

Formation of a three-dimensional hydrogen-bonding network by self-assembly of the Cu^{II} complex of a semi-bidentate Schiff base



Noboru Yoshida,* Naohito Ito and Kazuhiko Ichikawa

Laboratory of Molecular Functional Chemistry, Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan

Three-dimensional hydrogen-bonding networks have been found in the crystal structure of the Cu^{II} complex of the semi-*N,O*-bidentate Schiff base L₁₄, having both hydrogen donor and acceptor sites. The infinite one-dimensional channels and cavities and the helical structure are presented as a result of the complementary intermolecular hydrogen-bonding interaction (–SO₂···H₂N–). Molecular mechanics calculations show the difference between calculated and X-ray structures of the Cu^{II}–L₁₄ complex.

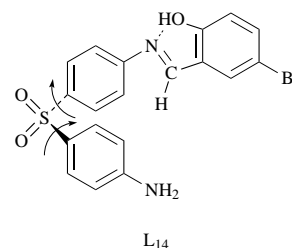
In aqueous solution, weak non-covalent interactions such as hydrophobic and hydrogen bonds play an important role in molecular recognition by cyclodextrin¹ and the fluorescence detection of an anionic guest by a charged amino-β-cyclodextrin.² In the solid state, the control of supramolecular organization using these weak interactions has been a subject of special interest because of both its technological significance and its scientific challenge to chemists.³

Recent crystal engineering of functional solids closely relates to solid-state structural and separation chemistry such as enantiomer resolutions and modifications of physical and chemical properties of solid materials.⁴ Hydrogen bonding involves directional weak interactions that may be useful in generating specific supramolecular architectures.⁵ Self-assembly *via* recognition between complementary hydrogen-bonding components has been developing rapidly in solid-state chemistry.⁶ The choice of molecular shape and size and the arrangement of hydrogen-bonding donor and acceptor sites are crucial to build up the supramolecular architecture in the solid.

Many organic components having hydrogen-bonding donor–acceptor sites have been extensively studied in the programmable lattice clathrates, such as barbituric acid–2,4,6-triaminopyrimidine,⁷ benzene-1,3,5-tricarboxylic acid–pyrene–EtOH,⁸ benzene-1,3,5-tricarboxylic acid–*N,N*-dicyclohexylamine,⁹ tetrakis{4-[2-(6-oxo-1,6-dihydropyridin-2-yl)ethynyl]phenyl}-methane ('Tectone')–butyric acid,^{5a} 4,4'-bis{[(6-methylpyridin-2-yl)amino]carbonyl}biphenyl–decanedioic acid,¹⁰ phenazine–3,5-dinitrobenzoic acid,¹¹ and isophthaloylaminopyridine–biphenyl diacid.¹²

Metal complexes are rarely used to design lattice clathrates with a predictable structure using hydrogen bonding, because the synthesis of metal complexes having both hydrogen-bonding acceptor and donor sites is difficult.¹³ However, the versatility of some chemically modified porphyrin compounds as hydrogen-bonding crystalline hosts appears to be adequate due to the large size, high symmetry, rigidity and thermal stability of the molecular framework.¹⁴ Metallo-supramolecular systems in which ligands are connected by a hydrogen-bonded network have been found recently in some metal complexes such as bis(thiosemicarbazide)Ni^{II}–dicarboxylate anions,^{15a} dicyclo-palladated 2,3-bis[6-(2-amino-4-phenylamino-1,3,5-triazinyl)]-pyrazine,^{15b} and Zn^{II}–tetra(4-carboxyphenyl)porphyrin.¹⁶

We report the three-dimensional hydrogen-bonding network of the copper(II) complex of the semi-*N,O*-bidentate Schiff base, L₁₄ (Scheme 1; the arrows denote the rotational freedom about the axes), having both hydrogen-bonding donor and acceptor sites. The construction of three-dimensional architecture requires the presence of two or more hydrogen subunits in the ligand.



