

# Preparation, Characterization, X-Ray Structure Determination and Solution Properties of some Novel Copper(I) Bisulfate and Sulfate Salts and Their Stable Derivatives

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Two highly unstable copper(I) salts, *i. e.* copper(I) bisulfate tetraacetonitrile,  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ , and dicopper(I) sulfate octaacetonitrile,  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ , and their stable derivatives with 2,9-dimethyl-1,10-phenanthroline (DMPhen) have been prepared in pure form and characterized by elemental, spectral and chemical analysis. Single-crystal X-ray studies of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  and its derivative  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  have been carried out. The solution behavior of both of these salts and their derivatives have been investigated using UV/Vis, IR,  $^{63}\text{Cu}$  NMR spectroscopy and molar conductance in a number of non-aqueous solvents. Furthermore, a simple method for the preparation of  $\text{Cu}_2\text{SO}_4$  is presented.

**Key words:** Acetonitrile, Copper(I) Salts, Copper(I) Bisulfate, Copper(I) Sulfate, UV/Vis Spectra, Molar Conductance,  $^{63}\text{Cu}$  NMR

## Introduction

Highly ionic copper(I) salts (salts with very large non-coordinating anions and devoid of ion-association in solution) are known to be unstable in the solid form as well as in the solution state [1, 2]. The stability of copper(I) complexes depends upon the nature of the anion, the ligands, the neighboring atoms, and considerably upon the choice of solvent. Concentrated copper(I) solutions find applications in the hydrometallurgical purification of copper and silver [2–4], therefore stabilization of copper(I) is an industrially important subject. Some highly ionic copper(I) salts like the tetraacetonitrile copper(I) perchlorate  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  and the related nitrate, tetrafluoroborate and hexafluorophosphate, as well as the more stable bis(2,9-dimethyl-1,10-phenanthroline) copper(I) salts  $[\text{Cu}(\text{DMPhen})_2]^+$  with anions  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{BF}_4^-$  and  $\text{PF}_6^-$ , have been prepared and extensively investigated in solution [5–11]. Whereas *N*-donor ligands stabilize the above copper(I) salts, those with the anion  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{CN}^-$  gain stability from more covalent bonding interactions with the counterions. Such “covalent copper salts” can also form polynuclear species [1, 12–15]. As we are inter-

ested in solid and solution properties of only highly ionic copper(I) salts, we investigated Cu(I) in combination with sulfates as weakly coordinating counterions. Copper(I) bisulfate and copper(I) sulfate are both highly ionic, however, have never been prepared in the solid form [2]. We report here a simple and quick method for the preparation of the acetonitrile solvates  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ ,  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$  and their derivatives with DMPhen as a bidentate ligand, as well as for the solvent-free  $\text{Cu}_2\text{SO}_4$ .

## Experimental Section

All organic solvents were AR grade and obtained from various sources already reported [16]. They were further purified by literature methods [17]. Copper(I) bisulfate tetraacetonitrile and copper(I) sulfate octaacetonitrile were prepared by adopting methods reported by Hathaway *et al.* [5] and Gill *et al.* [18] for the preparation of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  (details are given below).

### Preparation of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$

10.0 g (40.0 mmol) of copper(II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was dissolved in a minimum quantity of hot water (5 mL) containing 3–5 mL of concentrated  $\text{H}_2\text{SO}_4$ . The solution was stirred at 70–80 °C, and 40 mL of acetonitrile

