

Two Different Compounds Formed from Copper(II) tetrafluoridoborate and [1,2,4]triazolo[1,5-a]pyrimidine. Synthesis, Spectroscopy and Single-Crystal Structures

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Abstract Two coordination compounds copper(II) with tetrafluoridoborate as the anion and [1,2,4]triazolo[1,5-a]pyrimidine (abbreviated as tp) as the ligand are presented, together with their crystal structure and spectroscopic properties. A light blue compound $[\text{Cu}(\text{tp})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (**1**) with a tetragonal chromophore and a dark blue compound $[\text{Cu}(\text{tp})_5](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (**2**) are formed from the same batch. Compound (**2**) has a quite unusual geometry for Cu(II) with just 5 tp ligands, homoleptically coordinated to the metal ion. Both compounds show interesting hydrogen-bond interactions in the solid state, where coordinated water is intramolecularly bound to non-coordinated N atoms of tp (in **1**), and methanol is attached to the anion (in **2**).

Keywords Copper · Crystal structure ·
Triazolopyrimidine

Introduction

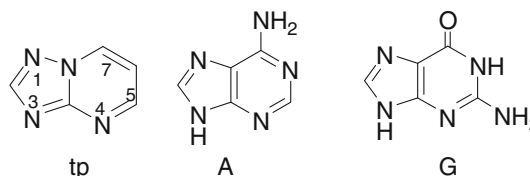
Triazolopyrimidines (IUPAC recommended name: [1,2,4]triazolo[1,5-a]pyrimidines) are versatile ligands, as they have several nitrogen atoms with accessible lone pairs to bind to Lewis acids like metal ions.

These ligands have a fused 5-membered and 6-membered ring system and as such resemble the nucleobases adenine and guanine of DNA (Scheme 1). A variety of coordination compounds of metals salts with the parent ligand and other triazoles is already known and reviewed [1, 2]. Previous work from this laboratory has mainly been focusing on methyl substituted tp-based ligands [2–11]. Also other research groups have been studying this type of ligands [12–17]. Triazoles and pyrimidines may in some cases act as bridging ligands between metals, but they may also coordinate monodentately [18–20].

In a more recent papers we reported on transition-metal compounds with the ligands (5,7-diethyl[1,2,4]triazolo[1,5-a]pyrimidine), (5-methyl,7-phenyl[1,2,4]triazolo[1,5-a]pyrimidine) and (5,6,7-trimethyl[1,2,4]triazolo[1,5-a]pyrimidine) [21]; [22] and (7-isobutyl-5-methyl-1,2,4]triazolo[1,5-a]pyrimidine) [23]. In the present study we report the X-ray crystal structures of two different copper BF_4 compounds with the ligand [1,2,4]triazolo[1,5-a]pyrimidine (abbreviated as tp), i.e. $[\text{Cu}(\text{tp})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (**1**) and $[\text{Cu}(\text{tp})_5](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (**2**). Surprisingly with Cu(II) as the metal and tp as the only ligand, just a few X-ray crystal structures have been reported in the literature, i.e. with the anions NCS^- and Cl^- [24], Br^- [10] and ClO_4^- [25].

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Scheme 1 The ligand [1,2,4]triazolo[1,5-a]pyrimidine (tp) and its IUPAC recommended ring-atom numbering system, together with adenine (A) and guanine (G)

Experimental Part

Starting Materials

Hydrated metal salts, solvents, 1,3-propane-dione and 5-amino-1,2,4-triazole were used as commercially available, without further purification.

Synthesis of the Ligand

The synthesis of the ligand tp was carried out by a known condensation procedure [2, 26] at 160 °C, from 1,3-propane-dione and 3-amino-1,2,4-triazole. Yield was found to be about 55%. Characterisation of the free tp ligand was performed by elemental analysis, IR and NMR spectroscopy.

Synthesis of the Coordination Compounds

Synthesis of (1): A solution of 2 mmol of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in 20 mL water was added to a warm aqueous solution of 2 mmol of tp. Upon standing at room temperature blue crystals appeared after one or 2 weeks, which were collected by filtration. Yields were found to be about 40%. By inspection under the microscope two different blue coloured (blue or light blue and other more dark blue) crystals were observed in the solution, which taken out of the solution very quickly disintegrated (by loss of lattice methanol), so that the difference of the two types could not be distinguished any more by eye. The two different types could not be synthesized separately, despite several attempts by changing the solvent, the metal–ligand ratio and the temperature.

Physical and Analytical Methods

Infrared spectra of the compounds were recorded on a PerkinElmer Paragon 1,000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4,000–300 cm^{-1} , res. 4 cm^{-1}).

