# Synthesis, Crystallographic and Spectroscopic Studies of Dimeric $Cu^{I}$ Complexes with Schiff-Base-Containing Triazole Ligands

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New $Cu^{I}$ complexes of the Schiff-base-containing triazole ligands *N*-[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (ClPhtrz) and *N*-[(*E*)-phenylmethylidene]-4*H*-1,2,4-triazol-4-amine (Phtrz) have been synthesised and characterised. Depending on the reaction conditions ClPhtrz forms two different dimeric complexes **1** and **2**. X-ray crystallography revealed that each copper centre exhibits a planar trigonal coordination in **1**, while the tetrahedral coordination sphere of the copper centre in **2** is completed by a solvent molecule. In dimeric complex **3** the tetrahedral coordination of the $Cu^{I}$ ions is formed by two monodentate and two bidentate (bridging) Phtrz ligands. Complexes **1**–**3** are unstable and easily lose coordinating and/or solvating acetonitrile molecules giving **4** (from **1** and **2**) and **5** (from **3**). On the basis of ESI MS and $^{1}H$ NMR and UV/Vis spectroscopy, it was shown that dimeric complexes **1**–**5** do not survive upon dissolution and dissociate rapidly forming mainly a 1:2 monomeric complex, along with a minor 1:1 complex.


## Introduction

Binuclear and multinuclear transition metal complexes containing two or more metal centres bridged by multidentate ligands have been the subject of great interest in coordination chemistry.[1] Particular interest has been focused on five-membered aromatic nitrogen heterocycles (azoles) as ligands because of their ability to form complexes in which two metal centres are bridged by one, two or three azole groups.[1,2] The most studied bridging ligand of this type is the pyrazolate anion.[3,4] Recently, copper(I) complexes containing pyrazolate ligands have been extensively studied due to their ability to act as selective catalysts in the oxidation of organic substrates such as aliphatic and aromatic amines.[5,6] Different pyrazoles modified by introducing substituents on the heterocyclic ring have been involved in these studies.[5–7] Depending on the ring substituent copper(I) forms a large series of derivatives: neutral 1-D polymers $[Cu(pz)]_{\infty}$ for unsubstituted pyrazole,[8] cyclic trimers $[Cu(pz')]_3$ [pz′ = 3,5-dimethyl-4-nitropyrazole (Hdmnpz),[6] 3,5-dimethylpyrazole (Hdmpz),[9] 3,5-diphenylpyrazole (Hdppz),[10] 3,4,5-trimethylpyrazole (tmpzH)[11]] and cyclic neutral $[Cu(dppz)]_4$ [5] and anionic tetramers $[Cu_4(dmnpz)_6]^{-2}$.[6] However, the most frequently observed structure is a dimer $[Cu_2(pz'')_2X_n]$ [where pz″ = dmpz, dcmpz, dppz, dmnpz (Hdcmpz = 3,5-dicarbomethoxy pyrazole); X = isocyanide, pyridine, $PPh_3$].[5–8,12] The common feature of all these compounds is that pyrazole ligands are always connected to two adjacent copper(I) ions in an $N^1,N^2$-bridging mode.

Similar coordination properties could be expected for $N^4$-substituted 1,2,4-triazole as a ligand. In fact, a number of coordination compounds with this group of ligands coordinated to transition metal ions have been reported.[2] However, to the best of our knowledge, $Cu^{I}$ complexes of $N^4$-substituted 1,2,4-triazoles are unknown. A limited number of structurally characterised systems based on copper(I) and deprotonated 1,2,4-triazolates have been reported.[13,14] In these systems the nitrogen atoms of the triazolate anion are coordinated to three different $Cu^{I}$ ions, forming polynuclear species; copper(I) complexes with a 1,2,4-triazole moiety as a part of an organic ligand have also been reported.[15–18]

In this work we describe the synthesis of dimeric copper(I) complexes with Schiff-base-containing triazole ligands (Scheme 1). The complexes were characterised by X-ray crystallography. The results are compared with those reported for pyrazole-bridged $Cu^{I}$ dimers. We also report the results of our study on the behaviour of these systems upon dissolution in acetonitrile.

