



Copper(II) complexes with 1,2,4-triazolo[1,5-*a*] pyrimidine and its 5,7-dimethyl derivative

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ABSTRACT

Several Cu(II) complexes with 1,2,4-triazolo[1,5-*a*]pyrimidine (tp) and its 5,7-dimethyl derivative (dmt) have been isolated and structurally characterized. Five of them are mononuclear and contain 1,10-phenanthroline (phen) or ethylenediamine (en) as auxiliary ligands, their formula being $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{tp})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{dmt})_2](\text{ClO}_4)_2$, $[\text{Cu}(\text{NO}_3)(\text{H}_2\text{O})(\text{phen})(\text{tp})](\text{NO}_3)$, $[\text{Cu}(\text{H}_2\text{O})_2(\text{en})(\text{tp})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{H}_2\text{O})_2(\text{en})(\text{dmt})_2](\text{ClO}_4)_2$. In all these compounds the tp or dmt ligand is monodentately coordinated via the nitrogen atom in position 3. The auxiliary ligand influences the coordination number, which is five when this ligand is phen and six when it is en whereas the number of triazolopyrimidine ligands linked to the metal seems to be influenced by the nature of the counteranion. A dinuclear compound with tp has also been isolated, its formula being $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})_{2.5}(\text{tp})_5](\text{ClO}_4)_3 \cdot (\text{H}_2\text{O})_{1.5}$, with both metal atoms linked by an hydroxydo group and by a tp bridging ligand, coordinated to one of the copper atoms via N3 and to the other via N4. This compound has several unusual features among the metal complexes with triazolopyrimidine derivatives: the presence of two different kinds of bridging moieties, the coexistence of bridging and terminal ligands and the formation of a N3–N4 bridge for a Cu(II) dinuclear compound for a derivative without exocyclic oxygen atoms.

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1. Introduction

Transition metal complexes with 1,2,4-triazolo[1,5-*a*]pyrimidines can be used as models for the study of metal–ligand interactions like those observed in biological systems. These heterocycles can be regarded as purine analogues since their fused ring system differs from purine skeleton mainly in having the pyrimidine nitrogen atom in a bridge-head position (see Fig. 1) with the disappearance of the acidic proton of the five-membered ring [1].

An appreciable number of copper(II) complexes with 1,2,4-triazolo[1,5-*a*]pyrimidine ligands are known, their crystal structures having been solved by X-ray diffraction [2–16]. Most of these complexes present octahedral or square-pyramidal geometry, with four strongly coordinated atoms at the equatorial plane and one or two atoms weakly interacting at apical positions with three exceptions: $[\text{Cu}(\text{NCS})_2(6\text{mtp})_2]$ [2], distorted tetrahedral and $[\text{CuBr}_2(\text{tp})_2(\text{H}_2\text{O})]$ [3] and $[\text{Cu}_2\text{Br}_4(\text{dmt})_4] \cdot 2\text{H}_2\text{O}$ [4], trigonal bipyramidal (where tp is unsubstituted 1,2,4-triazolo[1,5-*a*]pyrimidine, dmt is its 5,7-dimethyl derivative and 6mtp, its 6-methyl derivative). The preferred binding site of the heterocycle in these compounds is N3, which is analogous to the N9 position (in bio-

chemical numbering scheme) of purines, with an average Cu–N3 distance of 2.03 Å. Apart from monodentate N3 coordination, other binding modes have been found: N1,N3-bridging mode gives rise to the formation of chains in $[\text{Cu}(\text{NCS})_2(5\text{mtp})_2]$ [2], $[\text{CuCl}_2(\text{tp})_2]$ and $[\text{Cu}(\text{NCS})_2(\text{tp})_2]$ [14] (5mtp is the 5-methyl derivative of tp), whereas dinuclear compounds are generated by N3,N4-bridging mode in $[\text{Cu}_2(5\text{tpO})_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{biim})_2(5\text{tpO})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 5.5\text{H}_2\text{O}$ and by N3,O5-bridging mode in $[\text{Cu}_2(\text{phen})_2(5\text{tpO})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ [15] (5tpO[−] is the anionic form of 4,5-dihydro-5-oxo-1,2,4-triazolo[1,5-*a*]pyrimidine, biim is 2,2'-bisimidazole and phen is 1,10-phenanthroline).

