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Cite this: *CrystEngComm*, 2011, **13**, 5342

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**PAPER**

# Two unusual mixed-valent trinuclear $Cu^{II}_2Cu^{I}$ complexes containing copper(I) tribromide dianion as bridging ligand: Identification of an unprecedented doubly hydrogen-bonded water dimer†

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***Received 28th October 2010, Accepted 5th January 2011***
**DOI: 10.1039/c0ce00784f**

Two very rare mixed-valent $Cu^{II}_2Cu^{I}$ trinuclear complexes, $[Cu_2(Br–L^1)_2CuBr_3]\cdot 2H_2O$ (**1**) and $[Cu_2(L^2)_2CuBr_3]\cdot 2CH_3OH$ (**2**) have been synthesized using $CuBr_2$ and the tridentate reduced Schiff-base ligands $HL^1$ (2-[(2-dimethylamino-ethylamino)-methyl]-phenol) and $HL^2$ (2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol), respectively. The complexes have been characterized by X-ray structural analyses. In both complexes, the deprotonated tridentate reduced Schiff base forms a di-μ-phenoxo bridge between the two $Cu^{II}$ centers and the $CuBr_3^{2-}$ anion acts as an additional bridge between them to result in the trinuclear structures. During complex formation, ligand $HL^1$ has been brominated at the five position of the aromatic ring but $HL^2$ did not undergo any such reaction. In complex **1** an unprecedented doubly hydrogen-bonded water dimer, which is considered as an important transition state for the interchange of hydrogen atoms within the water dimer, has been identified. The dimensions of this water dimer agree quite well to those obtained from theoretical calculations.

## Introduction

Recently, much attention has been focused on water dimers[1] since the water dimer appears to be an important species in the atmosphere,[1f,2] where it may influence the energy balance of the earth. A supramolecular water dimer was first identified by Pimentel and co-workers long ago by infrared spectroscopy.[3] Later with the help of various other experimental techniques,[4–6] it has been clearly established that the water dimer is linear with one water acting as a proton acceptor and the other as a proton donor. Theoretical calculations also supported the linear structure.[7] On the other hand, study of water dimers with the help of X-ray crystal structure analysis in restricted environments such as organic and inorganic host lattices are very rare.[8] Moreover, the few water dimers which have been fully characterized by crystallography in the solid state are in conformity with the near-linear structure as proposed by the spectral evidences and theoretical calculations. To our knowledge, until now identification of a doubly hydrogen-bonded water dimer is unprecedented.

The mixed-valent $Cu^{I}/Cu^{II}$ coordination compounds are gaining popularity due to their great biological importance for their structural application in certain metallo-enzymes and interesting electronic properties,[9] as well as the good electrical conductivity[10] and bistability of the compounds.[11] However, there are great difficulties in controlling the final product with two different oxidation states, which is reflected in the literature of mixed-valent copper coordination compounds.[12–14] As a result, the number of mixed-valent copper complexes are limited and among them there is only one example of mixed-valent $Cu^{I}/Cu^{II}$ coordination compounds where a copper(I) trihalide dianion acts as a bridging ligand between two $Cu^{II}$ ions in a trinuclear structure.[14] The compound was prepared by using a resorcinol-substituted trimethylethylenediamine ligand. The tridentate reduced Schiff base ligands derived from the mono-condensation of diamines with salicylaldehyde has a very similar structure to that of this resorcinol-substituted trimethylethylenediamine ligand. Therefore, it is of interest to find out whether such ligands can also lead to this type of rare mixed-valence species.