trile was added. Excess of pure copper powder (10–12 g, 99.5 % purity) was then added to the vigorously stirred solution. Completeness of the reaction was indicated when the solution became colorless (occasionally the excess copper metal powder was allowed to settle). The solution was then filtered and cooled at  $-10$  to  $-20$  °C, but no solid separated out. To increase the concentration of the solution, there were two alternatives. One was to concentrate the solution by evaporating the solvent by heating. This method was not preferred because on heating most of the acetonitrile evaporates, thus destabilizing the solution. The second alternative which we followed was to reduce copper(II) to copper(I) by adding increasing amounts of copper(II) sulfate pentahydrate (10 g was added in five installments of 2 g each along with 2–3 g of Cu powder at regular intervals) to the solution (50 mL, 47 mL solution + 3 ml added acetonitrile) till a very concentrated ( $> 3$  M) solution of copper(I) salts was obtained. To know the exact copper(I) concentration, the solution was titrated against  $\text{KMnO}_4$  or cerium ammonium sulfate. On cooling this solution, crystalline copper(I) bisulfate separated out as the acetonitrile complex. By repeated recrystallization (three times) of this crude product from acetonitrile (dissolution by heating and crystallization upon cooling), pure copper(I) bisulfate tetracetonitrile with composition  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  was obtained as a crystalline solid (yield: 42 g, 81 %). The salt was found to be very stable in absence of air (but could be handled in air for a few minutes) and could be stored for a long time in a dry box. Its m. p. is  $78-80$  °C, which is similar to that of the corresponding nitrate, *i. e.*, m. p.  $79-81$  °C [5]. Elemental analysis for  $\text{C}_8\text{H}_{13}\text{CuN}_4\text{O}_4\text{S}$  (324.8): calcd. C 29.56, H 4.00, N 17.24; found C 29.25, H 4.23, N 17.52.

#### Preparation of $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ and $\text{Cu}_2\text{SO}_4$

For the preparation of  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$  the same method as for the preparation of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  was applied, the only alteration being the use of only a few drops of concentrated  $\text{H}_2\text{SO}_4$  just to keep the solution highly acidic. The amount of  $\text{H}_2\text{SO}_4$  used was not sufficient to form a significant fraction of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ . The resulting solution, on cooling at low temperature ( $-10$  to  $-20$  °C), gave a colorless solid mass, which was rich in  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ . The compound was purified by three repeated cycles of dissolving in acetonitrile and then separating out the solid mass by cooling under the same conditions as mentioned above. The final product was briefly exposed to a vacuum. Yield: 17.3 g, 78.5 %, m. p.  $163-165$  °C. This melting point is comparable with that of the corresponding perchlorate ( $164-166$  °C) and tetrafluoroborate salt ( $159-161$  °C) [5]. In order to remove traces of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ , this fraction was recrystallized once again (from acetonitrile), and the precipitate was dried under vacuum to give a colorless non-crystalline mass

(microscopy at a 100-fold magnification did not reveal any crystals) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ . When the purified fraction was dried under vacuum at  $70-80$  °C, it lost all the acetonitrile molecules and changed into a powdery mass with composition  $\text{Cu}_2\text{SO}_4$  (calcd. Cu 56.95,  $\text{SO}_4$  43.05; found Cu 56.90,  $\text{SO}_4$  43.00 by volumetric and gravimetric estimation of  $\text{Cu}^+$  and  $\text{SO}_4^{2-}$  [19], respectively), which was extremely unstable in the solid form, but remained stable in solutions of dried acetonitrile for a relatively long time and could be handled for further studies. Elemental analysis for  $\text{C}_{16}\text{H}_{24}\text{Cu}_2\text{N}_8\text{O}_4\text{S}$  (551.6): calcd. C 34.81, H 4.35, N 20.30; found C 33.98, H 4.22, N 20.51.

#### Preparation of $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$ and $[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$

Bis(2,9-dimethyl-1,10-phenanthroline) copper(I) bisulfate and bis(2,9-dimethyl-1,10-phenanthroline) copper(I) sulfate were prepared by mixing hot solutions of DMPhen (5.00 g, 24.0 mmol) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  (3.90 g, 12.0 mmol) or  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$  (6.60 g, 12.0 mmol), respectively, in acetonitrile and heating at  $70-80$  °C for half an hour. The solution was then cooled to r. t. Both derivatives were separated out by adding anhydrous toluene. The salts were crystallized from acetonitrile and dried under vacuum. The details of the method are given elsewhere [20]. Elemental analysis for  $\text{C}_{30}\text{H}_{28}\text{CuN}_5\text{O}_4\text{S}$  (618.2): calcd. C 58.25, H 4.50, N 11.33; found C 58.22, H 4.26, N 11.22. Yield: 5.6 g, 75.3 %. Elemental analysis for  $\text{C}_{28}\text{H}_{24}\text{Cu}_2\text{N}_4\text{O}_4\text{S}$  (1055.0): calcd. C 31.85, H 2.27, N 5.31; found C 31.23, H 2.29, N 4.89. Yield: 9.0 g, 71.4 %.

