

Red and Blue Compounds Formed from Copper(II) Bromide and the Ligand 7-Isobutyl-5-methyl-[1,2,4]triazolo[1,5-*a*]pyrimidine: Synthesis, Spectroscopy and Single-Crystal Structures

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Abstract Two newly synthesized coordination compounds copper(II) bromide with the ligand 7-isobutyl-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (abbreviated as *ibmtp*) are presented, together with their 3D crystal structure and spectroscopic and magnetic properties. The compounds are $\text{CuBr}_2(\text{ibmtp})_2$ (**1**) (red crystals) and $[\text{CuBr}(\text{ibmtp})_4]\text{Br}(\text{H}_2\text{O})_3$ (**2**) (blue crystals). In (**1**) the Cu(II) ion is present in a distorted tetrahedral environment, while in (**2**) the Cu(II) ion has a square pyramidal geometry. These crystal structures are also the first ones reported with the ligand *ibmtp*.

Keywords Copper · Bromide · 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. The unsubstituted ligand is abbreviated as *tp*.

These ligands have a fused 5-membered and 6-membered ring system and as such resemble the nucleobases adenine

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and guanine of DNA. 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 triazolopyrimidine-based ligands [2–11]. Also other groups have been studying these types of ligands [12–17]. Triazoles and pyrimidines may act as bridging ligands between metals via N3–N4 (see Scheme 1), but may also coordinate monodentately via N3 [18–20].

In a more recent paper 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) [21] and most recently (5,6,7-trimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine) [22]. The steric effects of substituents in these ligands are interesting and had not yet been explored before in great detail. In the present study we report on two different copper bromide compounds with the new ligand (7-isobutyl-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine) (abbreviated as *ibmtp*).

The ligand *ibmtp* was selected, as it contains a large isobutyl substituent on the seventh position. So far, to the best of our knowledge, no other coordination compounds have been reported with the ligand *ibmtp*.

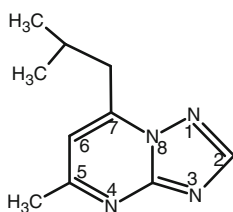
In this study we report on two Cu(II) compounds, prepared via different synthetic routes, i.e. $\text{CuBr}_2(\text{ibmtp})_2$ (**1**) (red crystals) and $[\text{CuBr}(\text{ibmtp})_4]\text{Br}(\text{H}_2\text{O})_3$ (**2**) (blue crystals).

Experimental Part

Starting Materials

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

Scheme 1 The ligand 7-isobutyl-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine (ibmtp) and its IUPAC recommended ring-atom numbering system



Synthesis of the Ligand

The synthesis of the ligand ibmtp was carried out by a known condensation procedure [2, 23] at 160 °C, from 6-methylheptane-2,4-dione and 3-amino-1,2,4-triazole. Details: 21 g (0.25 mol) of 3-amino-1,2,4-triazole and 35.6 g (0.25 mol) 6-methyl-2,4-heptanedione were put into a beaker glass and about 100 mL of ethylene glycol was added. The mixture was heated for about 1 h at around 160 °C. The mixture was cooled at RT and about 100 mL of ethanol was added and stirred. Overnight in the refrigerator the product separated and was subsequently filtered and washed with cold ethanol. Yield ca. 50%. Elemental Analysis calc. (found) for C₁₀H₁₄N₄: 62.9 (63.1) %C, 7.2 (7.4) % H, 29.3 (29.5) % N. For the IR spectrum see Fig. S1; the characterization of the specific isomer was made by X-ray diffraction (vide infra).

Synthesis of the Coordination Compounds

Synthesis of (1): A solution of 2 mmol (450 mg) of CuBr₂ in 20 mL of water was added to a warm aqueous solution of 2 mmol (380 mg) of ibmtp. Upon standing at room temperature red crystals appeared after one or 2 weeks, which were collected by filtration. Yield: about 30%. Anal. Calcd for C₂₀H₂₈Br₂CuN₈: C, 39.8; H, 4.7; N, 18.6%; Found: C, 39.7; H, 4.6; N, 18.6%.