X-ray Diffraction Studies

For each coordination compound a suitable crystal was selected from the mother liquid and quickly mounted to a glass fibre using the oil-drop method [27]. Diffraction data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated $\text{MoK}\alpha$ radiation). The structures were solved by direct methods. The programs COLLECT [28], SHELXS-97 [29] SHELXL-97 [29] were used for data reduction, structure solution and structure refinement, respectively. Refinement of F^2 was performed against all reflections. All non-hydrogen atoms were refined

anisotropically. Details for compound **1**: The tetrafluoroborate anion was found to be disordered and was refined in two positions with an SOF of 0.5. The oxygen atom of the methanol was also found disordered and given an SOF of 0.5. The carbon atom of the methanol molecule was refined in two positions each with an SOF of <0.5. The hydrogen atoms of the coordinated water molecule were taken from a Fourier-map. The hydrogen atoms of the methanol molecule were not located nor fixed. All other H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Crystallographic data for both compounds are summarized in Table 1.

Table 1 Crystallographic data for compounds **1** and **2**

Compound	(1)	(2)
Formula	$\text{C}_{21}\text{H}_{24}\text{B}_2\text{CuF}_8\text{N}_{16}\text{O}_3$	$\text{C}_{26}\text{H}_{24}\text{B}_2\text{CuF}_8\text{N}_{20}\text{O}$
Molecular weight	785.72	869.81
Crystal system	Monoclinic	Triclinic
Space group	C2/m	P-1
<i>a</i> , (Å)	19.498(2)	10.2984(5)
<i>b</i> , (Å)	13.305(2)	11.777(1)
<i>c</i> , (Å)	7.217(1)	15.522(2)
α , (°)	90	72.804(8)
β , (°)	110.84(1)	82.058(8)
γ , (°)	90	73.711(6)
<i>V</i> , (Å ³)	1749.8(4)	1723.1(3)
<i>Z</i>	2	2
<i>D</i> _{calc} , (g cm ⁻³)	1.491	1.676
<i>F</i> (000)	794	878
μ (cm ⁻¹)	0.717	0.736
Crystal size (mm)	0.40 × 0.40 × 0.40	0.40 × 0.20 × 0.20
Colour, shape	Light blue, block	Dark blue, block
θ min, θ max ^o	3.21; 27.52	2.88; 25.50
Total reflections	15291	26292
Total unique refl.	2090 ($R_{\text{int}} = 0.0280$)	6287 ($R_{\text{int}} = 0.0266$)
No. of refined parameters	145	524
R^a , wR_2^b	0.0461, 0.1308	0.0416, 0.1086
S^c	1.231	1.067
Min. and max. resd.dens., e/Å ³	1.086; -0.450	1.144; -0.878

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right]^{1/2}$$

$$^c \text{Goodness-of-fit } S = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{(n - p)} \right]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ the number of parameters}$$

Results and Discussion

Description of the X-ray Structures Crystal Structure of $[\text{Cu}(\text{tp})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (1)

An ORTEP perspective view of **1** is presented in Fig. 1. Selected bond lengths and angles are given in Table 2. The unit cell consists of a $[\text{Cu}(\text{tp})_4(\text{H}_2\text{O})_2]^{2+}$ moiety, two uncoordinating (disordered) tetrafluoridoborate anions and a (disordered) lattice methanol molecule. A centre of symmetry is located at Cu, and a mirror plane is running through the O–Cu–O axis, bisecting the N–Cu–N angle. The Cu(II) ion has a distorted octahedral environment, of which the basal plane is formed by four nitrogen atoms of four tp ligands with Cu–N distance 2.017(2) Å. The apical positions are formed by an oxygen atom of the water molecules with a Cu–O distance 2.472(3) Å. All angles are 180°, due to the symmetry. The lattice structure is stabilised by bifurcated hydrogen bonding of the water hydrogen atoms to the N4 of each tp ligand (O···N distance 2.870(3) Å) and to the fluorine atoms of the BF_4 anion (O···F distance 3.033(5) Å). (see Fig. 2) No other hydrogen