#### Measurements

Molar conductances were measured immediately after preparation of very dilute solutions, at 1 kHz frequency using a conductometer supplied by Naina Electronics, Chandigarh with an accuracy of  $\pm 0.2\%$ .  $^{63}\text{Cu}$  NMR spectra were recorded on a Jeol FT NMR (AL 300 MHz) broad band spectrometer at 79.585 MHz. For achieving better sensitivity, the measurements were performed in 10 mm sample tubes. IR spectra were recorded on a Perkin Elmer RX-I FT IR spectrophotometer. UV/Vis measurements were performed on a Hitachi 330 double beam spectrometer with  $1\text{ cm}^3$  quartz cells. All solutions of copper(I) salts for chemical analyses were prepared in acetonitrile. For the quantitative estimation of the copper(I) contents, a sample of the salt (of known weight, range 0.2–0.4 g) was dissolved in 5 mL of acetonitrile and then 2 mL of dilute  $\text{H}_2\text{SO}_4$  was added to the solution. This solution was titrated against standard N/50 aqueous  $\text{KMnO}_4$  or aqueous ceric ammonium sulfate using *N*-phenylanthranilic acid as indicator in the second case. The titration with ceric ammonium sulfate was found to be highly sensitive and more suitable for the estimation of copper(I) salts [19, 21, 22].

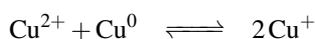
### Crystal structure determination

Single-crystal X-ray structure analyses were carried out on a Stoe IPDS-2 diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by Direct Methods (SHELXS-97 [23]) and refined with full-matrix least-squares methods (refinement on  $F^2$  of all reflections using SHELXL-97 [23]). All non-hydrogen atoms were refined anisotropically; C-bound H atoms were refined in idealized positions, the H atoms of the HSO $_4^-$  ions were located from residual electron density peaks.

CCDC 826964 and 826965 contain the supplementary crystallographic data for [Cu(CH $_3$ CN) $_4$ ]HSO $_4$  and [Cu(DMPhen) $_2$ ]HSO $_4$ , respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Results and Discussion

The formation of copper(I) salts takes place in water/acetonitrile mixtures by the reaction



This reaction yields a mixture of copper(I) bisulfate and copper(I) sulfate in different ratio, depending on the quantity of H $_2$ SO $_4$  added. When H $_2$ SO $_4$  was used in excess, the bisulfate was predominantly formed and *vice versa*. Parker and co-workers [2] have also found that in the presence of H $_2$ SO $_4$ , both copper(I) bisulfate and copper(I) sulfate were formed in the same solution, but they were not able to separate these two salts and obtain them in the pure solid form due to the following difficulties: (i) because of extremely high solubilities of copper(I) bisulfate and copper(I) sulfate, the solid samples of bisulfate and sulfate could not be separated out from the solution even from rather highly concentrated solutions on cooling or by adding an inert solvent; (ii) the concentrated copper(I) solutions could not be stored even for a short time because they undergo disproportionation rather quickly to give copper powder and copper(II) salts; (iii) the solution was to be maintained acidic in all cases to suppress the hydrolysis of copper(I) salts under formation of CuOH which separates out as a yellow mass; (iv) while preparing the concentrated copper(I) solutions from dilute solutions by heating, most of the acetonitrile was lost, and thus copper(I) solutions became unstable. In the present work we took care of all these difficulties by preparing copper(I) bisulfate or sulfate solutions by following a different protocol for obtaining highly concentrated

copper(I) solutions, *i. e.*, by adding increasing amounts of solid copper(II) sulfate pentahydrate and H $_2$ O an acetonitrile mixture and H $_2$ SO $_4$  proportionately to the same solution till a very concentrated (nearly 3 M) solution of the mixture was obtained from which a solid mass was separated out on cooling. Whereas the identities of the bisulfate-containing products were confirmed crystallographically, we were not able to obtain single-crystals of Cu(I) sulfate or its acetonitrile complex for X-ray studies. Chemical analyses, however, are in support of their composition.