Scheme 1

Experimental

Materials and synthesis

The synthesis, isolation and purification of L₁₄ have been carried out by the usual Schiff base condensation¹⁷ of 5-bromosalicylaldehyde and bis(4-aminophenyl) sulfone. Reaction of L₁₄ with Cu(CH₃COO)₂·H₂O in a 2 : 1 or 1 : 1 molar ratio in hot ethanol afforded an olive-green solid **1**. The suspended ethanol solution (60 ml) of L₁₄ (1.06 g, 2.46 mmol) was added to the ethanol solution (50 ml) of Cu(CH₃COO)₂·H₂O (0.34 g, 1.70 mmol). The resultant solution was warmed gently to 60–70 °C with stirring. The olive-green solid was collected and washed with ethanol and dried under vacuum for 24 h to give 0.689 g (60% yield). This solid was quite soluble in DMF, forming a black coloured solution, but was only sparingly soluble in acetonitrile and CHCl₃. Other metal complexes, such as Co^{II}, Ni^{II}, Zn^{II} and Pd^{II} were also synthesized by a similar method, but no crystals suitable for X-ray analysis were obtained. Crystals suitable for X-ray single-crystal analysis were obtained by diffusing a diethyl ether solution into the DMF solution of the Cu^{II}–L₁₄ complex (Found: C, 49.37; H, 3.95; N, 7.85; S, 5.99. C₃₈H₂₈N₄O₆S₂Br₂Cu·2DMF requires: C, 48.11; H, 3.92; N, 7.70; S, 5.57%). Elementary analysis and fast atom bombardment mass spectroscopy (FABMS) support the formation of Cu²⁺ : L₁₄ = 1 : 2 complex for **1**. FABMS also shows the presence of ligand L₁₄ and other Cu^{II} complex species such as Cu²⁺ : L₁₄ = 1 : 1 and 2 : 4.

X-Ray analysis

Crystal data for (L₁₄H₁)₂Cu²⁺·2DMF: C₄₄H₄₂N₆O₈S₂Br₂Cu with crystal size 0.30 × 0.25 × 0.20 mm, *M* = 1070.33, dark brown prismatic crystal, monoclinic, space group *P*2₁/*c*, *a* = 8.434(3), *b* = 20.760(4), *c* = 13.250(3) Å, β = 101.00(2)°, *V* = 2277.3(8) Å³, *Z* = 2, ρ_{calc} = 1.561 g cm^{–3}, μ(Cu-Kα) = 40.82 cm^{–1}, *F*(000) = 1086.00. Data were collected on a Rigaku AFC7R diffractometer, 3781 reflections, 3517 unique, 2294 observed [*I* > 3.00 σ(*I*)]. The structure was solved by a direct

method and expanded using Fourier techniques. The final cycle of full-matrix least-squares refinement was based on 2294 observed reflections [$I > 3.00 \sigma(I)$] and 255 variable parameters, and converged at $R = 0.060$, $R_w = 0.096$. Maximum/minimum residual electron density: $+0.56/-0.54 \text{ e } \text{Å}^3$. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.

Results and discussion

Absorption spectrum

Fig. 1 shows the change in absorption spectrum which occurred when L_{14} coordinated to the copper(II) ion. Upon addition of the copper(II) ion, the band at 355 nm decreased and the one at 410 nm increased. Mole ratio plots (the inset in Fig. 1) using the change in absorbance of these two bands demonstrated the

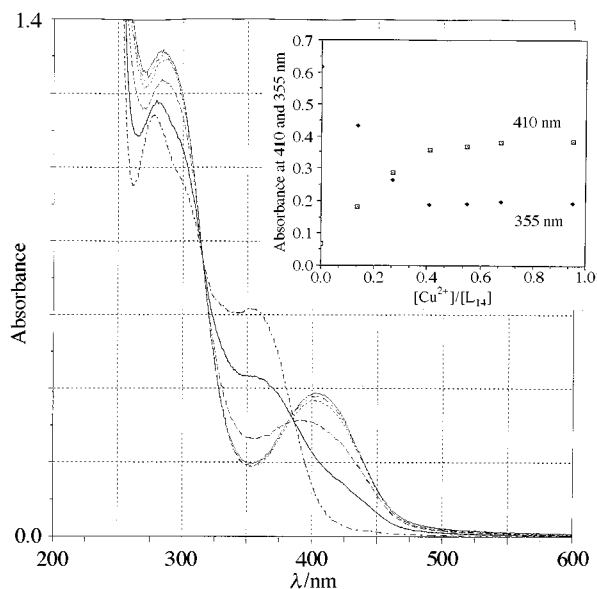


Fig. 1 Spectral change of the ligand L_{14} in ethanol upon addition of $Cu(CH_3COO)_2 \cdot H_2O$. $[L_{14}] = 5.03 \times 10^{-5} \text{ mol dm}^{-3}$. $[Cu^{II}] = 0, 0.687, 1.37, 2.06, 2.75, 3.43, 4.80, 6.18, 7.55 \times 10^{-5} \text{ mol dm}^{-3}$.