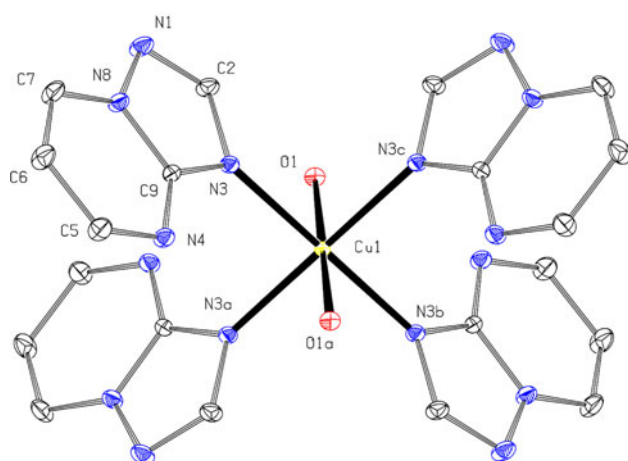


Fig. 1 ORTEP drawing (30% probability level) of $\text{Cu}(\text{tp})_4(\text{H}_2\text{O})_2(\text{BF}_4)_2(\text{CH}_3\text{OH})$ (**1**). The uncoordinating tetrafluoridoborate and methanol molecules, as well as the hydrogen atoms, are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) of (**1**)

Cu1–O1	2.472(3)	Cu1–N3	2.017(2)		
O1–Cu1–N3	86.20(8)	O1–Cu1–O1a	180.0		
O1–Cu1–N3a	93.80(8)	N3–Cu1–N3a	88.67(10)		
N3–Cu1–N3b	180.00	N3–Cu1–N3c	91.33(10)		
O1a–Cu1–N3a	86.20(8)				
Hydrogen bonds: (bifurcated H bond)		D–H	H···A	D···A	D–H···A
O(1)–H(1)···F(11) [–x, –y, –z]		0.78(4)	2.55(4)	3.033(5)	122(4)
O(1)–H(1)···N(4) [–x, –y, –z]		0.78(4)	2.17(4)	2.870(3)	150(4)

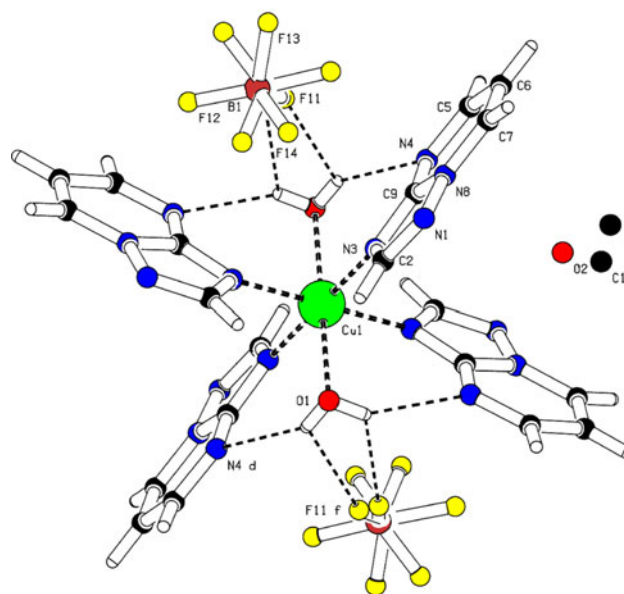


Fig. 2 H-bond system of (**1**)

bonds could be observed due to the severe disorder of the methanol molecule. Details are given in Table 2.

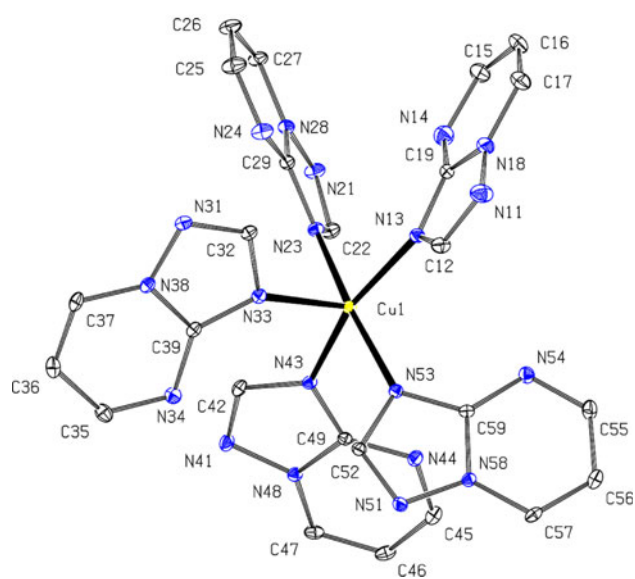
Crystal Structure of $[\text{Cu}(\text{tp})_5](\text{BF}_4)_2(\text{CH}_3\text{OH})$ (2)

An ORTEP perspective view of **2** is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. The unit cell contains the square pyramidal $[\text{Cu}(\text{tp})_5]^{2+}$ moiety, two non-coordinating tetrafluoridoborate anions and one uncoordinating methanol molecule. The Cu(II) ion has a square pyramidal geometry formed by four nitrogen atoms of four tp ligands (Cu–N distances from 2.009(2) to 2.028(2) Å) and one nitrogen atom of a fifth tp ligand (Cu–N distance 2.256(2) Å). The largest N–Cu–N angles are 162.58(10), 168.54(10)° (Fig. 3).