Using this method, two novel copper(I) salts, namely [Cu(CH $_3$ CN) $_4$ ]HSO $_4$  and [Cu(CH $_3$ CN) $_4$ ] $_2$ SO $_4$ , have been prepared and isolated in pure form. Both have been isolated from the concentrated solutions and purified by repeated cycles of dissolving and separating out from acetonitrile. The more stable complexes [Cu(DMPhen) $_2$ ]HSO $_4$  and [Cu(DMPhen) $_2$ ] $_2$ SO $_4$  have also been prepared and characterized.

As the diamagnetism of copper(I) salts allows for determination of their  $^{63}\text{Cu}$  NMR properties, we recorded the spectra of solutions of [Cu(CH $_3$ CN) $_4$ ]HSO $_4$  and [Cu(CH $_3$ CN) $_4$ ] $_2$ SO $_4$ , each of which shows a signal of rather narrow line width (found 500 Hz, comparable to a signal width of 480 Hz found for 0.064 M [Cu(CH $_3$ CN) $_4$ ]ClO $_4$  solution in acetonitrile taken as a reference in all of our previous NMR measure-

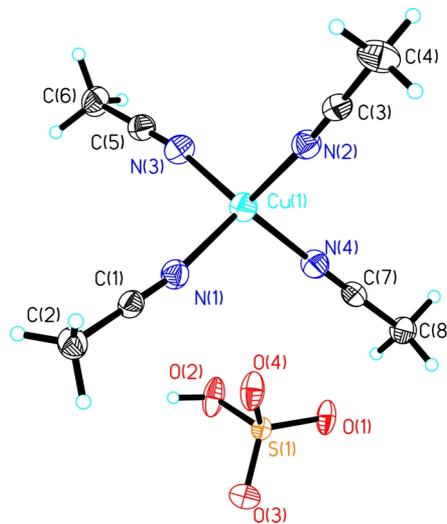


Fig. 1 (color online). Molecular structure of [Cu(MeCN) $_4$ ]HSO $_4$  in the crystal (ellipsoids with 50% probability). The anions form O–H $\cdots$ O-bridged dimers (not shown) about a crystallographic center of inversion, thus underlining the position of the H atom. The anions are two-fold disordered (only predominant site depicted).

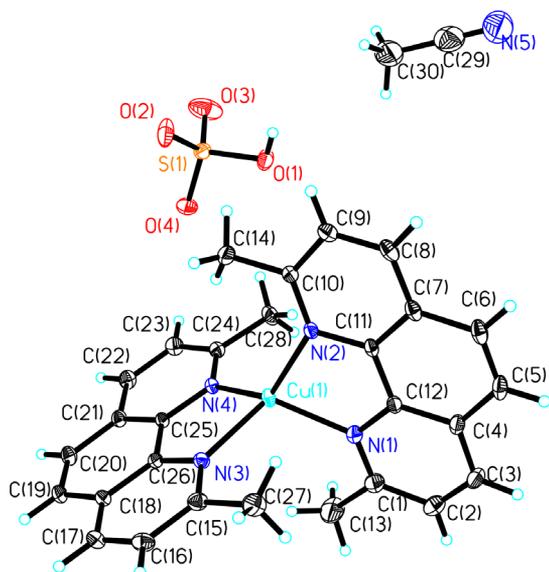


Fig. 2 (color online). Molecular structure of the acetonitrile solvate of  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  in the crystal (ellipsoids with 50% probability). The anions form O–H···O-bridged dimers (not shown) about a crystallographic center of inversion, thus underlining the position of the H atom. The anions are two-fold disordered (only predominant site depicted).

ments) [24–28]. This line width confirms the symmetrical (tetrahedral) geometry of the copper coordination sphere in solution. In sharp contrast, the  $^{63}\text{Cu}$  NMR signals of the complexes  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$  in acetonitrile were much broader ( $> 3$  kHz), thus indicating lower symmetry of the Cu coordination sphere. These results are further supported by single-crystal X-ray studies of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  (Figs. 1 and 2), which underline the less and more distorted  $\text{CuN}_4$  tetrahedral coordination of the two cations, respectively.