$Cu^{2+}:L_{14} = 1:2$ stoichiometry. The reaction in hot ethanol of L_{14} and copper(II) acetate resulted in the formation of an olive-green powder in good yield. The electronic absorption spectrum of this solid shows a $\pi-\pi^*$ band at 410 nm indicating the deprotonation of the OH group and the N,O -coordination of L_{14} to a Cu^{2+} ion.^{17a}

Mass spectra

The positive FAB mass spectrum in Fig. 2 of **1** in DMF (NBA matrices) shows a signal at $m/z = 923$ whose experimental isotope pattern very closely matches the calculated value of the $Cu^{2+}:L_{14} = (1:2)^+$ complex. However, the characteristic peaks that could be assigned to the $(L_{14})^+$, $Cu^{2+}:L_{14} = (1:1)^+$ and $(2:4)^+$ complexes are also observed at $m/z = 431, 495$ and 1843, respectively, showing the presence of complicated equilibria in the matrix solution. Many unidentified peaks are also observed. It is possible that the hydrogen-bonded cluster species is present in solution. Electrospray ionization mass spectrometry (ESIMS) has emerged as a mild ionization method for the characterization of many systems, e.g. proteins, oligonucleotides and coordination compounds.¹⁸ Since no energy is required to ionize the sample, ESIMS with no matrix is suitable for investigating the weak supramolecular assembly in solution.¹⁹ Fig. 3 shows the positive ESIMS of **1**. The strong peaks due to $(L_{14})^+$, $Cu^{2+}:L_{14} = (1:1)^+$ and $(2:3)^+$ complexes are found at $m/z = 431.0, 493.9$ and 1416.6, respectively, in addition to the peak at 923.8 of the $(1:2)^+$ complex. Thus, the presence of some metal-ligand species of **1** in equilibrium conditions could be detected by FABMS and ESIMS methods.

IR spectra

Fig. 4 shows the IR spectrum of L_{14} (KBr pellet). The two sharp peaks at 3421 and 3349 cm^{-1} are attributed to the N-H stretching frequencies (ν_{sym} and ν_{asym}) of the free primary amino group. These peaks nearly disappear in the Cu^{II} and Zn^{II} complexes of L_{14} . Since the UV-VIS spectrum of the $Zn^{II}-L_{14}$ complex shows no deprotonation of the OH group, the amino group of L_{14} would coordinate directly to the Zn^{II} ion. In the $Cu^{II}-L_{14}$ complex, the disappearance of the free amino groups would be correlated with the formation of intermolecular hydrogen bonds in the solid state. In other metal complexes, such as Ni^{II} and Pd^{II}

