10)\\ 161.42(10)\\ 76.85(10)\\ 92.42(10) \end{array}$	N1A—Cu1—N8C N8B—Cu1—N8C N1C—Cu1—N1B N8A—Cu1—N1B N1A—Cu1—N1B N8B—Cu1—N1B N8C—Cu1—N1B	101.25(10) 97.11(10) 98.65(10) 92.71(10) 85.10(10) 76.81(10) 172.38(9)

These anionic sheets (Fig. 7) are interspersed with cationic layers formed by mononuclear copper (II) entities united by $\pi-\pi$ stacking and sulphonate anion- π interactions. This cationic layer has stacking interactions among the "*phen* ligands" with a distance of 3.385 Å. The aromatic ring pertaining to 1,3-benzenedisulphonate anion posseses stacking interaction with the "*phen*" pertaining to the mononuclear copper (II) unit with a distance of 3.380 Å (Fig. 7). These are the interactions generating the three-dimensional supramolecular network in **1** and responsible for the stabilization of the crystal structure of this compound.

A note on the structural stability of a variety metal complexes of phen based on our experience [23-28] put forwards the importance of cooperative interplay of weak interactions in these family of complexes. Though an $\dots \pi$ and $\pi \dots \pi$ interactions lie at the bottom of the energetics of weak interactions for lattice stabilization, their synergistic behavior contribute significantly to the overall stability of the observed crystal packing. For example, in lattice stability of [Co(phen)₂CO₃]⁺ complexes, the crystal structure features the synergistic directional bonding interactions including cation to anion C–H···X (X = Cl, Br of the anion) bonds along with cation $Cl \cdots \pi$ and cation to cation $\pi \cdots \pi$ stacking interactions [23,24,26]. In the case of *phen* metal complexes, in which the counter anion is predominantly organic (such as arylcarboxylates), the layer formation (as observed here also) is also dictated by non-covalent interactions of the type O-H...O and C-H...O (carboxylate/water/carbonato) along with subtitle interplay of $\pi \cdots \pi$, C–H··· π and anion··· π interactions. In nutshell, in this family of phen metal complexes, though there are lattice stabilizing O/ N-H···O/N hydrogen bonding possibilities (including that from occluded water).

R.P. Sharma et al./Journal of Molecular Structure xxx (2014) xxx-xxx



Fig. 5. A view along *b* axis of supramolecular sheets generated by hydrogen bonds in 1.

Table 4Hydrogen – bonding parameters in 1 (Å, °).

D—H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	(<dha)< td=""><td>$d(D{\cdots}A)$</td></dha)<>	$d(D{\cdots}A)$
01W—H11W…031d	0.885	2.022	165.95	2.888
01W—H12W…0.13D	0.794	2.066	169.53	2.851 ^a
02W-H21W01W	0.834	1.970	169.88	2.794
02W-H22W03W	0.753	2.017	174.68	2.767
03W-H31W0.13D	0.701	2.174	169.79	2.866
03W-H32W0.32D	0.767	2.032	169.43	2.790 ^a
04W—H41W…0.5W	1.009	2.017	122.01	2.691
04W—H42W 0.6W	0.825	1.948	164.95	2.753 ^b
06W-H61W0.2W	0.883	1.893	168.12	2.762 ^c
06W-H62W05W	0.684	2.153	178.47	2.837
05W-H51W012D	0.938	1.933	167.75	2.857
05W-H52W033D	0.935	1.820	170.63	2.746 ^d
07W-H71W04W	0.842	2.118	161.26	2.927 ^e
07W-H72W011D	0.846	2.078	154.88	2.866 ^e

Symmetry transformations used to generate equivalent atoms:

^a [-x + 5/2, y - 1/2, -z + 1/2].

```
<sup>b</sup> [-x+2, -y+1, -z].
```

^c [x - 1/2, -y + 1/2, z - 1/2].

^d [-x + 2, -y, -z].

^e
$$[x - 1, y, z]$$
.



Fig. 6. The 2-D network of hydrogen bonding $(O-H \cdots O)$ interactions involving 1,3-benzenedisulphonate moiety of the anion and six water molecules that generates a cyclic arrangement.



Fig. 7. A view to the plane showing π - π stacking and anion- π interactions between 1,3-benzenedisulphonate anion in the cationic sheet in **1** along "**c**" **axis**. Hydrogen atoms are omitted for clarity.

Conclusion

A new copper(II) complex salt [Cu(phen)₃](1,3-benzenedisulphonate)·7H₂O has been synthesized and structurally characterized for the first time. A detailed packing analyses has revealed that non-covalent interactions like hydrogen bonding, π – π , anion– π , etc. stabilize the crystal lattice of this inorganic salt. The involvement of large number of water of crystallization through O–H···O hydrogen bonding has a profound influence in the layer formation and overall stability of the crystal lattice.