Both copper(I) salts and their DMPhen derivatives can be dissolved in acetonitrile giving colorless and orange-red solutions, respectively. The colorless solutions do not show any absorption band at 760 nm for the copper(II) ion. If this solution is stored for a long time it turns blue and shows an absorption band at 760 nm. The UV/Vis spectra of the  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$  complexes, which gave orange-red solutions in acetonitrile, showed a strong absorption band at 460 nm ( $\epsilon = 12500 \text{ dm}^2 \text{ mol}^{-1}$  in acetonitrile; also see Table 1), which is a typical charge transfer band for this kind of copper(I) complexes in various non-aqueous sol-

Table 1. Molar extinction coefficients  $\epsilon$  and wavelengths at maximum absorption  $\lambda_{\text{max}}$  of  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  in various organic solvents.

Parameter	AN	AC	MeOH	DMA	DMF	DMSO
$\epsilon, \text{ dm}^2 \text{ mol}^{-1}$	12500	11104	15732	13106	14310	13394
$\lambda_{\text{max}}, \text{ nm}$	460	460	450	456	456	457

Table 2. Molar conductance  $\Lambda_o$  ( $\text{S cm}^2 \text{ mol}^{-1}$ ) of copper(I) salts/complexes in organic solvents at 298 K.

Complex	AN	AC	MeOH	DMA	DMF	DMSO
$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$	179.9	228.2	132.0	92.3	98.2	43.5
$[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$	150.6	185.2	109.5	64.5	83.4	32.7
$[\text{Cu}_2(\text{CH}_3\text{CN})_8]\text{SO}_4$	199.9	248.9	142.0	97.2	104.2	45.5
$[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$	170.5	212.3	128.7	84.2	93.8	41.8
$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4^{\text{a}}$	168.0	202.2	115.7	62.8	81.8	34.6
$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{NO}_3^{\text{a}}$	176.7	202.3	115.7	68.4	87.3	34.5
$[\text{Cu}(\text{DMPhen})_2]\text{ClO}_4^{\text{a}}$	152.6	176.6	104.1	67.6	76.6	35.3

<sup>a</sup> The values for these salts for comparison with the present values have been taken from ref. [11].

vents (usually found in the range 420–460 nm) [29]. IR spectra confirmed the presence of the O–H group of bisulfate at  $\nu(\text{OH}) = 3414 \text{ cm}^{-1}$  and an acetonitrile band for  $\nu(\text{C}\equiv\text{N})$  at  $2271 \text{ cm}^{-1}$  in  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ , whereas the  $\nu(\text{OH})$  band was absent in sulfate complexes [30].

Molar conductances of very dilute solutions ( $1\text{--}100 \times 10^{-4} \text{ M}$ ) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ ,  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ ,  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$  were measured in a number of organic solvents like acetonitrile (AN), acetone (AC), methanol (MeOH), *N,N'*-dimethylacetamide (DMA), dimethylformamide (DMF), and dimethylsulfoxide (DMSO). Copper(I) salts with tetraacetonitrile solvates are relatively less stable in organic solvents while copper(I) complexes with DMPhen are very stable and were studied in many organic solvents without getting converted to copper(II) salts [11]. At high copper(I) concentrations, in the case of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  and  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$ , the solution turned slightly bluish in all of the solvents. The formation of copper(II) was very small as confirmed by UV/Vis and  $^{63}\text{Cu}$  NMR spectra in which no absorption band at 760 nm and not much line broadening was observed. In the cases of the colored complexes, the orange-red solution remained stable, and there was no copper(II) formation observed in all the solvents. Conductivity measurements of the two salts and their DMPhen complexes in different solvents delivered high values of molar conductance which indicate that the salts are very strong electrolytes. For comparison, the  $\Lambda_o$  values for various salts in different solvents are re-

Table 3. Crystal data and numbers pertinent to data collection and structure refinement of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$ .