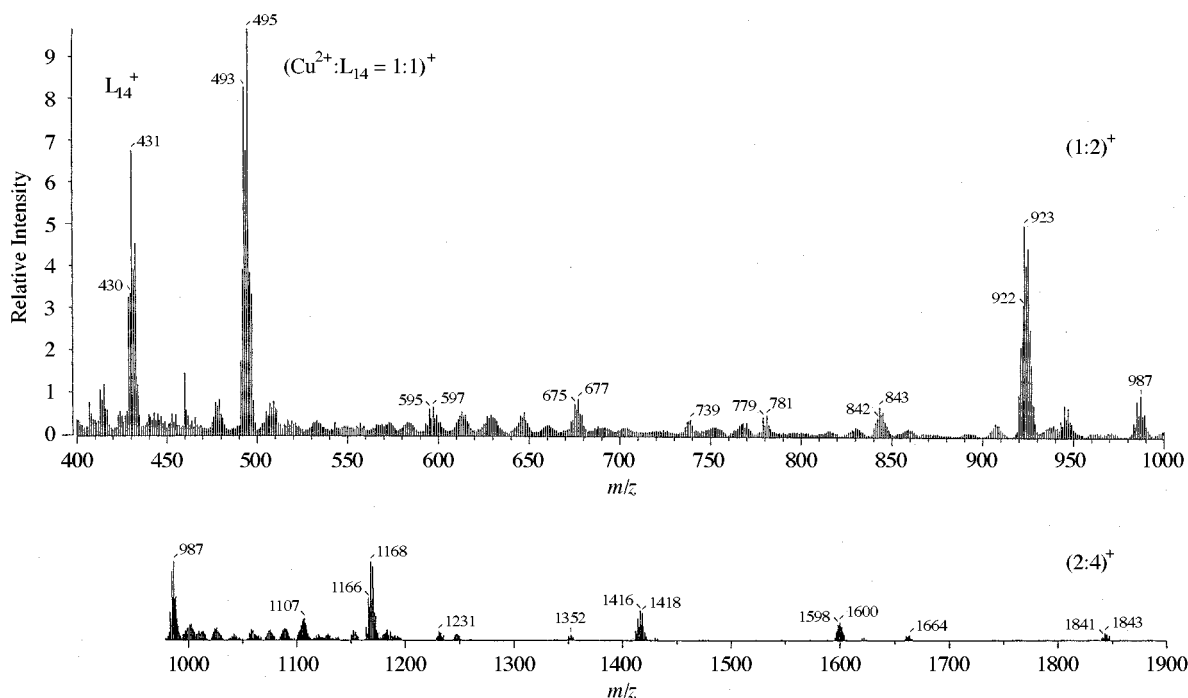


Fig. 2 FAB mass spectrum of **1** (NBA matrix)

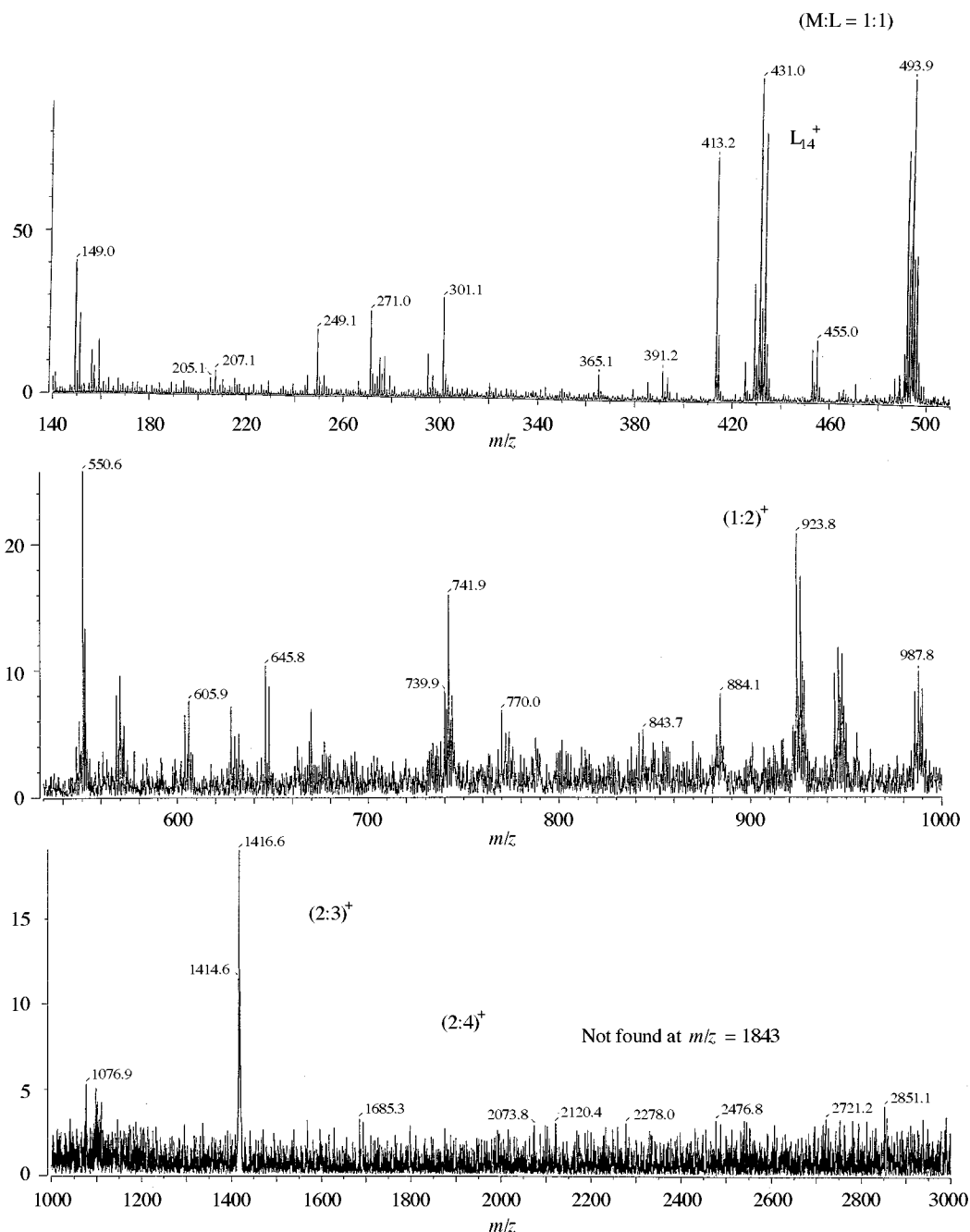


Fig. 3 ESI mass spectrum of a DMF solution of **1**

of L_{14} , a reduction in intensity and shift to lower frequency of the peak of the free amine are also observed.