Synthesis of (2): 1 mmol (240 mgr) of Cu(NO₃)₂·3H₂O and 2 mmol (380 mg) of ibmtp were each dissolved in mixture of 20 mL of water/ethanol (1:1) and put carefully together. The solution stays clear and after one day 2 mmol (240 mgr) of KBr dissolved in 5 mL water was added. After a few days blue crystals appeared. Yield ca. 60%. Anal. Calcd for C₄₀H₆₂Br₂CuN₁₆O₃: C, 46.3; H, 6.0; N, 21.6%; Found: C, 46.1; H, 5.9; N, 21.6%.

Physical and Analytical Methods

C, H, N determinations were performed on a PerkinElmer 2400 Series II analyzer. Ligand field spectra in the 300–2000 nm range were obtained on a PerkinElmer Lambda 900 spectrophotometer using the diffuse reflectance technique, using MgO as a reference. Infrared spectra of all compounds were recorded on a PerkinElmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique

(4000–300 cm⁻¹, res. 4 cm⁻¹). X-band powder EPR spectra were obtained on a Bruker EMXplus electron spin resonance spectrometer at room T and 77 K (Field calibrated with DPPH (g = 2.0036)).

X-Ray Diffraction Studies

For each coordination compound a suitable crystal was selected from the mother liquid and mounted to a glass fibre using the oil-drop method [24]. Diffraction data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated MoK α radiation). The structures were solved by direct methods. The programs COLLECT [25], SHELXS-97 [26] SHELXL-97 [26] were used for data reduction, structure solution and structure refinement, respectively. Refinement of F² was performed against all reflections. All non-hydrogen atoms were refined anisotropically. Details for compound **1**: All H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Details for compound **2**: One of the water molecules was found to be disordered and refined in two positions. The uncoordinated bromide anion was found to be severely disordered and was refined in four positions. The hydrogen atoms of the water molecules 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 of the compounds are summarized in Table 1.

Results and Discussion

Description of the X-Ray Structures

Crystal Structure of CuBr₂(ibmtp)₂ (1)

An ORTEP perspective view of **1** is presented in Fig. 1. Selected bond lengths and angles are given in Table 2. A two-fold axis relates the 2 halves of the molecule. The Cu(II) ion has a distorted tetrahedral environment formed by two nitrogen atoms of two ibmtp ligands (Cu–N distance 1.986(2) Å) and two coordinated bromide anions (Cu–Br distance 2.3602(4) Å). Such tetrahedrally-based distorted geometries are not uncommon for Cu(II) with N donor ligands [27]. The N–Cu–Br angle is 137.11(6)°. The Cu–N and Cu–Br bond distances are in typical ranges for this type of [CuN₂Br₂] tetrahedrally based compounds [28, 29]. This structure can also be compared with [CuBr₂(tmtp)₂] [22] (tmtp = 5,6,7-trimethyltriazolopyrimidine). The [CuBr₂(tmtp)₂] structure contains two almost identical independent crystallographic units, and each of them is very similar to compound 1. The N–Cu–Br and Br–Cu–Br

Table 1 Crystallographic data

	Compound (1)	Compound(2)
Formula	C ₂₀ H ₂₈ Br ₂ CuN ₈	C ₄₀ H ₅₆ Br ₂ CuN ₁₆ O ₃
Molecular weight	603.86	1032.36
Crystal system	Hexagonal	Tetragonal
Temp (K)	173(2)	173(2)
Space group	P3 ₁ 2 ₁	P4/nnc
<i>a</i> (Å)	8.9326(9)	13.413(2)
<i>b</i> (Å)	8.9326(9)	13.413(2)
<i>c</i> (Å)	26.3330(3)	28.006(5)
α (°)	90	90
β (°)	90	90
γ (°)	120	90
<i>V</i> (Å ³)	1819.6(3)	5038.5(14)
<i>Z</i>	3	4
<i>D</i> _{calc} (g cm ⁻³)	1.653	1.369
<i>F</i> (000)	909	2148
μ (mm ⁻¹)	4.218	2.071
Crystal size (mm)	0.28 × 0.22 × 0.15	0.35 × 0.20 × 0.08
colour, shape	Red, block	Blue, plate
θ min, θ max deg	3.08–26.50	2.66–25.05
Total refl.	23863	25938
Total unique refl.	2509 (<i>R</i> _{int} = 0.0514)	2220 (<i>R</i> _{int} = 0.0659)
No. of refined parameters	144	151
<i>R</i> ^a , <i>wR</i> ^{2b}	0.0240, 0.0521	0.0487, 0.1216
<i>S</i> ^c	1.101	1.093
min. and max. resd.dens. (e/Å ³)	0.210; -0.349	0.654; -0.817