	$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$	$[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$
Empirical formula	$\text{C}_8\text{H}_{13}\text{CuN}_4\text{O}_4\text{S}$	$\text{C}_{30}\text{H}_{28}\text{CuN}_5\text{O}_4\text{S}$
Formula weight	324.82	618.17
<i>T</i> , K	180(2)	150(2)
Crystal size, mm	$0.25 \times 0.20 \times 0.17$	$0.22 \times 0.18 \times 0.14$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
<i>a</i> , Å	8.7309(4)	10.1693(4)
<i>b</i> , Å	15.2187(5)	10.7454(4)
<i>c</i> , Å	10.3702(4)	13.3051(5)
$\alpha$ , deg	90	90.729(3)
$\beta$ , deg	92.611(3)	104.066(3)
$\gamma$ , deg	90	98.583(3)
<i>V</i> , Å <sup>3</sup>	1376.49(9)	1392.68(9)
<i>Z</i>	4	2
$\rho_{\text{calc.}}$ , mg m <sup>-3</sup>	1.57	1.47
$\mu(\text{MoK}\alpha)$ , mm <sup>-1</sup>	1.8	0.9
<i>F</i> (000), e	664	640
Limiting indices <i>hkl</i>	$\pm 12, \pm 21, \pm 14$	$\pm 14, \pm 15, -17 / + 18$
Refl. collected / unique	21483 / 4006	33508 / 8129
<i>R</i> <sub>int</sub>	0.0309	0.0328
$\theta_{\text{max}}$ , deg	30.0	30.0
Completeness, %	99.8	99.9
Absorption correction	integration	integration
Data / restraints	4006 / 4	8129 / 4
Refl. parameters	208	390
<i>R</i> 1 / <i>wR</i> 2 [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0332 / 0.0828	0.0417 / 0.1007
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0399 / 0.0857	0.0515 / 0.1061
GoF on <i>F</i> <sup>2</sup>	1.078	1.069
Largest diff. peak / hole, e Å <sup>-3</sup>	0.30 / -0.46	0.48 / -0.68

ported in Table 2. In general, the differences of the conductivities between the different Cu(I) complexes and in different solvents can be attributed to the different ionic sizes for  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  and  $[\text{Cu}(\text{DMPhen})_2]^+$  (0.49 and 0.61 nm, respectively) [11], which may also change from one solvent to the other. It is evident from Table 2 that the ranges of molar conductance of various copper(I) complexes are comparable to the values for other categories of salts like alkali metal halides and tetraalkylammonium salts which behave as 1 : 1 electrolytes in various solvent systems, while in the cases of  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2\text{SO}_4$  and  $[\text{Cu}(\text{DMPhen})_2]_2\text{SO}_4$  salts, the values indicate 1 : 2 electrolyte characteristics [31]. From Table 2 it becomes clear that  $\text{HSO}_4^-$  has a similar influence on conductivity as  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ . This hints at mono-anionic  $\text{HSO}_4^-$  as the predominant contributor to the conductivity, whereas its dissociation into sulfate and protons would provoke dramatically increased conductivity. Moreover the chances of ionization of  $\text{HSO}_4^-$  into  $\text{SO}_4^{2-}$  can occur only in water but not in dipolar aprotic solvents.

Table 4. Selected bond lengths (Å) and angles (deg) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$ .

Cu(1)–N(3)	1.9808(16)	Cu(1)–N(4)	1.9922(15)
Cu(1)–N(1)	2.0052(15)	Cu(1)–N(2)	2.0147(15)
N(1)–C(1)	1.137(2)	N(2)–C(3)	1.135(2)
N(3)–C(5)	1.136(2)	N(4)–C(7)	1.137(2)
S(1)–O(3)	1.414(4)	S(1)–O(1)	1.442(4)
S(1)–O(4)	1.477(4)	S(1)–O(2)	1.540(2)
N(3)–Cu(1)–N(4)	110.50(7)	N(3)–Cu(1)–N(1)	107.76(7)
N(4)–Cu(1)–N(1)	112.48(6)	N(3)–Cu(1)–N(2)	114.72(7)
N(4)–Cu(1)–N(2)	106.69(6)	N(1)–Cu(1)–N(2)	104.66(6)
C(1)–N(1)–Cu(1)	169.32(14)	C(3)–N(2)–Cu(1)	172.35(15)
C(5)–N(3)–Cu(1)	169.90(16)	C(7)–N(4)–Cu(1)	179.18(15)

Table 5. Selected bond lengths (Å) and angles (deg) of  $[\text{Cu}(\text{DMPhen})_2]\text{HSO}_4$ .