Force field calculated structure of Schiff base L_{14}

The Schiff base L_{14} is an interesting bifunctional ligand having both an *N,O*-bidentate coordination mode and hydrogen-bonding donor ($-\text{NH}_2$) and acceptor ($-\text{SO}_2-$) sites. Furthermore, two rotational freedoms about the $-\text{SO}_2-$ linkage are possible in the conformation of the aminophenyl moiety (see Scheme 1). Molecular mechanics gives an MM-2 minimized space-filling model of L_{14} (Fig. 5), showing that the amino-sulfone moiety is slightly twisted around the $-\text{SO}_2-$ linkage whereas the bromosalicylidene group is a co-planar unit.²⁰

X-Ray structure analysis of **1**

For X-ray crystallographic analysis, suitable single crystals of **1** were obtained by slow diffusion of diethyl ether into the DMF solution of the $\text{Cu}^{\text{II}}-L_{14}$ complex. The compound crystallized in the centrosymmetric monoclinic space group $P2_1/c$ (#14) with

two molecules per unit cell. An ORTEP representation of the structure of **1** is given in Fig. 6. Table 1 shows the selected bond lengths and angles of **1**.²¹ The Cu^{II} ion lies on a crystallographic center of symmetry and has square-planar geometry with two azomethine nitrogen atoms and two phenolate oxygen atoms in a *trans* configuration. The $\text{Cu}(1)-\text{N}(1)$ and $\text{Cu}(1)-\text{O}(1)$ bond lengths are 2.009(4) and 1.874(5) Å, respectively, and the $\text{O}(1)-\text{Cu}(1)-\text{N}(1)[\text{N}(1^*)]$ angles are 91.3(2) and 88.7(2)°. However, the phenyl sulfone moiety is nearly perpendicular with respect to the chelate plane. This conformation is appreciably different from that of ligand L_{14} inferred from the MM-2 calculation. Furthermore, two aminophenyl moieties are also lying perpendicular to the bromosalicylidene units. Molecular mechanics calculations were used to clarify the conformational preference of the crystal structure of **1**. The MM-2 energy minimized structure ($E_{\text{steric}} = -27.34 \text{ kcal mol}^{-1}$)²² for the $\text{Cu}^{2+}:L_{14} = 1:2$ complex favours the conformer in which two aromatic rings linked by an azomethine bond ($-\text{CH}=\text{N}-$) overlap each other, but the aminophenyl moiety is somewhat twisted out of the chelate plane (Fig. 7).²³