In this paper we report the synthesis, and crystal structures of two mixed-valent $Cu^{I}/Cu^{II}$ coordination compounds, $[Cu_2(Br–L^1)_2CuBr_3]\cdot 2H_2O$ (**1**) and $[Cu_2(L^2)_2CuBr_3]\cdot 2CH_3OH$ (**2**) obtained from the reduced Schiff base ligands 2-[(2-dimethylamino-ethylamino)-methyl]-phenol ($HL^1$) and 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol ($HL^2$) respectively. In compound **1**, an unprecedented doubly hydrogen-bonded water dimer which has been considered from theoretical calculation as

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† Electronic supplementary information (ESI) available. CCDC reference numbers 793723 (**1**) and 793724 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00784f

one of the intermediates for the interchange of hydrogen atoms within the water dimer, is identified.

## Experimental

### Materials

All the chemicals were of reagent grade and used without further purification.

### Synthesis of the reduced Schiff base ligands 2-[(2-dimethylamino-ethylamino)-methyl]-phenol ($HL^1$) and 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol ($HL^2$)

The Schiff base ligand has been synthesized by refluxing a solution of salicylaldehyde (0.52 mL, 5 mmol) and N,N-dimethylethylenediamine (0.54 mL, 5 mmol) in methanol (30 mL) for one hour.[15] The solution was cooled to 0 °C and solid sodium borohydride (210 mg, 6 mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution was acidified with concentrated HCl (5 mL) and then evaporated to dryness.[15] The reduced Schiff base ligand $HL^1$ was extracted from the solid mass with methanol and this methanol solution (*ca.* 20 mL) was used for preparation of the complexes. $HL^2$ was synthesized in the same way as $HL^1$ using 2-hydroxyacetophenone (0.60 mL, 5 mmol) instead of salicylaldehyde.

### Synthesis of $[Cu_2(Br–L^1)_2CuBr_3]\cdot 2H_2O$ (1) and $[Cu_2(L^2)_2CuBr_3]\cdot 2CH_3OH$ (2)

An extracted methanol solution of $HL^1$ as prepared above was added to a solution of $CuBr_2$ (1.672 g, 7.5 mmol) in methanol (20 mL). The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. Deep brown crystals of **1** suitable for X-ray diffraction were obtained after 24 h. The deep brown coloured single crystals of complexes **2** were obtained in the same way using $HL^2$ instead of $HL^1$.

**Complex 1.** (Yield: 1.920 g; 76%) Anal. Calc. for $C_{22}H_{36}Br_5Cu_3N_4O_4$: C, 26.14; H, 3.59; N, 5.54%. Found: C, 26.13; H, 3.51; N, 5.62%. $\lambda_{max}$ (nm), [$\varepsilon_{max}$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)] (acetonitrile), 685 (332), 422(2870); IR: $\nu$(N–H), 3155 cm$^{-1}$, $\nu$(C–N), 1595 cm$^{-1}$,

**Complex 2.** (Yield: 1.613 g; 71%) Anal. Calc. for $C_{26}H_{46}Br_3Cu_3N_4O_4$: C, 34.35; H, 5.10; N, 6.16%. Found: C, 34.31; H, 5.15; N, 6.09%. $\lambda_{max}$ (nm), [$\varepsilon_{max}$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)] (acetonitrile), 650 (335), 422(3231); IR: $\nu$(N–H), 3149 cm$^{-1}$, $\nu$(C–N), 1593 cm$^{-1}$.

### Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm$^{-1}$) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. Thermal analysis (TG-DTA) was carried out on a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate = 30 cm$^3$ min$^{-1}$). The samples were heated in an alumina crucible at a rate of 5 °C min$^{-1}$. Electrochemical studies were done using a PAR 273 potentiostat. The measurements were performed at 300 K in acetonitrile solutions containing 0.2 M TEAP and $10^{-3}$ M complex deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were a platinum wire, a platinum coil, and a SCE, respectively. The X-band EPR spectra were recorded using a Bruker E300 automatic spectrometer on solid samples at 293 K and frozen acetonitrile solutions at 77 K.