Acknowledgments

One of us (RPS) acknowledges the financial support of UGC, New Delhi (India) vide grant no. F. 40-60/2011 (SR) and the Junta de Andalucía FQM-3705 (Spain). Authors gratefully acknowledge the help of Prof. L. Lezama, Basque Country University, Bilbao (Spain) for EPR studies.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the reported structure have been deposited with the Cambridge

Crystallographic Data Centre as supplementary publication. CCDC reference number for the structure is 983322. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44 1223 336-033; e-mail, deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.molstruc.2014.04.046.

References

- [1] M. Muraki, Protein Pept, Lett. 9 (2002) 195.
- [2] J. Liu, T. Zhang, T. Lu, J. Inorg. Biochem. 91 (2002) 269.
- [3] J. Liu, T. Zhang, Dalton Trans. (2003) 114.
- [4] Z. Cao, K. Murayama, K. Aoki, Anal. Chim. Acta 448 (2001) 47.
- [5] N. Lanigan, X. Wang, Chem. Commun. 49 (2013) 8133.
- [6] J. Anastassopoulou, T. Theophanides, NATO ASI Ser. C. 459 (1995) 209.
- [7] E.A. Meyer, R.K. Castellano, F. Diederich, Angew. Chem. Int. Ed. 42 (2003) 1210.
- [8] J.M. Lehn, Supramolecular Chemistry, VCH publication, Weinheim, 1995.
- [9] J.W.G. Bloom, S.E. Wheeler, Angew. Chem. Int. Ed. 50 (2011) 7847.
- [10] S.-I. Noro, K. Fukuhara, K. Sugimoto, Y. Hijikata, K. Kuboab, T. Nakamura, Dalton. Trans. 42 (2013) 11100.
- [11] D. Escudero, A. Frontera, D. Quiñonero, P.M. Deyà, Chem. Phys. Lett. 45 (2008) 257.
- [12] J.W. Steed, D.R. Turner, K.J. Wallace, Core Concepts in Supramolecular Chemistry and Nanochemistry, John Wiley & Sons, Ltd., Chichester, 2007. p. 194
- [13] H. Xu, X. Zhang, J. Sun, S. Cui, Nanosciences and Nanotechnologies, Supramolecular Chemistry, Encyclopedia of Life Support Systems.
- (a) R.P. Sharma, A. Singh, P. Venugopalan, A.R. Diéguez, J.M. Salas, J. Mol. Struct. 1033 (2013) 208;
 - (b) R.P. Sharma, A. Saini, P. Venugopalan, V. Ferretti, J. Mol. Struct. 1015 (2012) 166;
 - (c) R.P. Sharma, A. Saini, S. Singh, P. Venugoplalan, V. Ferretti, J. Mol. Struct. 969 (2010) 128;
 - (d) R.P. Sharma, R. Bala, R. Sharma, J. Raczynskab, U. Rychlewska, J. Mol. Struct. 738 (2005) 247.
- [15] Q. Huo, D. Margolese, U. Ciesla, D. Demuth, P. Feng, T. Gier, P. Sieger, A. Firouzi, B. Chmelka, F. Schuth, G. Stucky, Chem. Mater. 6 (1994) 1176.
- [16] S. Marder, J. Perry, C. Yakymyshyn, Chem. Mater. 6 (1994) 1137.
- V. Russell, M. Etter, M. Ward, Chem. Mater. 6 (1994) 1206.
- [18] D. Natale, J.C. M-Rivas, Chem. Commun. (2008) 425.
- [19] P.D. Beer, E.J. Hayes, Coord. Chem. Rev. 204 (2003) 167.
- [20] S.L. Tobey, B.D. Jones, E.V. Anslyn, J. Am. Chem. Soc. 125 (2003) 4026.
- [21] B. Verdejo, J. Aguilar, A. Domenech, C. Miranda, P. Navarro, H.R. Jimenez, C. Soriano, E. Garcia-Espana, Chem. Commun. (2005) 3086.
- [22] R.P. Sharma, A. Saini, P. Venugopalan, S. Khullar, S. Mandal, Polyhedron 56 (12) (2013) 34.
- [23] R.P. Sharma, A. Singh, P. Brandão, V. Félix, P. Venugopalan, Polyhedron 30 (2011) 2759.
- [24] R.P. Sharma, A. Singh, P. Venugopalan, W.T.A. Harrison, J. Mol. Struct. 996 (2011) 82.