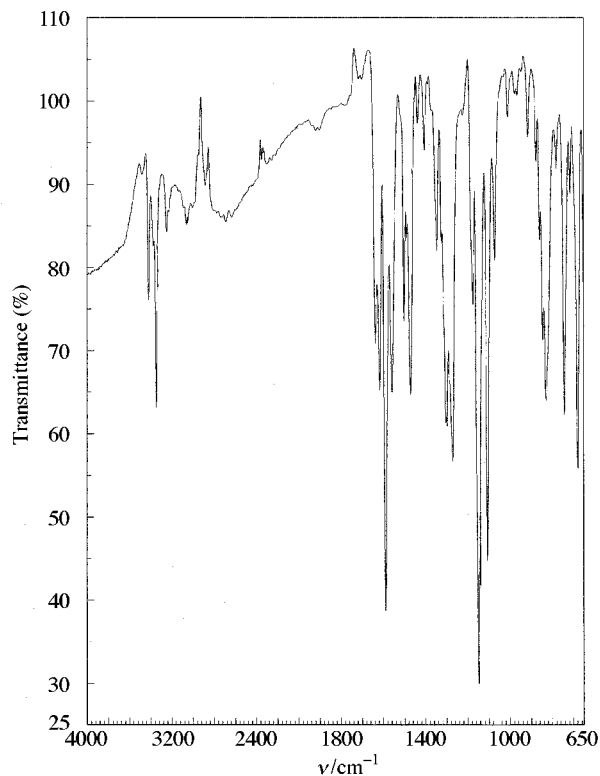


Fig. 4 IR spectrum of ligand L_{14}

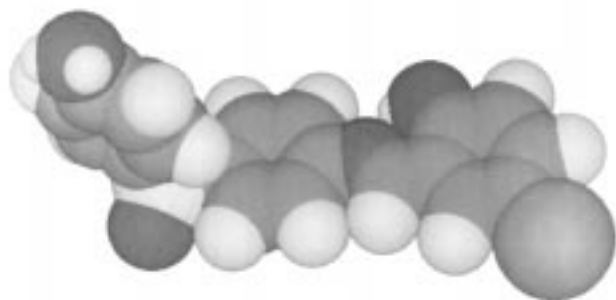


Fig. 5 Energy-minimized conformational isomer of ligand L_{14} calculated by MM-2 molecular mechanics

The fairly large steric energy ($E_{\text{steric}} = +271.0 \text{ kcal mol}^{-1}$) calculated for the X-ray crystal structure indicates the structure of **1** has a sterically-strained conformation.²⁴ This considerable strain is mainly reflected in the Cu–O and Cu–N bonds (Cu–O 1.874 Å, Cu–N 2.009 Å and C=N 1.291 Å for the X-ray structure). In the strain free Cu^{II} complex of an analogous Schiff base, the bond lengths of Cu–O, Cu–N and C=N have been reported as 1.910(9), 1.930(10) and 1.30(2) Å, respectively.²⁵ In the calculated structure in Fig. 7, the strain is relaxed particularly in the Cu–O bond length (Cu–O 1.897 Å, Cu–N 1.938 Å and C=N 1.268 Å for the MM-2 structure).²² This conformational strain may be compensated by edge-to-face $\text{CH}\cdots\pi$ aromatic interactions.²⁶ As shown in Table 2, the CH(aminophenyl) $\cdots\pi$ (bromosalicylidene) interatomic distances lie in the range 2.927–4.240 Å. This type of weak interaction would lead to the T-type edge-to-face $\text{CH}\cdots\pi$ interactions.

Three-dimensional hydrogen-bonding network

Hydrogen bonding is normally stronger and more directional than other non-bonding attractive forces²⁷ and can be exploited for the rational design of molecular crystals.^{3,28} The complex **1** is a unique building block similar to water which also has two hydrogen-bonding acceptor and two donor sites. These four sites would lead to the formation of 2-D or 3-D hydrogen-

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Cu(1)–O(1)	1.874(5)	Cu(1)–N(1)	2.009(14)
S(1)–O(2)	1.443(6)	S(1)–O(3)	1.441(6)
S(1)–C(11)	1.769(6)	S(1)–C(14)	1.741(8)
N(1)–C(7)	1.291(8)	N(1)–C(8)	1.442(7)
C(6)–C(7)	1.416(9)	C(6)–C(1)	1.403(8)
C(1)–O(1)	1.300(8)	N(2)–C(17)	1.35(2)
C(4)–Br(1)	1.905(8)		
O(1)–Cu(1)–O(1*)	180.0	O(1)–Cu(1)–N(1)	91.3(2)
O(1)–Cu(1)–N(1*)	88.7(2)	N(1)–Cu(1)–N(1*)	180.0
O(2)–S(1)–O(3)	119.5(3)	O(2)–S(1)–C(11)	107.8(3)
O(2)–S(1)–C(14)	108.6(4)	O(3)–S(1)–C(11)	106.7(3)
O(3)–S(1)–C(14)	108.0(3)	C(11)–S(1)–C(14)	105.3(3)
Cu(1)–O(1)–C(1)	130.9(4)	Cu(1)–N(1)–C(7)	124.1(4)
Cu(1)–N(1)–C(8)	118.8(4)	C(7)–N(1)–C(8)	117.0(5)
O(1)–C(1)–C(6)	123.3(5)	C(1)–C(6)–C(7)	123.3(6)

Table 2 CH $\cdots\pi$ lengths (Å) between the bromosalicylidene moiety [C(2)H and C(3)H] and the aminophenyl moiety (C*) for **1**

	C(17*)	C(18*)	C(19*)	C(14*)	C(15*)	C(16*)
C(3)H	2.927	3.251	3.919	4.240	3.962	3.329
C(2)H	3.777	3.413	3.234	3.356	3.677	3.856
	C(11*)	C(10*)	C(9*)	C(8*)	C(13*)	C(12*)
C(2)H	3.948	3.473	3.655	3.895	3.954	3.784