The geometry of 5-coordinated compounds can be expressed by the structural parameter τ (the structural parameter τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal) [30]. In this case $\tau = 0.10$, so the geometry can be described as distorted square pyramidal.

Table 3 Selected bond lengths (Å) and angles (°) of (**2**)

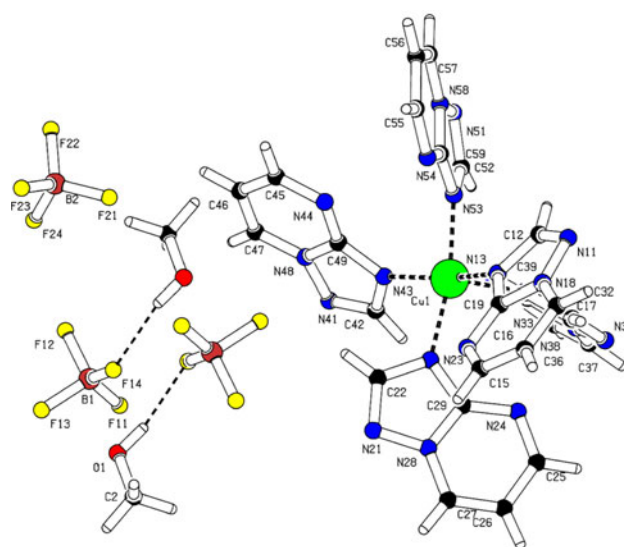
Cu1–N13	2.028(2)	Cu1–N23	2.012(2)	
Cu1–N33	2.256(2)	Cu1–N43	2.015(2)	
Cu1–N53	2.009(2)			
N13–Cu1–N23	92.14(10)	N13–Cu1–N33	93.87(9)	
N13–Cu1–N43	162.58(10)	N13–Cu1–N53	90.10(9)	
N23–Cu1–N33	98.80(9)	N23–Cu1–N43	87.60(9)	
N23–Cu1–N53	168.54(10)	N33–Cu1–N43	103.39(9)	
N33–Cu1–N53	92.27(9)	N43–Cu1–N53	86.92(9)	
Hydrogen bonds	D–H	H···A	D···A	D–H···A (°)
O(1)–H(1)···F(14) [1–x, –1–y, –z]	0.84	2.04	2.833(6)	157

**Fig. 3** ORTEP drawing (30% probability level) of [Cu(tp)₅](BF₄)₂ (CH₃OH) (**2**). The uncoordinating tetrafluoridoborate and methanol molecules, as well as the hydrogen atoms, are omitted for clarity

The lattice structure is stabilised by hydrogen bonding of the oxygen atom of the methanol molecule to the BF₄ anion (O···F distance 2.833(6) Å). Such hydrogen bonding with BF₄ is relatively rare, but easily detectable with IR for X–H groups binding to it [31]. Geometric details are given in Table 3 (Fig. 4).

IR Spectroscopy

Due to the fact that the two different compounds were very virtually impossible to be separated manually (see experimental part), only an overall IR spectrum could be recorded for characterisation (see Fig. S1). The characteristic ligand vibrations differ only slightly from the free ligand, as would be expected. The BF₄ anion vibrations are observed at 1051–1039 cm⁻¹ as a split band. At around 3348 cm⁻¹ a broad absorption is observed, which is

**Fig. 4** H-bond system in the lattice of (**2**)

ascribed to the ν_{OH} of the water and methanol molecules, hydrogen bonded to the BF₄ anions.

Concluding Remarks

The study described above has resulted in two new Cu(II) tetrafluoridoborate compounds with unsubstituted tp as a ligand. The two forms crystallise from the same batch, and despite several attempts, no conditions were found to obtain either one or the other compound in pure form. These two compounds appear to be the first compounds of Cu(II) and BF₄⁻ with tp as the ligand, which have been characterized by X-ray structures. Even with substituted tp ligands only one case is known [22].

Compound **2** has an unusual geometry with 5 tp ligands coordinated in an homoleptic manner, generating a five-coordinate geometry. Five-coordinate Cu(II) compounds are quite common, but with only a single type of a bulky ligand, they are rarely observed.

Supplementary Data

CIF files of both structures, and IR spectra of **1** and **2** and the complexes are given as supplementary material. The files CCDC-756398 and 756399 also contain the crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. A checkcif file for both compounds is also available.

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