### Crystallographic data collection and refinement

Suitable single crystals of each complex were mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) radiation. The structures were solved using the Patterson method by using the SHELXS97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atoms. The hydrogen atoms of the water molecule were located from a difference map and kept fixed during refinement. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations were carried out using SHELXS 97,[16] SHELXL 97,[17] PLATON 99,[18] ORTEP-32[19] and WinGX system Ver-1.64.[20] Data collection and structure refinement parameters and crystallographic data for the two complexes are given in Table 1. The selected bond lengths and bond angles are summarized in Table 2.

**Table 1** Crystal data and structure refinement of complexes **1** and **2**

| | 1 | 2 |
|---|---|---|
| Formula | $C_{22}H_{36}Br_5Cu_3N_4O_4$ | $C_{26}H_{46}Br_3Cu_3N_4O_4$ |
| M | 1010.72 | 909.02 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C*2/*c* (No. 15) | *C*2/*c* (No. 15) |
| *a*/Å | 22.979(10) | 23.267(3) |
| *b*/Å | 10.157(4) | 11.0415(16) |
| *c*/Å | 15.902(7) | 15.727(2) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 118.944(4) | 122.907(2) |
| $\gamma$ (°) | 90 | 90 |
| *V*/Å$^3$ | 3248(2) | 3392.1(8) |
| Z | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 2.067 | 1.780 |
| $\mu$/mm$^{-1}$ | 8.131 | 5.433 |
| *F*(000) | 1960 | 1816 |
| R(int) | 0.043 | 0.047 |
| Total reflections | 6068 | 12417 |
| Unique reflections | 2239 | 3359 |
| $I > 2\sigma(I)$ | 1508 | 1873 |
| $R_1$, $wR_2$ | 0.0624, 0.2024 | 0.0712, 0.2423 |
| *T*/K | 296 | 293 |

**Table 2** Bond distances (Å) and angles (°) for complexes **1** and **2**

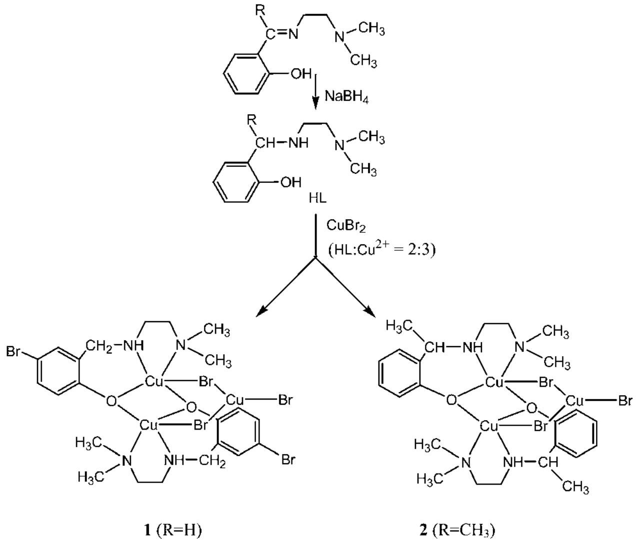
| | 1 | 2 |
|---|---|---|
| Cu(1)–O(1) | 1.959(7) | 1.965(6) |
| Cu(1)–N(1) | 1.994(10) | 2.007(9) |
| Cu(1)–N(2) | 2.047(10) | 2.048(9) |
| Cu(1)–O(1)$^a$ | 1.947(8) | 1.947(7) |
| Br(1)–Cu(1) | 2.701(2) | 2.6818(16) |
| Br(1)–Cu(2) | 2.392(2) | 2.3810(16) |
| Br(2)–Cu(2) | 2.346(4) | 2.420(7) |
| O(1)–Cu(1)–N(1) | 91.1(4) | 90.2(3) |
| O(1)–Cu(1)–N(2) | 165.5(4) | 162.7(3) |
| O(1)–Cu(1)–O(1)$^a$ | 76.6(3) | 77.4(3) |
| N(1)–Cu(1)–N(2) | 85.5(4) | 86.5(4) |
| N(1)–Cu(1)–O(1)$^a$ | 157.5(4) | 157.5(3) |
| N(2)–Cu(1)–O(1)$^a$ | 101.7(4) | 99.9(3) |
| Br(1)–Cu(1)–O(1) | 92.3(2) | 94.05(17) |
| Br(1)–Cu(1)–N(1) | 101.5(3) | 100.2(2) |
| Br(1)–Cu(1)–N(2) | 102.2(3) | 103.3(2) |
| Br(1)–Cu(1)–O(1)$^a$ | 97.8(2) | 99.32(17) |
| Cu(1)–Br(1)–Cu(2) | 106.96(8) | 106.02(7) |
| Br(1)–Cu(2)–Br(2) | 119.19(7) | 118.47(5) |
| Br(1)–Cu(2)–Br(1)$^a$ | 121.62(14) | 123.06(10) |
| Br(2)–Cu(2)–Br(1)$^a$ | 119.19(7) | 118.47(5) |