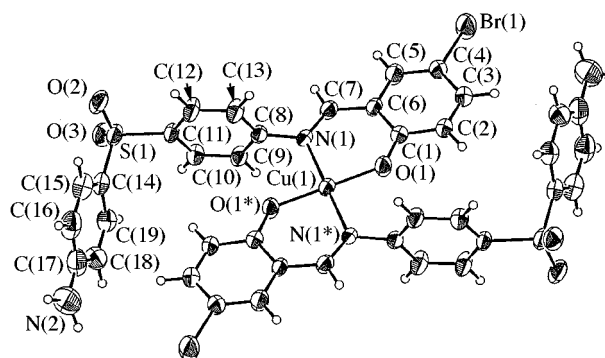


Fig. 6 ORTEP representation of the structure of **1**

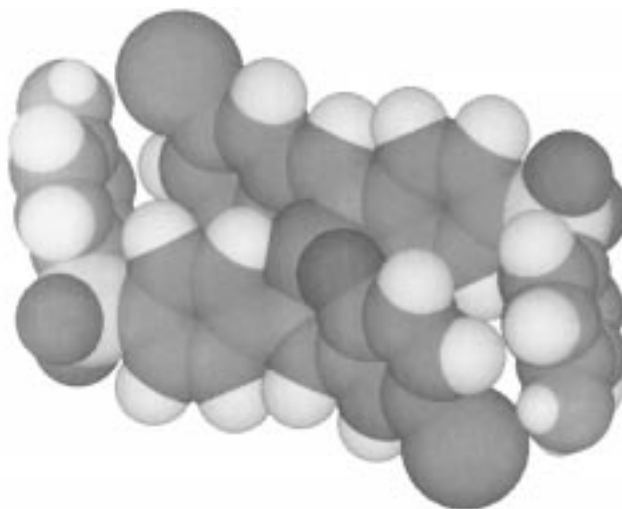


Fig. 7 Minimum-energy structure of the 1:2 = $\text{Cu}^{2+}:L_{14}$ complex calculated by MM-2

bonding arrays in the solid. Fig. 8 shows the specific intermolecular hydrogen bonding (types A–F) which is often used to design the hydrogen-bonding co-crystals. The intermolecular hydrogen bond of type G is utilized for the construction of the new hydrogen-bonding network.

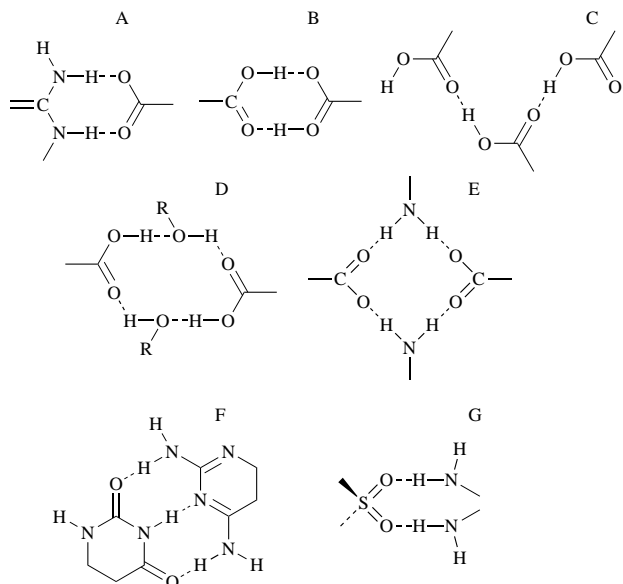


Fig. 8 Some hydrogen-bonding motifs for crystalline nomenclature

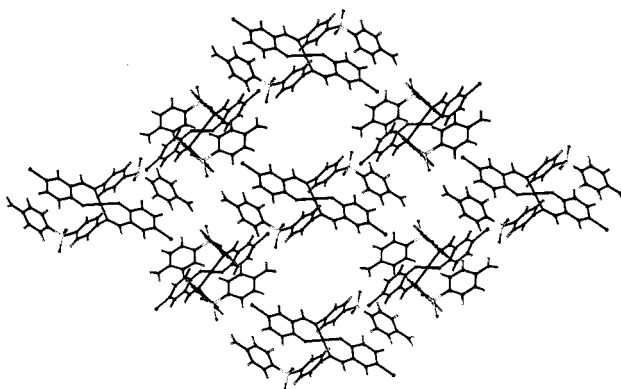


Fig. 9 The four-fold two-dimensional view of the chicken-wire network of **1**. Part of the three-dimensional hydrogen-bonding network of **1** is showing the four cavities. DMF solvents were removed for clarity.