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$,

^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^{1/2}]^{1/2}$

^c Goodness-of-fit

$S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$,

where *n* is the number of reflections and *p* the number of parameters

only differ slightly (ca. <4% difference) with respect to compound (1).

Crystal Structure of [CuBr(ibmtp)₄]Br(H₂O)₃ (2)

An ORTEP perspective view of **2** is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. Compound **2** crystallizes in the tetragonal space group *P4/nnc*. The unit cell contains the square pyramidal CuBr(ibmtp)₄ moiety, one disordered uncoordinated bromide anion and three uncoordinated lattice water molecules of which one is disordered. The Cu(II) ion has a square-pyramidal geometry formed by four nitrogen atoms of four ibmtp ligands (Cu–N distance 2.020(3) Å) and one bromide anion (Cu–Br distance 2.569(1) Å). The N–Cu–N angle is 161.8(2)°. The angle between the bromide and the least-squares plane of the Cu and the 4 N atoms, is 88.2 degrees.

The lattice structure is stabilised by hydrogen bonding of the bromide anion to the oxygen atoms of the water molecules (Br(1)⋯O(1) distance 3.33(3) Å). Due to the fact that the second bromide anion and the other water molecules are disordered and the hydrogen atoms could not be located nor fixed (see experimental) no further detailed information could be obtained.

IR, Ligand Field and EPR Spectroscopy

For characterisation purpose the IR spectra are given in the supplementary material (Figs. S2, S3), the characteristic the ligand vibrations differ only slightly as can be expected. In compound (2) at around 3420 cm⁻¹ a broad absorption is observed, which is due to νOH of the lattice water molecules.

The powder EPR spectra of both compounds (see Figs. S4, S5) reveal at RT a typical *S* = 1/2 spectrum with a *g*_{perp} of 2.08 and a strong unresolved *g*_{||} of 2.31 for compound (1) and with a *g*_{perp} of 2.07 and a very weak unresolved *g*_{||} of 2.31 for compound (2). These signals are in agreement with a d_{x²-y²} configuration for the ground state [30].

The ligand-field transitions measured as a solid with the diffuse reflectance technique (see Figs. S6, S7) observed for compound (1) a very broad tail shaped band which a centre around 9.9 (7.7 sh) × 10³ cm⁻¹, and is assigned to the split but unresolved d–d transition ²T_{2g} → ²E_g. For compound (2) a broad band at 14.3 × 10³ cm⁻¹, assigned to the d–d transition ²E_g → ²T_{2g}, with a shoulder at about 10.1 × 10³ cm⁻¹, assigned to a split component of the d–d transition ²E_g → ²T_{2g} was observed. These bands are not uncommon for ligand field transitions of tetrahedrally-based