$^a$ Symmetry Operation: 1−x, y, 0.5−z for complex **1** and **2**.

## Results and discussion

### Synthesis of the complexes

The condensation of N,N-dimethylethylenediamine in 1 : 1 molar ratio with salicylaldehyde and 2-hydroxyacetophenone afforded the Schiff bases, 2-[(2-dimethylamino-ethylimino)-methyl]-phenol and 2-[1-(2-dimethylamino-ethylimino)-ethyl]-phenol, respectively, which on reduction with sodium borohydride readily produced the reduced Schiff bases, $HL^1$ and $HL^2$ (Scheme 1). Complexes **1** and **2** were prepared by reacting a methanol solution of copper(II)bromide and the ligands ($HL^1$) and ($HL^2$), respectively, in a 3 : 2 molar ratio.



**1** (R=H) **2** (R=CH₃)

**Scheme 1** Formation of the complexes.

### Infrared and electronic spectra

All four compounds show a moderately strong, sharp peak due to N–H stretching vibration at 3155, and 3149 cm$^{-1}$ for the complexes **1**, and **2**, respectively, which shows that an imine group of the Schiff base is reduced. The reduction of the imine group is also very clearly indicated by the absence of the strong band due to imine vibration which appears in the region of 1620–1650 cm$^{-1}$ for the complexes of the corresponding unreduced Schiff bases.[21]

The electronic spectra of these two compounds are recorded in acetonitrile solution. The electronic spectra show single absorption bands at 685 and 650 nm for compounds **1** and **2**, respectively. The positions of these bands are of typical d–d transitions in the square-pyramidal $Cu^{II}$ surroundings.[22] At a higher energy region, the ligand to metal charge transfer bands were located at 422 nm for both the complexes.

### Description of structures of complexes 1 and 2

Both complexes consist of mixed valent $Cu^{II}_2Cu^I$ trinuclear units which sit on a twofold axis. The structure $[Cu_2(Br–L^1)_2CuBr_3]\cdot 2H_2O$ (**1**) is shown in Fig. 1 together with the atomic numbering scheme.

The asymmetric unit consists of a $Cu^{II}$ atom, a ligand and half of a copper(I) tribromide unit. The copper(II) atom is five-coordinate being bonded equatorially to three donor atoms of one ligand $L^1$ together with a bridging oxygen atom $O(1)^a$ ($^a$ = 1−x, y, 0.5−z) from a second ligand $L^1$ that forms a di-μ-phenoxo bridge between the two $Cu^{II}$ centers. A copper(I) tribromide unit acts as an additional bridge between the copper(II) centers by coordinating weakly to the axial position of each copper(II) and thus forms the mixed-valent $Cu^{II}_2Cu^I$ trinuclear entity. Bond lengths in the $Cu^{II}$ coordination sphere are Cu(1)–O(1) 1.959(7) Å, Cu(1)–N(1) 1.994(10) Å and Cu(1)–N(2) 2.047(10) Å to the chelating terdentate ligand $L^1$ and Cu(1)–O(1$^a$) ($^a$ = 1−x, y, 0.5−z) 1.947(8) Å to the bridging oxygen in the equatorial plane. The axial Cu(1)–Br(1) 2.701(2) Å to the copper(I) tribromide unit is rather long as is expected for $Cu^{II}$ ion with Jahn–Teller distortion. The deviations of the coordinating atoms O(1), N(1), N(2), O(1$^a$) from the least-square mean plane through them are 0.052(8), −0.046(9), 0.042(11) and −0.047(8) Å, respectively. The deviation of copper(II) from the same plane is 0.2988(14) Å in the direction of the coordinated bromide Br(1) of $CuBr_3^{2-}$. The Addison parameter (τ)[23] of the penta-coordinated $Cu^{II}$ is 0.13