Cu(1)–N(4)	2.0147(14)	Cu(1)–N(1)	2.0355(15)
Cu(1)–N(2)	2.0415(14)	Cu(1)–N(3)	2.0708(14)
S(1)–O(3)	1.429(2)	S(1)–O(4)	1.4413(18)
S(1)–O(2)	1.4675(19)	S(1)–O(1)	1.5694(16)
N(4)–Cu(1)–N(1)	130.11(6)	N(4)–Cu(1)–N(2)	127.31(6)
N(1)–Cu(1)–N(2)	82.59(6)	N(4)–Cu(1)–N(3)	82.22(6)
N(1)–Cu(1)–N(3)	112.41(6)	N(2)–Cu(1)–N(3)	127.32(6)
C(1)–N(1)–C(12)	118.63(16)	C(1)–N(1)–Cu(1)	130.01(13)
C(12)–N(1)–Cu(1)	111.03(12)	C(10)–N(2)–C(11)	118.28(14)
C(10)–N(2)–Cu(1)	131.10(11)	C(11)–N(2)–Cu(1)	110.62(11)
C(15)–N(3)–C(26)	118.32(14)	C(15)–N(3)–Cu(1)	130.86(12)
C(26)–N(3)–Cu(1)	110.81(11)	C(24)–N(4)–C(25)	118.54(14)

Single crystal X-ray studies (Figs. 1 and 2, Tables 3–5) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{HSO}_4$  have shown that each copper(I) ion is interacting with four acetonitrile molecules. Despite some deformation, most likely caused by packing effects, the environment of Cu is rather tetrahedral (N–Cu–N angles ranging between  $104.7(1)^\circ$  and  $114.7(1)^\circ$ ), with the bisulfate anion being well separated from the Cu(I) complex (Fig. 1). As to deformation phenomena, we need to point out that only one of the Cu–N–C bond angles is nearly linear, *i. e.*  $179.18(15)^\circ$  whereas the other three Cu–N–C angles range from  $169.32(14)$  to  $172.35(15)^\circ$ , while in case of the benzonitrile complex  $[\text{Cu}(\text{PhCN})_4]\text{ClO}_4$  such values are reported to be almost equal. Hence, fluxional behavior of these nitrile ligands can be expected for  $[\text{Cu}(\text{RCN})_4]^+$  in solution, thus generating an average tetrahedral  $\text{CuN}_4$  coordination sphere. Some X-ray diffraction studies of similar highly ionic copper(I) complexes have been reported in the literature where the tetrahedral geometry is maintained around the  $\text{Cu}^+$  ion [10, 32, 33]. In the 1 : 2 complex with the bidentate ligand 2,9-dimethyl-1,10-phenanthroline (Fig. 2) the tetracoordination of copper(I) is maintained. The N–Cu–N angles, however, clearly deviate from tetrahedral (Table 5). As the five-membered

DMPPhen chelate rings cause the sharp bite angles of *ca.* 82° (which are similar to intra-chelate N–Cu–N angles of other phenanthroline and bipyridine Cu(I) complexes) [34, 35], this deformation is retained in solution, thus rendering the <sup>63</sup>Cu NMR line width of these chelate complexes much broader than that for the acetonitrile complex.

## Conclusion

Copper(I) bisulfate and sulfate are two unstable and sensitive salts which suffer oxidation in air and disproportionation in aqueous solution. They can, however, form very stable derivatives with 2,9-dimethyl-1,10-phenanthroline. The crystal structures of the bisulfate salt and its DMPPhen complex have been determined.

The rather soft N-donor atoms of both acetonitrile and 2,9-dimethyl-1,10-phenanthroline set up a more or less distorted tetrahedral coordination sphere around the Cu<sup>+</sup> ion. Higher symmetry is found in the case of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]HSO<sub>4</sub> than in its derivative. Both salts and their derivatives with 2,9-dimethyl-1,10-phenanthroline behave as strong electrolytes. Most notably, the acetonitrile solvate of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>2</sub>SO<sub>4</sub> can be converted into pure Cu<sub>2</sub>SO<sub>4</sub>, thus providing an easy route for the preparation of this otherwise hardly accessible salt.