It is interesting to note what type of 2-D or 3-D hydrogen-bonding array emerges with the use of type G (having the sulfone acceptor) instead of types A–F with the carboxylate (or carbonyl) acceptor.

The infinite overall structure of **1** is found to be organized by a three-dimensional hydrogen-bonding network in which the $\text{-NH}_2 \cdots \text{O}_2\text{S-}$ type intermolecular hydrogen bonds play an important role, as shown in Fig. 9. One complex molecule is surrounded by four adjacent complexed molecules through four $\text{-NH}_2 \cdots \text{O}_2\text{S-}$ hydrogen bonds. These hydrogen bonds would be strong judging from the $\text{NH} \cdots \text{O}$ distances in the range 2.032–2.941 Å. From the neutron diffraction study of sulfamic acid ($^+\text{NH}_3\text{SO}_3^-$), a comparably strong hydrogen bond has been observed ($\text{-N}^+\text{H} \cdots \text{O-S}$ distances in the range 1.95–2.56 Å).²⁹ Recently, similar hydrogen bonds between sulfone and hydroxy groups [2.898(6) Å] have been found in a supramolecular carpet formed *via* self-assembly of bis(4,4'-dihydroxyphenyl) sulfone.³⁰ Furthermore, four weak $\text{Br} \cdots \text{H}$ hydrogen bonds may participate in the hydrogen-bonding arrays as shown in Fig. 10.

The voids formed by four complex molecules are filled with two DMF solvent molecules within one layer. The very short hydrogen bonds between $\text{O}(\text{DMF})$ and $\text{H}_2\text{N}(\text{L}_{14})$ are also observed [$\text{NH} \cdots \text{O}(\text{DMF})$ lengths: 1.889 Å]. The one-dimensional channel thus formed along the crystallographic *a* axis could be organized by the complementary hydrogen bonding and filled with the DMF solvent molecules. The very large solubility of **1** in DMF is due to the occlusion by this

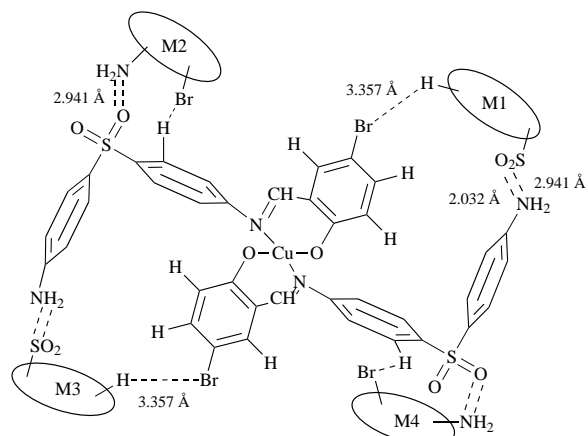


Fig. 10 Schematic representation of the mutual hydrogen-bonding arrays of **1**



Fig. 11 CPK model representation of a helical structure of **1** along the crystallographic *b* axis

channel structure. The unusual role of the DMF solvent in the crystal packing has also been observed in the dimeric magnesium phenylphosphatosulfate.³¹

The other interesting projection of the crystal packing diagram is shown in Fig. 11, which corresponds roughly to the view along the crystallographic *b* axis. In Fig. 11, the unique helical structure through the strong $\text{-NH}_2 \cdots \text{O}_2\text{S-}$ hydrogen bond and weak $\text{Br} \cdots \text{H}$ hydrogen bonds is shown.

Super-tetrahedral crystal architectures have been observed in molecular recognition among simple alcohols and amines.³² Furthermore, a triple-stranded helical structure has been reported by Hanessian *et al.* in the hydrogen-bonded co-crystal formed by *trans*-1,2-diaminocyclohexane and butane-2,3-diol.³³

Long-range crystal packing in complex **1** might be controlled through short-range interactions such as complementary inter-

molecular hydrogen bonding. The first step in the long-range ordering is the formation of the self-assembled organized species by weak interactions such as hydrogen bonds in solution. These structural results have clearly demonstrated that the complementary double hydrogen bonds ($-\text{NH}_2 \cdots \text{O}_2\text{S}-$ and $\text{Br} \cdots \text{H}$) can form the supramolecular arrays of a three-dimensional hydrogen-bond network and the one-dimensional channel. Further study on complementary intermolecular hydrogen bonding leading to three-dimensional supramolecular architectures is now in progress using an analogous Schiff base ligand.

Acknowledgements

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