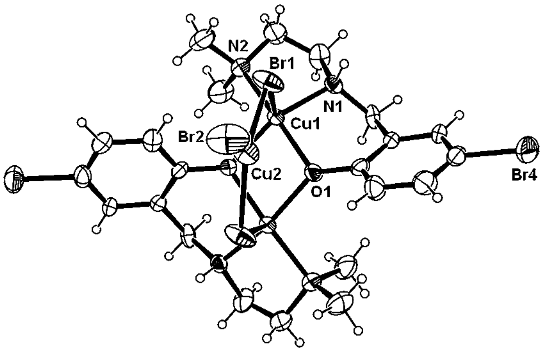


**Fig. 1** The structure of **1** with ellipsoids at 30% probability.

indicating that the geometry is nearly square pyramidal with a slight distortion towards being trigonal bipyramidal. The $CuBr_3$ unit is trigonal planar with Cu–Br bond lengths and Br–Cu–Br bond angles typical of the well known and characterized copper(I) anion,[24–26] $CuBr_3^{2-}$: Cu(2)–Br(1) 2.392(2) Å and Cu(2)–Br(2) 2.346(4) Å and ∠Br(1)–Cu(2)–Br(2) 119.19(7)° and ∠Br(1)–Cu(2)–Br($1^a$) ($^a$ = 1−x, y, 0.5−z) 121.62(14)°.

The molecular structure of **2**, $[Cu_2(L^2)_2CuBr_3]\cdot 2CH_3OH$ is equivalent to that of **1** as shown in Fig. 2 together with the atomic numbering scheme. The copper(II) atom is bonded in a similar fashion to that in **1** with three equatorial bonds to the ligand $L^2$, another one to an oxygen atom of a second ligand that forms the phenoxo bridge and one axial bond to a bromine Br(1) of a bridging copper(I) tribromide unit. The deviations of the coordinating atoms O(1), N(1), N(2), O($1^a$) from the least-square mean plane through them are 0.026(6), −0.023(8), 0.021(9) and −0.024(6) Å, respectively. The deviation of copper(II) from the same plane is 0.3252(11) Å towards the axially coordinated bromide ion Br(1). The overall geometry around copper(II) is nearly square pyramidal with Addison parameter (τ) = 0.08. Bond lengths in the $Cu^{II}$ coordination sphere are Cu(1)–O(1) 1.965(6) Å, Cu(1)–N(1) 2.007(9) Å and Cu(1)–N(2) 2.048(9) Å to the terdentate ligand $L^2$ with Cu(1)–O($1^a$) ($^a$ = 1−x, y, 0.5−z) 1.947(7) Å and Cu(1)–Br(1) 2.6818(16) Å to the copper(I) tribromide unit—all are very similar to those in **1**. The bond lengths in the trigonal planar $CuBr_3^{2-}$ are: Cu(2)–Br(1) 2.3810(16) and Cu(2)–Br(2) 2.420(7) Å. The Br–Cu–Br bond angles are: ∠Br(1)–Cu(2)–Br(2) 118.47(5)° and ∠Br(1)–Cu(2)–Br($1^a$) ($^a$ = 1−x, y, 0.5−z) 123.06(10)°.