## Results and Discussion

Depending on the experimental conditions two products were obtained from the reaction between $[Cu(CH_3CN)_4](ClO_4)$ and *N*-[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (ClPhtrz) in acetonitrile. Colourless, needle-shaped crystals of $[Cu_2(ClPhtrz)_4](ClO_4)_2\cdot 2CH_3CN$ (**1**) were grown overnight from a concentrated solution. When the crystallisation was carried on from a very dilute solution light-yellow, prismatic crystals of $[Cu_2(ClPhtrz)_4$-

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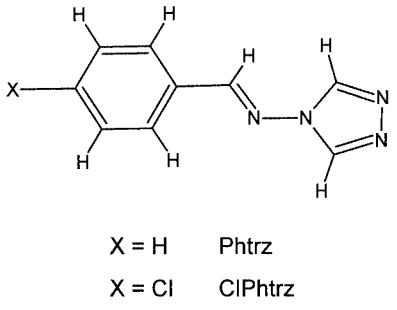


Scheme 1

$(CH_3CN)_2](ClO_4)_2 \cdot CH_3CN$ (**2**) were formed after a much longer time (about 1 month).

The main difference between dimers **1** and **2** is the coordination mode around each copper atom: in **1** the metal ion is coordinated by three triazole ligands whereas in **2** additional coordination of an acetonitrile molecule gives a tetrahedral environment for the copper(I) ion.

The procedure described above is valid for a 1:2 metal-to-ligand ratio or with an excess of ligand in solution. When an excess of metal ion is used only **2** is formed. In the case of $[Cu_2(Phtrz)_6](ClO_4)_2 \cdot 2CH_3CN$ (**3**) the complex is formed in any metal-to-ligand molar ratio. When crystals of **1**−**3** are removed from acetonitrile solution they rapidly lose acetonitrile molecules (within a few minutes; see Exp. Sect.). In this way crystals of **1** and **2** give $[Cu_2(ClPhtrz)_4](ClO_4)_2$ (**4**), whereas **3** gives $[Cu_2(Phtrz)_6](ClO_4)_2$ (**5**). Crystals of **1**−**3** were characterised crystallographically, while complexes **4** and **5** were studied by spectroscopic methods (UV, $^1H$ NMR, ESI-MS).

## Structural Studies

### *X-ray Structure of 1*

The molecular structure of **1** is shown in Figure 1. It consists of a discrete binuclear copper(I) centre bridged by two $N^1,N^2$-coordinated ClPhtrz ligands. Surprisingly, an additional triazole ligand is bound to the $Cu^I$ ion in a monodentate fashion. This unprecedented coordination mode results in almost *planar* tricoordinate, trigonal coordination environment with a small deviation [0.073(2) Å] of the metal centre from the plane defined by the N11, N12A and N21 atoms. The non-bonding Cu···Cu distance is equal to 3.508(1) Å. A slight deviation from planarity toward a chair-like configuration is observed due to the asymmetric triazole ligands forming a six-membered Cu-$[N\text{-}N]_2$-Cu ring. The copper atoms are located only 0.202(6) Å off the mean plane defined by four triazole nitrogens, well below the value reported for the $Cu^I$-pyrazole system (0.62 Å).[5] Furthermore, the Cu-N-N-Cu dihedral angle of 13.8(4)° is considerably smaller than that observed (41.7°) for the pyrazole-containing complex $[Cu(dppz)(RNC)]_2$ with the same conformation.[5] In the latter compound it has been suggested that the large value of the dihedral angle is due to the presence of steric interactions between the phenyl groups in the 3,5-positions of the ligand and the cyclohexyl isocyanide groups attached to the copper ions.

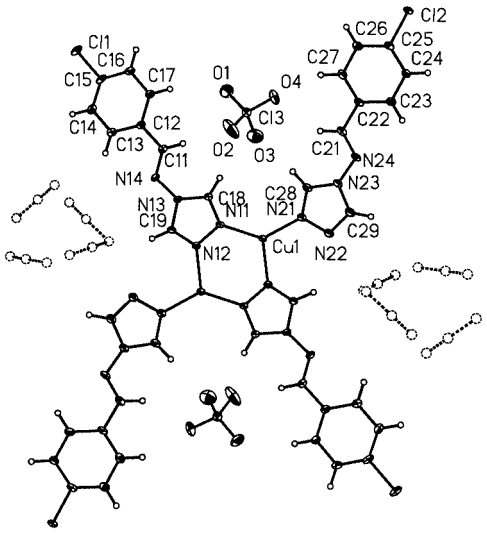


Figure 1. Molecular structure of the dimeric compound **1**; selected bond lengths [Å] and angles [°]: Cu1···Cu1a 3.508(1), Cu1−N11 1.948(3), Cu1−N21 1.937(3), Cu1−N12a 2.012(3); N21−Cu1−N11 131.57(13), N21−Cu1−N12 113.12(13), N11−Cu1−N12 114.89(12), Cu1−N11−N12−Cu1 13.8(4)