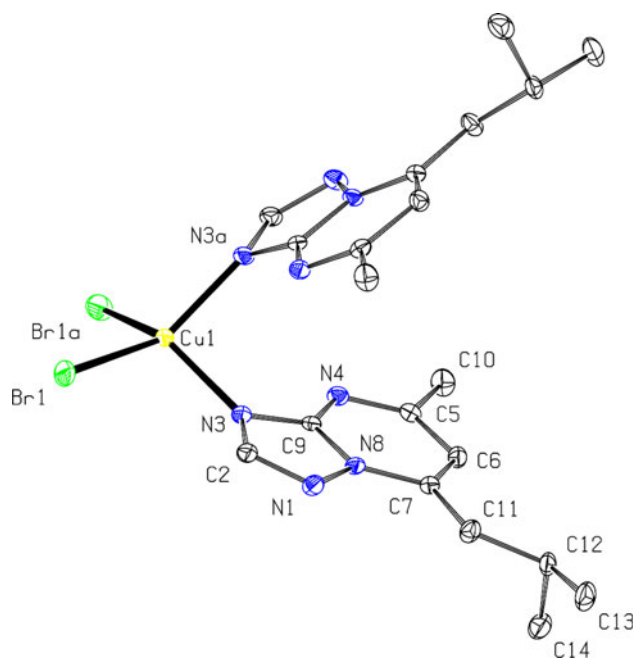


Fig. 1 ORTEP drawing (50% probability level) of $[\text{CuBr}_2(\text{ibtmp})_2]$ (**1**). Hydrogen atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) of $\text{CuBr}_2(\text{ibtmp})_2$ (**1**)

Cu(1)–N(3)	1.986(2)	Cu(1)–Br(1)	2.3602(4)
N(3)–Cu(1)–N(3)a	91.98(11)	N(3)–Cu(1)–Br(1)	97.57(5)
N(3)a–Cu(1)–Br(1)	137.11(6)	Br(1)–Cu(1)–Br(1)a	103.06(2)

a = y, x, -z

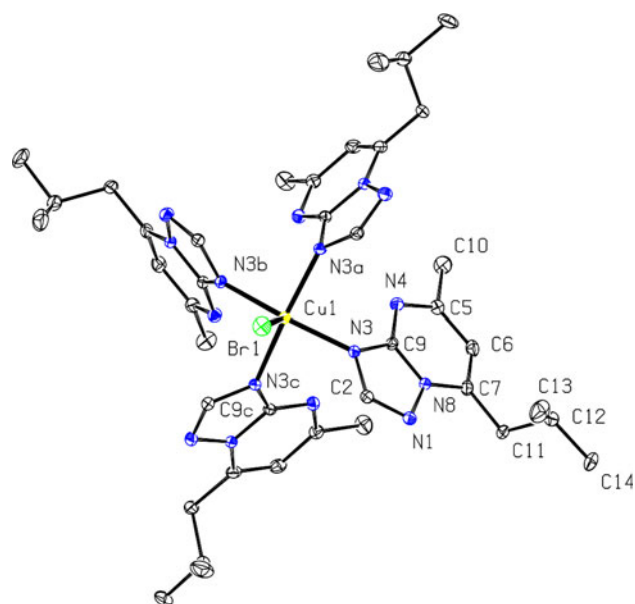


Fig. 2 ORTEP drawing (50% probability level) of $[\text{CuBr}(\text{ibtmp})_4]\text{Br}(\text{H}_2\text{O})_3$ (**2**). Hydrogen atoms, the uncoordinated bromide anion and lattice water molecules are omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) of $[\text{CuBr}(\text{ibtmp})_4]\text{Br}(\text{H}_2\text{O})_3$ (**2**)

Cu(1)–N(3)	2.020(3)	Cu(1)–Br(1)	2.569(1)
N(3)a–Cu(1)–N(3)	88.56(3)	N(3)–Cu(1)–N(3)b	161.6(2)
N(3)–Cu(1)–N(3)c	88.56(3)	N(3)–Cu(1)–Br(1)	99.13(9)

a = y, -x + 1/2, z; b = -x + 1/2, -y + 1/2, z; c = -y + 1/2, x, z

and square-planar based geometries, respectively and in agreement with the crystal structures found [30, 31].

Concluding Remarks

The study described above has presented two new Cu(II) compounds with a triazolopyrimidine ligand. The metal–ligand ratio determines the stoichiometry of the formed compounds. The anhydrous compound (**1**) shows no lattice hydrogen bonding, whereas the hydrate shows an interesting Br–O hydrogen bonding pattern. The ligand synthesis, although in potential yielding two isomers, i.e. with the methyl group at either five or seven position, only yields a single isomer. The structure of the isomer is intrinsically also proven by the structure of the formed Cu(II) coordination compounds.

Supplementary Data

IR, LF and EPR spectra are given as supplementary material, Figs. S1–S7. CCDC- 751873 & 751874 contains the supplementary 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.

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