It should be noted that the $[CuBr_3]^{2-}$ ion is well documented in the literature. However, there are only two previous examples in which the $CuBr_3^{2-}$ anion acts as a bridge between two copper(II) centres. Between these two examples, one is a polymeric chain compound, (1,4,8,11-tetraazacyclotetradecane)copper(II) tribromocuprate(I)[27] and the other is a discrete trinuclear compound[14] that has a very similar structure to that of **1** and **2**. Interestingly, this reported trinuclear compound was formed with a resorcinol-substituted trimethylethylenediamine ligand (L) which is very similar to those used for complexes **1** and **2** and the ligand has been brominated at the five-position of the aromatic ring during complex formation with $CuBr_2$, just like the present complex **1**. The bromination of the ligands is not surprising as $CuBr_2$ is an effective reagent for the bromination of activated aromatics.[28,29] The aryl bromination reaction produces cuprous bromide and hydrogen bromide as side-products (according to: Ar–H + 2CuBr₂ = Ar–Br + H–Br + 2CuBr). However, rather surprisingly bromination of the ligand ($L^2$) did not take place in the case of complex **2** indicating that substitution of the H-atom of the aldehyde by a methyl group prevents the ligand from bromination *i.e.* this bromination is very much susceptible to the constitution of the ligands. It should also be noted that the $CuBr_3^{2-}$ ion is also formed in complex **2** although no bromination takes place. Formation of the $CuBr_3^{2-}$ ion without any bromination has also been observed previously.[27] Although the mechanism of the formation of cuprous bromide is not certain in these cases, the solvent perhaps is responsible for its generation.

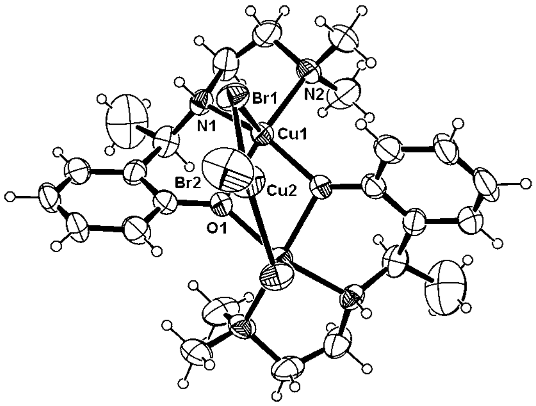


**Fig. 2** The structure of **2** with ellipsoids at 30% probability.

## Hydrogen bonding in the complexes and identification of a doubly hydrogen-bonded water dimer in 1

A very interesting feature of complex **1** is that there is a doubly hydrogen-bonded water dimer as shown in Fig. 3.

The two water molecules O(2W) and O($2W^b$) ($^b$ = 0.5−x, 1.5−y, 1−z) arrange themselves to form a non-linear doubly hydrogen-bonded water dimer [O(2W)–H(1W2)···O($2W^b$)]. The geometrical parameter of the water dimer is provided in Table 3. The O···O distance in the $(H_2O)_2$ dimer is 2.93(5) Å. For comparison, the corresponding values in regular ice, in liquid water, and in the vapor phase are 2.74, 2.85, and 2.98 Å, respectively.[30] The value in the linear water dimer which has been determined previously by X-ray crystal structure is 2.84 Å. To our knowledge no doubly hydrogen-bonded water dimer has been characterized by X-ray structural analysis. However, the dimensions of the doubly hydrogen-bonded water dimer have been proposed by a variety of density functional theories and the calculated dimensions (the O···O separation, 2.917 Å, H(1W)···O distance, 2.37 Å and ∠O–H(1W)···O is 115°) are in good agreement with the values found in the present compound (Table 3).