Because all the ClPhtrz ligands are coordinated in an almost planar *E* configuration the resulting binuclear unit can be described as an X-shaped dimer. These X-shaped dimers strongly influence the packing of the discrete units in the crystal (Figure 2). The dimers form sheets with an average distance of 3.04 Å between the planes. The chlorine atoms of the ligands (see Scheme 1) are located above and below each copper(I) ion [Cu···Cl = 3.129(1) and 3.242(1) Å, respectively; Cl···Cu···Cl = 158.44(3)°] and are believed to stabilise the packing. As a result rhomboidal channels, defined by the separation of the centre of Cu-$[N\text{-}N]_2$-Cu fragments, are observed parallel to the crystallographic [100] direction with a cross-section of about 15 × 15 Å. The $ClO_4^-$ anions and solvent (acetonitrile) molecules are positioned in these channels (see Figure 2). Location of the non-coordinating solvent molecules in the channels makes them potentially labile and easy to remove from the crystals. The free-pore volume of the unit cell was estimated to be 696 $Å^3$ (25.2% of the total) with the PLATON[19] program (squeeze).

A trigonal environment of $Cu^I$ such as that observed in **1** is rare for dinuclear compounds, but not unknown, and has been reported previously for complexes with pyrazole bridges.[5−7,12,20] However, in all those systems at least one other ligand coordinates to the copper ion. Three-coordinate copper(I) has also been detected in polymeric systems with different ligands.[14,21,22] The dimers derived from tris(pyrazolyl)borate[23] and tris(imidazole)methoxymethane[24] are rare examples of tricoordinate $Cu^I$ complexes without bridges between the metals.

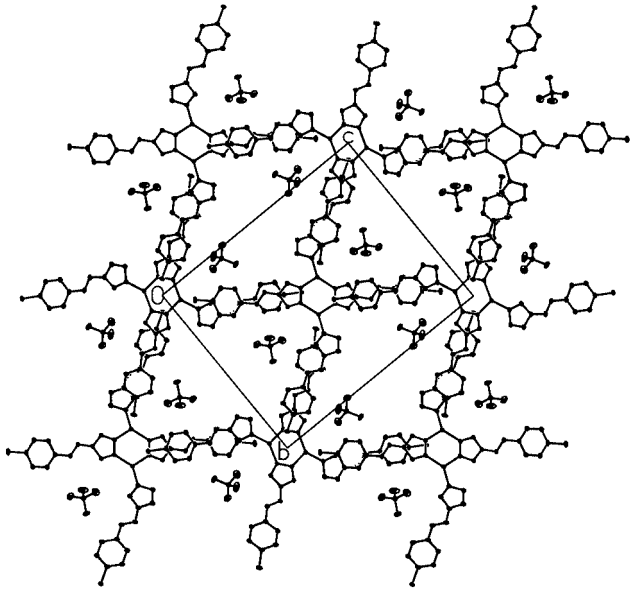

Figure 2. View of **1** along the crystallographic axis *a* illustrating the channels; the disordered acetonitrile molecules have been omitted for clarity

### *X-ray Structure of 2*

When a dilute solution of $[Cu(CH_3CN)_4](ClO_4)$ and ClPhtrz ligand in acetonitrile was allowed to stand for a long time (about one month) light-yellow crystals of **2** were formed. The molecular structure of **2** is shown in Figure 3. The crystals of **2** contain discrete dimeric complexes of $Cu^I$ bridged by two ClPhtrz ligands. Another triazole ligand is bonded in a monodentate fashion to each copper atom, as was observed for **1**. A molecule of acetonitrile completes the distorted tetrahedral coordination geometry. The increased steric crowding around the metal atoms considerably disturbs the planarity of the six-membered cycle defined by two copper and the four nitrogen atoms of bridging ligands. The observed chair-like conformation in **2** is more pronounced than in **1** and the Cu-N-N-Cu torsion angle is 34.2(3)°. The copper atoms are located 0.516(5) Å out of the plane defined by the four nitrogens of the bridging triazole ligands. Each metal ion is moved towards the coordinated acetonitrile molecules. The observed Cu−N distances [1.990(3) to 2.083(3) Å] lie well within the range for tetracoordinate copper(I) complexes[6,25] and are about 0.1 Å longer than the Cu−N bond lengths observed in **1** and other tricoordinate $Cu^I$ structures.[5−8,12] The nonbonding Cu···Cu distance increases from 3.508(1) Å in **1** to 3.685(1) Å in **2**. The same tendency was reported previously for tri- and tetracoordinate pyrazole-containing dimers of $Cu^I$.[6]