- [25] R.P. Sharma, A. Singh, P. Venugopalan, V. Ferretti, J. Fluorine Chem. 132 (2011) 453
- [26] R.P. Sharma, A. Singh, P. Venugopalan, W.T.A. Harrison, J. Mol. Struct. 994 (2011) 6.
- [27] A. Singh, R.P. Sharma, T. Aree, P. Venugopalan, CrystEngComm. 15 (2013) 1153.
- [28] (a) R.P. Sharma, A. Singh, T. Aree, P. Venugopalan, J. Chem. Sci. 122 (2010) 1; (b) R.P. Sharma, A. Saini, S. Singh, P. Venugopalan, W.T.A. Harrison, J. Fluorine Chem. 131 (2010) 456.
- [29] C.R. Bondy, P.A. Gale, S.J. Loeb, J. Am. Chem. Soc. 126 (2004) 5030.
- [30] (a) G. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, Oxford, 1999; (b) Fitzsimons, M. Lavelle, J.F. Gallagher, Acta Cryst. C55 (1999) 472;
- (c) T. Liu, Z.-W. Wang, Y.-X. Wang, Z.-P. Xie, Acta Cryst. E63 (2007) m2027.
 [31] B.S. Furmiss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell,
- Vogel'sTextbook of Practical Organic Chemistry Including Quantitative Organic Analysis, fourth ed., Longman Group Ltd., London, 1978. p. 802.
- [32] Bruker Apex2, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
- [33] G.M. Sheldrick, SADABS, Program for Empirical Adsorption Correction, Institute for Inorganic Chemistry, University of Gottingen, Germany, 1996.
- A. Altomare, M.C. Burla, M. Camilla, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
- [35] G.M. Sheldrick, SHELX97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [36] J. Bellamy, second ed., The Infrared Spectra of Complex Molecules, vol. 2, Chapman & Hall, London, 1980.
- [37] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., John Wiley & Sons, New York, USA, 1997.
- S.M. Holmes, S.G. Mckinley, G.S. Girolami, Inorg. Synth. 33 (2002) 91.
- [39] Z.H. Chohan, H.A. Shad, F.H. Nasim, Appl. Organometal. Chem. 23 (2009) 319.
- [40] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advance Inorganic Chemistry, sixth ed., Wiley-Interscience publication, USA, 1999.
- [41] (a) J.M. Seco, M.J.G. Garmendia, M. Quiros, J. Coord. Chem. 53 (3) (2002) 345; (b) A.T. Baker, J. Chem. Educ. 75 (1998) 98.
- [42] C. Detoni, N.M.F. Carvalho, R.O.M.A. deSouza, D.A.G. Aranda, Q.A.C. Antunes, Catal. Lett. 129 (2009) 79.
- [43] B.J. Hathaway, Coord. Chem. Rev. 41 (1982) 423.
- [44] J.V. Folgado, W. Henke, R. Allman, H. Stratemeier, D. Beltran-Porter, T. Rojo, D. Reine, Inorg. Chem. 29 (1990) 2035.
 - [45] B.J. Hathaway, D. Billing, Coord. Chem. Rev. 5 (1970) 143.
 - [46] I. Unamuno, J.M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, R. Calvo, T. Rojo, Inorg. Chem. 37 (1998) 6452.
 - [47] a) S. Youngme, N. Wannarit, C. Pakawatchai, N. Chaichit, E. Somsook, U. Turpeinen, I. Mutkainen, Polyhedron 26 (2007) 1459; b Jian, F. Fang, Lin, J. Hua, Zhang, S. Sheng, Chienese J. Chem. 19 (2001) 772; c) O.P. Anderson, J. Chem. Soc. Dalton Trans. (1973) 1237; d) J.M. Seco, M.J. Garmendia, M. Quiros, J. Coord. Chem. 55 (2002) 345;
 - e) J. Sletten, M. Julve, Acta Chem. Scand. 53 (1999) 631;
 - (f) I. Potocnak, M. Pohlova, C. Wagner, L. Jager, Acta Cryst. E58 (2002) 595.
 - [48] a) N. Nagel, P. Eller, H. Bock, Acta Cryst. B52 (1996) 562;

 - b) Z.X. Lian, Hao-Hong, Acta Cryst. E63 (2007) m731; c) X.F. Zheng, L.G. Zhu, Polyhedron 30 (2011) 666;

 - d) L.W. Zhang, S. Gao, S. Weng, Ng. Acta Cryst. E67 (2011) m1780;
 - e) J. Cai, C.H. Chen, C.-Z. Liao, X.L. Feng, X.M. Chen, Acta Cryst. B57 (2001) 520.