The amine hydrogen atom, H(1) of the trinuclear unit forms an intermolecular hydrogen bond, N(1)–H(1)···Br($1^c$) ($^c$ = 1−x, 2−y, 1−z) with the coordinated bromide (Br($1^c$)) of a neighboring molecule with N(1)···Br(1) 3.357(9) Å, H(1)···Br(1) 2.54 Å and ∠N(1)–H···Br(1) 149° to result in a zig-zag 1D supramolecular structure (Fig. 4). The trinuclear units of complex **2** are also connected by the H–bond, N(1)–H(1)···Br($1^d$) ($^d$ = 1−x, 2−y, −z) with dimensions, N(1)···Br(1) 3.352(8) Å, H(1)···Br(1) 2.52 Å and ∠N(1)–H···Br(1) 152° to form a 1D chain as in **1** (Fig. S1†). However, unlike **1** the solvent molecule is methanol in **2**.

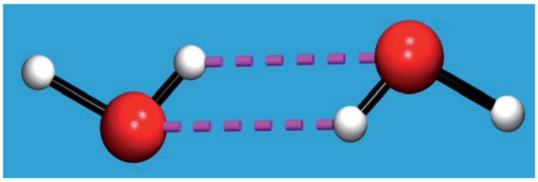


**Fig. 3** Hydrogen bonding water dimer in compound **1**.

**Table 3** Hydrogen bonding distances (Å) and angles (°) for the complexes **1** and **2**[a]

| Complex | D–H···A | D–H (Å) | A···H (Å) | D···A (Å) | ∠D–H–A (°) |
|---|---|---|---|---|---|
| **1** | O(2W)–H(1W2)···O(2W)[b] | 0.85 | 2.29 | 2.93(5) | 132 |
| | N(1)–H(1)···Br(1)[c] | 0.91 | 2.54 | 3.357(9) | 149 |
| **2** | N(1)–H(1)···Br(1)[d] | 0.91 | 2.52 | 3.352(8) | 152 |

[a] Symmetry Operation: [b] 0.5−x, 1.5−y, 1−z, [c] 1−x, 2−y, 1−z, [d] 1−x, 2−y, −z.

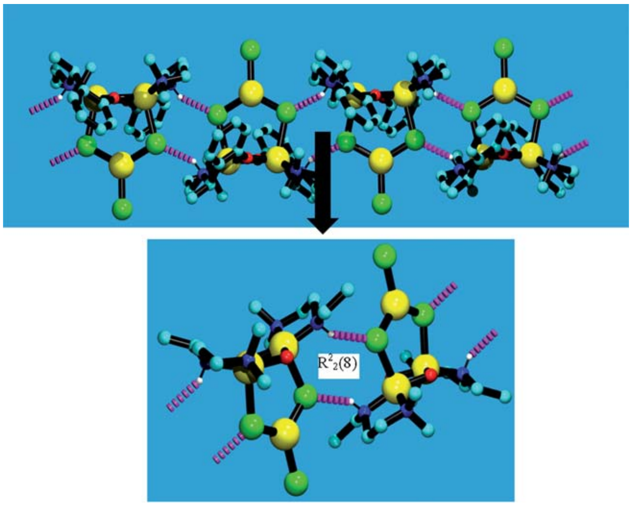


**Fig. 4** Hydrogen bonding polymeric structure of compound **1**.

### Thermal analysis

The simultaneous TG-DTA curves for complex **1** reveal that upon heating it starts to lose water molecules at 80 °C and becomes dehydrated at *ca.* 110 °C in a single step. The observed weight loss (3.9%) corroborates the loss of two water molecules (calcd. 3.5%). The compound does not show any color change on deaquation. Complex **2** starts to lose methanol molecules at *ca.* 55 °C and becomes desolvated at *ca.* 80 °C in a single step. The observed weight loss (7.1%) corroborates the loss of two methanol molecules (calcd. 7.0%). Both the complexes start to decompose at 150 °C. (Fig. S2 and S3†)