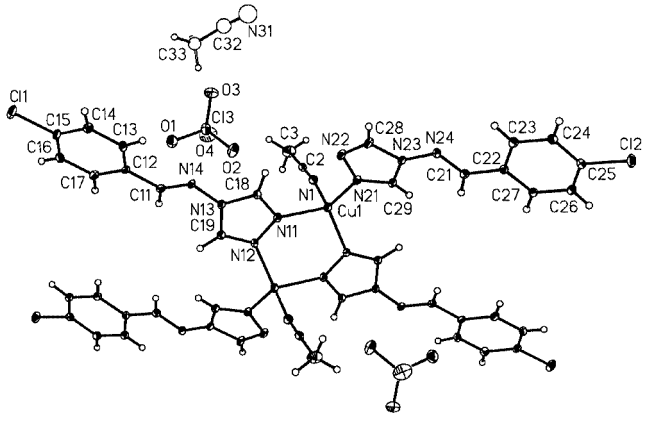


Figure 3. Molecular structure of the dimeric compound **2**; selected bond lengths [Å] and angles [°]: Cu1···Cu1a 3.685(1), Cu1−N11 2.082(3), Cu1−N21 1.991(3), Cu1−N12a 2.028(3), Cu1−N1 2.013(3); N21−Cu1−N1 116.02(11), N21−Cu1−N12 120.68(10), N1−Cu1−N12 102.33(10), N21−Cu1−N11 106.58(10), N1−Cu1−N11 100.12(10), N12−Cu1−N11 109.16(10), Cu1−N11−N12−Cu1 34.2(3)

### *X-ray Structure of 3*

Another tetracoordinate complex **3** was obtained when the 4-chlorophenyl group in the triazole ligand was replaced by a phenyl substituent. A view of the molecule is shown in Figure 4. Compound **3** is a dinuclear $Cu^I$ complex containing two bridging triazole groups as in the case of **1** and **2**. Surprisingly two additional triazole ligands are coordinated to each copper(I) ion in a monodentate fashion to give a coordination number of four, with all four coordination sites being occupied by triazole ligands. The more-regular tetrahedral surrounding of the $Cu^I$ centres causes a less-pronounced chair-like configuration of the Cu-$[N\text{-}N]_2$-Cu ring and, in fact, the copper atoms are located only 0.152(3) Å out of the plane defined by the bridging triazole nitrogens. It is worth noting that this value matches well

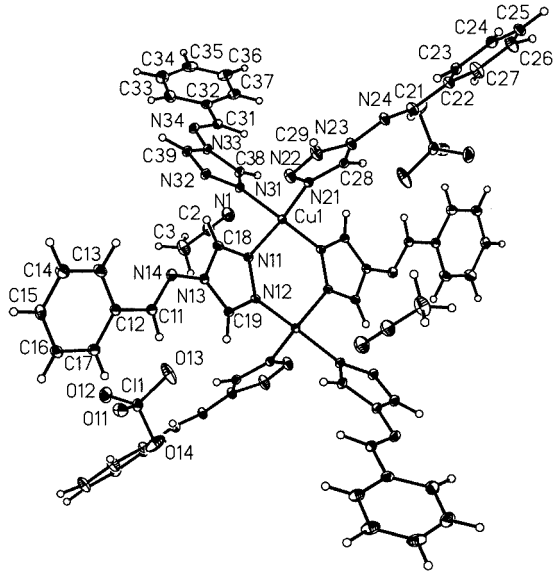


Figure 4. Molecular structure of the dimeric compound **3**; selected bond lengths [Å] and angles [°]: Cu1···Cu1a 3.6606(5), Cu1−N11 2.0737(15), Cu1−N21 2.0376(16), Cu1−N31 2.0220(16), Cu1−N12 1.9923(15); N12−Cu1−N31 119.72(6), N12−Cu1−N21 113.46(6), N31−Cu1−N21 107.02(6), N12−Cu1−N11 112.01(6), N31−Cu1−N11 102.58(6), N21−Cu1−N11 99.71(6), Cu1−N11−N12−Cu1 −10.3(2)

with the value observed in the tricoordinate compound **1**, although the Cu−N bond lengths [1.992(2) to 2.074(2) Å] and the nonbonding Cu···Cu distance [3.6606(5) Å] are closer to those observed in **2**.