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- [1] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 2<sup>nd</sup> ed., Interscience, New York, **1966**.
- [2] I. D. Macleod, D. M. Muir, A. J. Parker, P. Singh, *Aust. J. Chem.* **1977**, *30*, 1423–1437.
- [3] A. J. Parker, D. Muir, *Hydrometallurgy* **1981**, *6*, 239–260.
- [4] D. S. Gill, R. Srivastava, *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1533–1538.
- [5] B. J. Hathaway, D. G. Holah, J. D. Postlewaite, *J. Chem. Soc.* **1961**, 3215–3218.
- [6] H. L. Yeager, B. Kratochvil, *J. Phys. Chem.* **1969**, *73*, 1963–1974.
- [7] K. Miyoshi, *J. Phys. Chem.* **1972**, *76*, 3029–3033.
- [8] U. Ochsenbein, C. W. Schlaefer, *Helv. Chim. Acta* **1980**, *63*, 1926–1931.
- [9] D. S. Gill, L. Rodehueser, P. Rubini, J. J. Delpuech, *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2307–2312.
- [10] P. G. Jones, O. Crespo, *Acta Crystallogr.* **1998**, *54C*, 18–20.
- [11] D. S. Gill, D. Rana, *Z. Naturforsch.* **2009**, *64a*, 269–272.
- [12] S. Ahrland, B. Tagesson, *Acta Chem. Scand.* **1977**, *A31*, 615–624.
- [13] T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* **2003**, *42*, 5340–5347.
- [14] J. R. Black, W. Levason, M. D. Spicer, M. Webster, *J. Chem. Soc., Dalton Trans.* **1993**, *20*, 3129–3136.
- [15] S. Chowdhury, P. B. Iveson, M. G. B. Drew, D. A. Tocher, D. Datta, *New J. Chem.* **2003**, *27*, 193–196.
- [16] D. S. Gill, *J. Sol. Chem.* **1979**, *8*, 691–699.
- [17] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents, physical properties and methods of purification*, 4<sup>th</sup> ed., Wiley Interscience, New York, **1986**.
- [18] D. S. Gill, J. S. Cheema, *Electrochim. Acta* **1982**, *27*, 1267–1271.
- [19] D. S. Gill, K. S. Arora, J. Tewari, B. Singh, *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1729–1736.
- [20] D. S. Gill, K. S. Arora, B. Singh, M. S. Bakshi, M. S. Chauhan, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1159–1162.
- [21] D. S. Gill, J. Tewari, G. Singh, M. S. Bakshi, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1155–1157.
- [22] J. Bassett, R. G. Denney, G. H. Jaffery, J. Mandhem, *Vogel's Text Book of Quantitative Inorganic Analysis*, 4<sup>th</sup> ed., ELBS Longman, London, **1978**.
- [23] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473; *ibid.* **2008**, *A64*, 112–122.
- [24] D. S. Gill, U. Kamp, A. Doelle, M. D. Zeidler, *Ind. J. Chem.* **2001**, *40A*, 693–699.
- [25] D. S. Gill, T. I. Quickenden, L. Byrne, V. Pathania, B. K. Vermani, *J. Mol. Liq.* **2004**, *111*, 85–93.
- [26] P. Kroneck, J. Kodweis, O. Lutz, A. Nolle, D. Zepf, *Z. Naturforsch.* **1982**, *37a*, 186–192.
- [27] J. K. Irangu, R. B. Jordan, *Inorg. Chem.* **2003**, *42*, 3934–3942.
- [28] S. Kitigawa, M. Munakata, *Inorg. Chem.* **1988**, *23*, 4388–4390.
- [29] R. T. Pflaum, V. V. Brandt, *J. Am. Chem. Soc.* **1955**, *77*, 2019–2022.
- [30] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, 6<sup>th</sup> ed., John Wiley, **2009**.
- [31] B. Kratochvil, H. L. Yeager, *Top. Curr. Chem.* **1972**, *27*, 1–58.

- [32] G. A. Bowmaker, D. S. Gill, B. W. Skelton, N. Somers, A. H. White, *Z. Naturforsch.* **2004**, *59b*, 1307–1313.
- [33] I. Csoregh, P. Kierkegaard, R. Norrestam, *Acta Crystallogr.* **1975**, *B31*, 314–317.
- [34] G. Dessy, V. Sare, *Cryst. Struct. Commun.* **1979**, *8*, 507–510.
- [35] M. Munakata, M. Maekawa, S. Kitagawa, S. Matsuyama, H. Masuda, *Inorg. Chem.* **1989**, *28*, 4300–4302.