### Electrochemical study

The cyclovoltammograms of the copper complexes **1** and **2** in acetonitrile solution display irreversible reductive responses ($E_{pc}$ at −1.11 and −1.10 V, respectively) during cathodic scanning, attributed to the $Cu^{II}/Cu^{I}$ couple. During the anodic potential scan, both the complexes show an oxidative response at *ca.* −0.08 V with a very narrow width and high peak current and another quasi-reversible oxidative response at 1.12 and 1.17 V for **1** and **2**, respectively. On reversing the potential scan just after completion of the peak, the corresponding cathodic peak is observed at 0.90 and 0.92 V for complexes **1** and **2**, respectively (Fig. 5). The response at −0.08 V is typical of the anodic stripping of copper. Therefore, it may be inferred that both the copper(II) species undergo reduction to their respective $Cu^{I}$ complexes which subsequently undergo disproportionation to $Cu^{0}$ and $Cu^{2+}$. The oxidative responses around 1.2 V may be due to the $Cu^{II}/Cu^{III}$ couple.

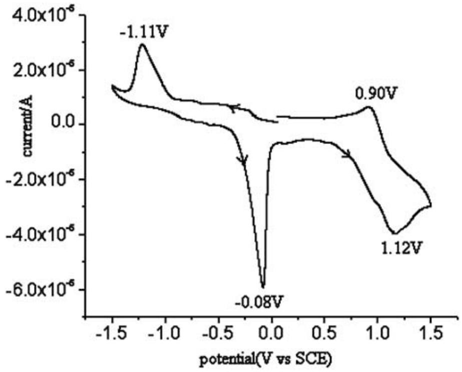


**Fig. 5** The cyclic voltammogram of **1** in acetonitrile solution (scan rate 100 mV s⁻¹).

### EPR studies

X-band EPR spectra were recorded for complexes **1** and **2** in solid state at room temperature and at 77 K. The spectra at 293 K show only one broad signal. This type of spectra unfortunately gives no information about the electronic ground state of the Cu(II) ion present in the complexes. At 77 K both the complexes are EPR-silent, suggestive of strong antiferromagnetic coupling between the two Cu(II) centres as is found for many similar phenoxo-bridged copper(II) dimers.[31] Considering the large bridging angles (>102°) in both complexes strong antiferromagnetic coupling is expected.[32] The EPR spectra of frozen acetonitrile solutions at 77 K of both the complexes show four-line spectrum which is indicative of localized unpaired electrons in the Cu(II) centre *i.e.* of Class I mixed valence complex (Fig. S4 and S5†). However, these signals seem to appear from the break-up of the trinuclear compound, at least partially upon dissolution in acetonitrile as was also found in the reported similar complex.[14]

## Conclusions

Two unusual mixed-valent trinuclear $Cu^{II}_2Cu^{I}$ complexes containing a copper(I) tribromide dianion as a bridging ligand have been synthesized using $CuBr_2$ and two tridentate reduced Schiff-base ligands $HL^1$ and $HL^2$. In both cases, a portion of $CuBr_2$ was reduced *in situ* to $CuBr_3^{2-}$ which acted as a bridging ligand between the two $Cu^{II}$ centers generating the very rare trinuclear $Cu^{II}_2Cu^{I}$ species. During complex formation, ligand $HL^1$ has been brominated at the five position of the aromatic ring but $HL^2$

did not undergo any such reaction indicating that substitution of the H-atom of the aldehyde by a methyl group prevents the ligand from bromination. In compound **1**, a doubly hydrogen-bonded water dimer, which is considered as one of the intermediates for the interchange of hydrogen atoms within the water dimer from theoretical calculations, has been identified. To our knowledge, to date there is no crystallographic evidence in the literature for the existence of such a water dimer. Thus, the present example should be valuable for verification of the results of theoretical calculations regarding water dimers.

## Acknowledgements

We thank CSIR, the Government of India for Junior Research Fellowship to A. Biswas, Sanction No. [09/028(0717)/2008-EMR-I], and DST FIST for financial support for the X-ray diffraction facility. We are also thankful to Prof. Shyamal Kumar Chattopadhyay, Bengal Engineering and Science University for cyclic voltammetry experiments.

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