This diversity in coordination modes found in copper(II) complexes with triazolopyrimidines prompted us to continue this research line by studying the complexes formed by Cu(II) with tp and dmt in the presence of aliphatic (ethylenediamine, en) and aromatic (1,10-phenanthroline, phen) amines as auxiliary ligands, five new Cu(II) ternary complexes having been isolated and structurally characterized. The nature of the auxiliary ligand and the counteranion influences the geometry around the metal centre.

Seeking the formation of dinuclear species analogous to the above mentioned with ligands containing exocyclic oxygen atoms in which metal–metal interactions may be studied, we have raised the pH of solutions containing tp or dmt and Cu(II). For tp, we have been successful in isolating a dinuclear complex with a structural type different to the previously known.

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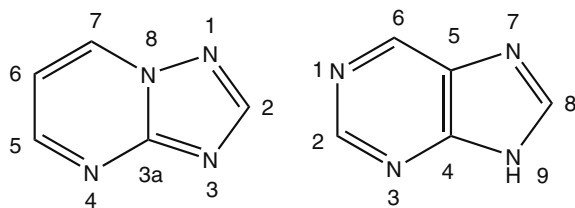


Fig. 1. The basic skeleton of 1,2,4-triazolo[1,5-*a*]pyrimidines and purines.

2. Experimental

2.1. Synthesis of the compounds

1,2,4-Triazolo-[1,5-*a*]pyrimidine (tp), 5,7-dimethyl-1,2,4-triazolo-[1,5-*a*]pyrimidine (dmtp), 1,10-phenanthroline (phen), ethylenediamine (en), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were purchased from Aldrich and used without further purification.

2.1.1. $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{tp})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{dmtp})_2](\text{ClO}_4)_2$ (**2**)

Firstly a green solution was obtained by mixing an aqueous solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 10 mL) and another one of the appropriate ligand tp (**1**) or dmtp (**2**) (1 mmol, 10 mL). After adding 1,10-phenanthroline dissolved in ethanol (1 mmol, 5 mL) a green precipitate of $\text{Cu}(\text{phen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ immediately appeared, which was filtered, washed with water and ethanol. The filtered solution was allowed to evaporate at room temperature and, after several days, blue crystals suitable for X-ray studies were isolated. Elemental analysis data: Compound **1**: *Anal. Calc.* for $\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{CuN}_{10}\text{O}_{10}$: C, 36.8; H, 2.8; N, 19.5. Found: C, 37.4; H, 2.6; N, 19.8%. Compound **2**: *Anal. Calc.* for $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{CuN}_{10}\text{O}_9$: C, 41.3; H, 3.5; N, 18.5. Found: C, 41.3; H, 3.5; N, 18.4%.

2.1.2. $[\text{Cu}(\text{NO}_3)(\text{H}_2\text{O})(\text{phen})(\text{tp})](\text{NO}_3)$ (**3**)

The complex was obtained by mixing three solutions, 10 mL each, one containing 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, other 1 mmol of tp and the third 1 mmol of 1,10-phenanthroline. The two first solutions are aqueous and the last is ethanolic. After few days blue crystals suitable for X-ray study were obtained. Elemental analysis data: *Anal. Calc.* for $\text{C}_{17}\text{H}_{14}\text{CuN}_8\text{O}_7$: C, 40.4; H, 2.8; N, 22.2. Found: C, 40.8; H, 2.7; N, 22.6%.

2.1.3. $[\text{Cu}(\text{H}_2\text{O})_2(\text{en})(\text{tp})_2](\text{ClO}_4)_2$ (**4**) and $[\text{Cu}(\text{H}_2\text{O})_2(\text{en})(\text{dmtp})_2](\text{ClO}_4)_2$ (**5**)

Firstly two aqueous solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 10 mL) and the appropriate ligand (tp (**4**) or dmtp (**5**)) (1 mmol, 10 mL) were mixed. After adding 0.5 mmol (34 μL) of ethylenediamine, it was left to stand at room temperature, blue crystals suitable for X-ray studies were isolated. Elemental analysis data: Compound **4**: *Anal. Calc.* for $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{CuN}_{10}\text{O}_{10}$: C, 24.1; H, 3.4; N, 23.4. Found: C, 24.3; H, 4.0; N, 23.8%. Compound **5**: *Anal. Calc.* for $\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{CuN}_{10}\text{O}_{10}$: C, 29.3; H, 4.3; N, 21.4. Found: C, 29.6; H, 4.6; N, 22.0%.