### Solution Studies

#### *Mass Spectrometry*

Formation of monomeric 1:2 and 1:1 complexes from the dimer has been observed by ESI mass spectrometry upon dissolution of original samples of **1**, **2** or **4**. Peaks at *m*/*z* (%) = 475.3 (100), 309.9 (70), 206.6 (10) and 144.5 (10) are observed in the ESI mass spectra independently of the sample used (see above). The isotopic peaks are separated by 1.0 amu, revealing a charge state of +1 for the corresponding ions. Therefore, the peaks at 475.3 and 309.9 correspond to $[Cu(ClPhtrz)_2]^+$ and $[Cu(ClPhtrz)(CH_3CN)]^+$ species, respectively. No peaks characteristic of the dimer entities could be detected in the ESI-MS spectra. The formation of the 1:2 and 1:1 complexes from the pure dimeric complexes should be accompanied by the release of both free ligand and free $Cu^{I}$ cation. Indeed, weak peaks at 206.6 (for $[ClPhtrz]^+$) and at 144.5 (for $[Cu(CH_3CN)_2]^+$) are observed during the ESI-MS analysis.

Unexpected ESI-MS spectra were obtained for complexes **3** and **5**. Despite the different metal to triazole ligand ratio in dimer **3** (2:6) than in dimers **1** and **2** (2:4) the fragmentation led to the same pattern in the mass spectrum, i.e. a monomeric 1:2 species at 406.9 (attributed to $[Cu(Phtrz)_2]^+$) and a 1:1 species at 276.2 (attributed to $[Cu(Phtrz)(CH_3CN)]^+$). Dissociation of the parent dimer results in two additional peaks at 172.2 and 144.1 corresponding to free ligand $[Phtrz]^+$ and solvated copper(I) cation $[Cu(CH_3CN)_2]^+$, respectively

On the basis of the electrospray mass spectrometry results it can be concluded that the dimeric complexes $[Cu_2(ClPhtrz)_4]^{+2}$, $[Cu_2(ClPhtrz)_4(CH_3CN)_2]^{+2}$, and $[Cu_2(Phtrz)_6]^{+2}$ do not survive upon dissolution and dissociate rapidly to mainly form a 1:2 monomeric complex, along with a minor 1:1 complex. Similar phenomena have been observed for other $Cu^{I}$ dimers.[23,24,26]

#### *Spectroscopic Studies*

The competitive equilibria related with dissociation of the complexes can also be observed by UV/Vis and $^1H$ NMR spectroscopy. The UV spectra of **4** or **5** in acetonitrile consist of two major bands: one centred at 210 nm and the other at 283 nm. Both bands contain several shoulders. Comparison of the spectrum obtained for the complex with that of the free ligand reveals a close similarity of the lower energy bands for each of the systems under study. In fact, these spectra are superimposable in this region after normalisation of the absorbance. The band at 210 nm can be reproduced by a superposition of the spectra of an appropriate free ligand and that of $[Cu(CH_3CN)_4]^+$ (Figure 5). Evidently, at the concentration level of electronic spectroscopy the overwhelming excess of acetonitrile ligand causes the complete substitution of Phtrz or ClPhtrz by $CH_3CN$ in the first coordination sphere of the copper(I) ion.

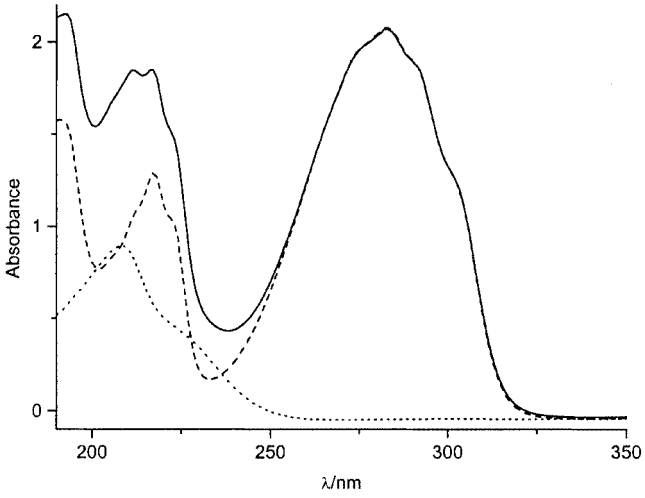


Figure 5. Electronic spectra of acetonitrile solutions of **4** (solid line), ClPhtrz (dashed line), and $[Cu(CH_3CN)_4]ClO_4$ (dotted line)

The $^1H$ NMR spectra of saturated solutions of the complexes in $CD_3CN$ are consistent with the labile character of the complexes and also reveal the dissociation of the dimers upon dissolution in acetonitrile. The number of signals indicates the degeneracy of the respective resonances, i.e. there is only one peak for the azomethine group (N=CH), the triazole (trz) ring and each type of aryl ring proton (Figure 6). Differentiation of the chemical shifts is expected particularly for these protons that are in the vicinity of the coordination sites if the solid-state structure of the complex is retained in solution. Although the number of peaks is the same for both the complex and for the appropriate free ligand, the positions of the peaks differ considerably [**5** (Phtrz): δ = 8.869 (8.844) ppm (N=CH), 8.864 (8.791) (trz); **4** (ClPhtrz): δ = 8.845 (8.825) (N=CH), 8.838 (8.777) (trz) ppm; $CD_3CN$, 233 K]. This suggests an equilibrium between coordinated and free ligand in solution. Such an equilibrium, which is fast on the NMR timescale, causes an averaging of the chemical shifts. The considerable broadening of the triazole signal of the complex at low temperature is also consistent with the presence of a fast chemical exchange between coordinated and uncoordinated ligand. Titration of the complex solution with free ligand does not result in the appearance of any additional signals. Instead, it gradually shifts the position of all the peaks to those of the free ligand (Figure 6).

## Conclusion

The results discussed here demonstrate that reaction between $[Cu(CH_3CN)_4](ClO_4)$ and Schiff-base-containing triazole ligands in acetonitrile gives various dimeric copper(I) complexes. The composition and geometry of these complexes depend on the reaction conditions (compounds

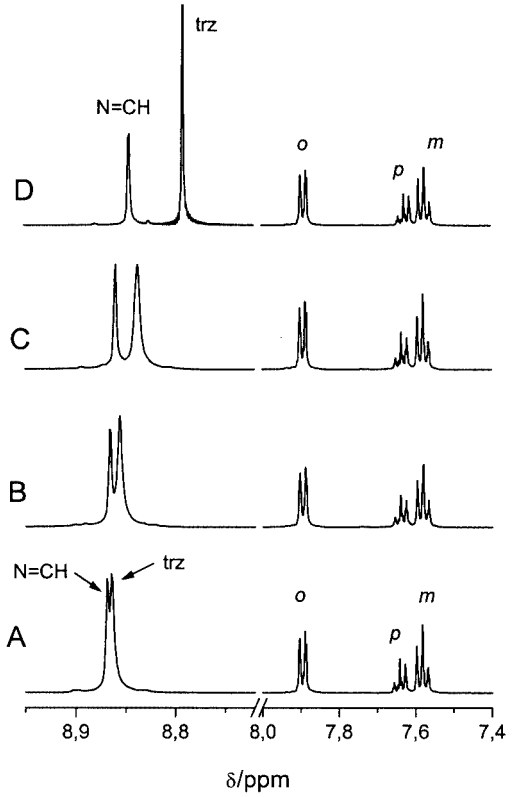


Figure 6. $^1$H NMR spectra (500 MHz, $CD_3CN$, 233 K) of a saturated solution of **5** (A), mixtures of **5** and Phtrz (B and C) and Phtrz (D); assignments: N=CH − azomethine proton, trz − triazole protons, *o*, *m*, *p* − *ortho*, *meta*, *para* protons of phenyl substituent

**1** and **2**) and/or type of ligand used (**3**), as confirmed by single-crystal X-ray diffraction. Our studies show that Schiff-base-containing triazole ligands coordinate simultaneously in the monodentate and bidentate mode. The latter results in them bridging two metal centres. This is in contrast with pyrazolylcopper(I) complexes, in which a pyrazole molecule acts solely as a bridging ligand. All studied crystals are unstable and lose acetonitrile molecules (coordinated and solvated) forming **4** (from **1** and **2**) and **5** (from **3**). Regardless of the stoichiometry, the complexes dissociate rapidly to form monomeric species upon dissolution, unlike the pyrazole-bridged dimers, which retain their dimeric structure in solution.

## Experimental Section

**General Remarks:** ESI MS were performed on a Finnigan Mat type TSQ700 mass spectrometer. $^1$H NMR spectra were recorded on a Bruker AM500 spectrometer in $CD_3CN$. UV spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer. Elemental analyses were carried out at the Microanalytical Laboratory of this University.