2.1.4. $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})_{2.5}(\text{tp})_5](\text{ClO}_4)_3(\text{H}_2\text{O})_{1.5}$ (**6**)

Two solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 10 mL) and tp (1 mmol, 10 mL) in 0.01 M NaOH were mixed. The mixture was allowed to evaporate at room temperature and, after one week, light blue crystals suitable for X-ray studies were obtained. Elemental analysis data: *Anal. Calc.* for $\text{C}_{25}\text{H}_{29}\text{Cl}_3\text{Cu}_2\text{N}_{20}\text{O}_{17}$: C, 26.9; H, 2.6; N, 25.1. Found: C, 27.1; H, 2.9; N, 25.7%.

2.2. Instrumentation

Microanalysis of C, H and N were performed in a Fisons Instruments EA-1008 analyser. Thermal behaviour was studied under an air flow in Shimadzu TGA-50 and Shimadzu DSC-50 equipments, at heating rates of $20\text{ }^\circ\text{C min}^{-1}$ and $10\text{ }^\circ\text{C min}^{-1}$, respectively. Reflectance diffuse spectra were made on a VARIAN model CARY-5E spectrophotometer. EPR spectra of powdered samples were recorded at room temperature on a Bruker ESP-300E spectrometer, operating at X-band (9–10 GHz) while the magnetic susceptibility measurements, in the temperature range of 2–300 K, were carried out on powdered samples using a Quantum Design MPMS-XL SQUID (all this equipment is sited at the Centre of Scientific Instrumentation of the University of Granada). IR spectra were recorded on a ThermoNicolet IR 200 spectrometer using KBr pellets.

2.3. Crystallography

Data were collected, at room temperature for **3** and **4** and at 100 K for the rest of the samples, in a Bruker SMART APEX CCD system with Mo $K\alpha$ radiation ($\lambda = 0.7107\text{ \AA}$). Data were corrected for absorption (multi-scan, transmission ranges, 0.8305–0.7330, 0.7944–0.7122, 0.673–0.545, 0.822–0.614, 0.7013–0.6392 and 0.8659–0.7245 for **1–6**, respectively). The structures were solved by the heavy atom method and anisotropically refined in F^2 using SHELXL-97 [17]. There are two non-coordinated nitrate anions in **3** placed in binary axes, one of them disordered between two equally populated positions. Two water molecules in **6** have been refined with half occupancy. Hydrogen atoms of the heterocycles and auxiliary ligands were placed in ideal positions whereas those of water molecules (except the half occupancy ones in **6**) were refined with fixed O–H distance. Isotropic thermal parameters of all H atoms fixed to 1.2 times the equivalent isotropic thermal parameter of their parent atoms. Table 1 summarizes the crystallographic data for the six compounds.

3. Results and discussion

3.1. X-ray structure of the ternary copper complexes

All ternary copper(II) complexes (**1–5**) are mononuclear with the triazolopyrimidine ligands monodentately coordinated to the metal via the nitrogen atom at position 3 and the auxiliary ligand (ethylenediamine, en or 1,10-phenanthroline, phen) bidentately attached closing a five-member chelate ring. The geometry around the metal atom is square-pyramidal when the auxiliary ligand is phen (**1**, **2**, **3**) and tetragonally distorted octahedral when the auxiliary ligand is en (**4**, **5**). Figs. 2–4 display the structures of all these complexes. Distances and angles in the coordination sphere are listed in Table 2. These distances agree well with bibliographic data for Cu complexes of both triazolopyrimidine ligands and amine ligands [11]. The trigonality indexes [18] calculated for the five-coordinate compounds are 0.142, 0.187 and 0.022, respectively for **1**, **2** and **3** indicating that the geometries are in fact much closer to tetragonal pyramidal than to trigonal bipyramidal.

Both the triazolopyrimidine moiety and the auxiliary ligands occupy basal or equatorial coordination positions. For compound **3**, in which only one tp molecule is present, the fourth position in the basal plane is occupied by one oxygen atom of the coordinated nitrate anion. The axial positions are filled by one (**1**, **2**, **3**) or two (**4**, **5**) water molecules at a longer distance in typical Cu(II) Jahn–Teller distorted environments. In the two later compounds, distances Cu–water are long enough to let us consider the compounds as quasi-square planar (4+2). A weak interaction of the metal with a second oxygen atom of the coordinated nitrate anion

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