**Starting Materials:** Commercially available solvents, hydrazine monohydrate, formic acid, 4-chlorobenzaldehyde and benzaldehyde (Fluka) were used without further purification. $[Cu(CH_3CN)_4](ClO_4)$,[27] 4-amino-1,2,4-triazole,[28] and *N*-[(*E*)-(4-chlorophenyl)-methylidene]-4*H*-1,2,4-triazol-4-amine (ClPhtrz)[29] were prepared according to literature procedures. All reactions with $Cu^I$ were carried out under a dry nitrogen atmosphere using standard Schlenk techniques.

**Caution.** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compound should be prepared and handled with much care!*

***N*-[(*E*)-(phenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (Phtrz):** An ethanolic solution (20 mL) of benzaldehyde (2.12 g, 20 mM) was added to a warm ethanolic solution (25 mL) of 4-amino-1,2,4-triazole (1.69 g, 20 mM) and the resulting solution was refluxed for four hours. The reaction mixture was then cooled to room temperature. The solution was evaporated to dryness under reduced pressure, and the crude product was recrystallised from ethanol/diethyl ether. The resultant white solid was filtered off, washed with diethyl ether and dried under vacuum. Yield 2.55 g, 74%; M.p. 144 °C (subl.). $C_9H_8N_4$ (172.2): calcd. C 62.78, H 4.68, N 32.54; found C 62.71, H 4.66, N 32.54. MS: *m*/*z* = 173 $[MH]^+$. $^1$H NMR (500 MHz, $CD_3CN$, 298 K): δ = 8.84 (s, 1 H, N=CH) 8.74 (s, 2 H, triazole) 7.92 (m, 2 H, *ortho*) 7.64 (m, 1 H, *para*) 7.59 (m, 2 H, *meta*) ppm.

**$\{[Cu_2(ClPhtrz)_4](ClO_4)_2\}\cdot 2CH_3CN$ (1):** A solution of $[Cu(CH_3CN)_4](ClO_4)$ (164 mg, 0.5 mmol) in acetonitrile (5 mL) was added dropwise to an acetonitrile solution (15 mL) of ClPhtrz (207 mg, 1 mmol). The colourless solution was stirred for 15 min, then the volume of the solution was reduced by half over 4 hours in a stream of $N_2$. The resultant solution was allowed to stand overnight at room temperature, affording colourless, needle-shaped crystals of **1** which were collected by filtration, washed with acetonitrile and diethyl ether. The crystal used in the X-ray structure determination was selected from this sample. The molecular formula for **1** was established on the basis of X-ray crystallographic measurement (see Table 1). Elemental analysis data: vide infra.

**$\{[Cu_2(ClPhtrz)_4(CH_3CN)_2](ClO_4)_2\}\cdot CH_3CN$ (2).** ***Method A*:** The compound was obtained as described for **1**, but no reduction of solvent volume was done. The colourless solution was allowed to stand at room temperature for about one month. During this time light-yellow, prismatic crystals of **2** were formed.
***Method B*:** The compound was obtained as described in *method A*, but ClPhtrz (104 mg, 0.5 mmol) and $[Cu(CH_3CN)_4](ClO_4)$ (164 mg, 0.5 mmol) were used. After standing overnight at room temp. light-yellow, prismatic crystals were formed. The measured lattice parameters for the crystals obtained by *method B* were identical to those detected for **2** obtained by *method A*. The molecular formula for **2** was established on the basis of X-ray crystallographic measurement (see Table 1). Elemental analysis data: vide infra.

**$\{[Cu_2(Phtrz)_6](ClO_4)_2\}\cdot 2CH_3CN$ (3):** A solution of $[Cu(CH_3CN)_4](ClO_4)$ (164 mg, 0.5 mmol) in acetonitrile (10 mL) was added to an acetonitrile solution (10 mL) of Phtrz (172 mg, 1 mmol). The resultant light-yellow solution was stirred for 15 min, then about 4 mL of solvent was removed under a stream of dinitrogen. After 4 hours light-yellow crystals of **3** had formed. The crystals were filtered off, washed with acetonitrile and diethyl ether. The molecular formula for **3** was established on the basis of X-ray crystallographic measurement (see Table 1). Elemental analysis data: vide infra.

During the storage of the complexes even in a sealed vial under a dinitrogen atmosphere cracking of the crystals of **1** and **3** was detected, whereas crystals of **2** undergo complete powdering and become white. The analysis of the resulting products **4** and **5** indicated the loss of acetonitrile molecules, either independently solvated (**1** and **3**) or coordinated (**2**).[30] For **4**: $C_{36}H_{28}N_{16}Cl_6Cu_2O_8$ (1152.5):

Table 1. Crystal data and structure refinement

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{36}H_{28}N_{16}O_8Cl_6Cu_2{\cdot}2H_3CCN$ | $C_{40}H_{34}N_{18}O_8Cl_6Cu_2{\cdot}H_3CCN$ | $C_{54}H_{48}N_{24}O_8Cl_2Cu_2{\cdot}2H_3CCN$ |
| Molecular weight | 1234.63 | 1275.68 | 1441.25 |
| $T$ (K) | 100(2) | 100(2) | 100(2) |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 7.0205(8) | 9.3882(12) | 11.1666(10) |
| $b$ (Å) | 17.9760(14) | 11.0484(17) | 12.3458(11) |
| $c$ (Å) | 22.0379(17) | 13.5942(19) | 12.6112(11) |
| α (°) | 90 | 76.384(13) | 68.604(8) |
| β (°) | 96.995(8) | 71.686(12) | 88.132(7) |
| γ (°) | 90 | 84.439(12) | 80.316(8) |
| $V$ (Å$^3$) | 2760.5(4) | 1300.6(3) | 1594.9(2) |
| $Z$ | 2 | 1 | 1 |
| $D_c$ (Mg·m$^{-3}$) | 1.485 | 1.629 | 1.501 |
| μ (mm$^{-1}$) | 1.125 | 1.197 | 0.827 |
| $F$(000) | 1248 | 646 | 740 |
| Crystal size (mm) | 0.15 × 0.12 × 0.12 | 0.17 × 0.15 × 0.13 | 0.52 × 0.35 × 0.33 |
| θ range for data collection (°) | 3.17−28.51 | 3.35−28.36 | 3.64−28.37 |
| Ranges of $h,k,l$ | −9→6, −24→23, −29→29 | −12→11, −14→8, −18→18 | −14→8, −16→16, −16→16 |
| Reflections collected | 18818 | 9065 | 10983 |
| Independent reflections | 6492 (0.0406) | 5716 (0.0305) | 7019 (0.0200) |
| Data/parameters | 6492/320 | 5716/414 | 7019/562 |
| GOF($F^2$) | 1.099 | 1.021 | 1.047 |
| Final $R_1/wR_2$ indices [$I > 2\sigma(I)$] | 0.0579/0.1526 | 0.0456/0.1077 | 0.0346/0.0812 |
| Min/max. transmission factor | --- | --- | 0.6731/0.7720 |
| Extinction coefficient | --- | --- | 0.0021(5) |
| Largest diff. peak/hole (e·Å$^{-3}$) | 1.162/−0.462 | 1.416/−0.983 | 0.448/−0.500 |

calcd. C 37.52, H 2.45, N 19.44; (obtained from **1**) C 37.74, H 2.45, N 19.39; (obtained from **2**) C 37.38, H 2.47, N 19.43. For **5**: $C_{54}H_{48}Cl_2Cu_2N_{24}O_8$ (1359.1): calcd. C47.72, H 3.56, N 24.73; found C47.63, H 3.66, N 24.41. The elemental analytical data for **1** and **2** were analogous to that obtained for **4**, while elemental analysis showed that dried **3** and **5** were the same species.

**X-ray Crystallographic Study:** Crystal data of **1**−**3** are given in Table 1, together with refinement details. All measurements of crystals were performed at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation. The crystals were positioned 65 mm from the CCD camera. 612 frames were measured at 0.75° intervals with a counting time in the range 10−20 sec. Accurate cell parameters were determined and refined by least-squares fit of 1900 to 3100 of the strongest reflections. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) (formerly Kuma Diffraction Wrocław, Poland) programs. The data were corrected for Lorentz and polarisation effects. An analytical absorption correction was also applied for **3**. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o. o. (formerly Kuma Diffraction Wrocław, Poland) programs. The structures were solved by direct methods (program SHELXS-97[31]) and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXL-97[32] programs. In the studied crystals the acetonitrile solvent molecules are disordered, with occupancy parameters of 0.25 in **1**, and 0.5 in **2**, whereas in **3** one molecule has two different orientations in an 0.84:0.16 ratio. The $ClO_4^-$ ion in **3** is also slightly disordered, with two distinct orientations approximately in a 0.93:0.07 ratio. Non-hydrogen atoms were refined with anisotropic displacement parameters except for the disordered solvent molecules in **1** and **2** and the minor components of the disordered acetonitrile molecule and perchlorate ion. Hydrogen atoms were included from the geometry of the molecules and Δρ maps. During refinement their parameters were fixed.
CCDC-198765−198767 (**1**−**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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