



Coordination chemistry of 5,6,7-trimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidine with first-row transition-metal salts: Synthesis, spectroscopy and single-crystal structures, with counter-anion dependence of the structures

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ABSTRACT

A variety of new coordination compounds with transition-metal salts and the ligand trimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (abbreviated as tntp) is described, together with several of their 3D crystal structures and spectroscopic and magnetic properties. The compounds were selected based on the coordination ability of the counterion, halide, nitrate, sulfate, thiocyanate and perchlorate. The formed coordination compounds and their coordination numbers were found to be strongly dependent on both the cation and the used counter-anion. The several compounds studied have the following structural formulae: [CuCl₂(tntp)₂], [CuBr₂(tntp)₂], [ZnBr₂(tntp)₂], [Cu(NO₃)₂(tntp)₂], [CuSO₄(tntp)₂](H₂O)(MeOH), [Cu(H₂O)(NCS)₂(tntp)₂], [Zn(NCS)₂(tntp)₂], [Cd(NCS)₂(tntp)₂] and [M(H₂O)₂(tntp)₄](BF₄)₂, in which M = Co, Ni, Zn.

The new coordination compounds have been further characterized by NMR, (far-)IR and LF spectra, as well as by C, H, N element analyses, and EPR spectra for the Cu(II) compounds. The coordination around the metal varies from **4** (Zn, Cu), via **5** (Cu) to **6** (for Co, Cu and Cd). The anions usually complete the coordination sphere; only the Co and Zn compounds with the tetrafluoridoborate anions have no coordinated anions, but water ligands complete the octahedral coordination sphere. In the 5-coordinated [Cu(H₂O)(NCS)₂(tntp)₂] water completes the square pyramid geometry.

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1. Introduction

Triazolopyrimidines (traditional IUPAC 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, see the structure in Scheme 1, with the actual IUPAC ring numbering.

These ligands contain fused 5-membered and 6-membered rings and as such resemble the nucleobases adenine 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 symmetric, and methyl substituted tp-based ligands [2–11]. Also other groups have been studying this type of ligands [12–17]. Triazoles and pyrimidines may act as bridging ligands between metals, but may also coordinate monodentately [18–20].

In a recent paper [21] we reported on transition-metal compounds with the ligands (5,7-diethyl[1,2,4]triazolo[1,5-*a*]pyrimidine) and (5-methyl,7-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine).

The steric effects of substituents in these ligands are interesting and have not been explored before in great detail. Therefore in the present study the ligand tntp was selected, which has three methyl substituents on the 5, 6 and 7 position (ligand abbreviation tntp), by studying a variety of reactions with transition-metal(II) salts, with a focus upon both the metal and the different anions. Given the fact that N1 and N4 have bulky methyl groups nearby, coordination at N3 would be expected for steric reasons, whereas the other nitrogens might be more accessible for H-bond acceptance. Still a ligand bridging two metal ions via additional coordination by N1 or N4 cannot be excluded a priori. A selection of 11 different compounds were synthesised and characterized of which 10 delivered crystals suitable for single-crystal X-ray analysis.

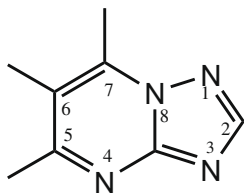
2. Experimental

2.1. Starting materials

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

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Scheme 1. The ligand tntp (5,6,7-trimethyl[1,2,4]triazolo[1,5-a]pyrimidine) and its IUPAC recommended ring-atom numbering system.

2.2. Synthesis of the ligand

The synthesis of the ligand tntp was carried out by a known condensation procedure [2,22] at 160 °C, from a diketone and 3-amino-1,2,4-triazole schematically as summarized in Scheme 2, followed by recrystallization using ethanol. Observed yields were 60–70% depending on small variations in the conditions. Characterisation of the free ligand was done by elemental analysis, IR and NMR spectroscopy.

2.3. Synthesis of the coordination compounds

The coordination compounds were prepared by the following general recipes:

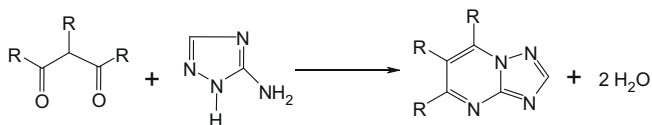
A solution of 1–2 mmol of the metal salt in 10–20 mL water was added to a warm aqueous solution of the ligand (1–5 mmol). Upon standing at room temperature crystals appeared, which were collected by filtration. In some cases, MeOH/water or pure MeOH were used as a solvent. To prepare the thiocyanate compounds a metathesis reaction was used, starting from the aqueous metal nitrate and ammonium thiocyanate (1:2). Yields were found to be between 30% and 60% depending on the metal and anion. Satisfactory elemental analysis was obtained for all compounds.

2.4. 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}). (Far-)FTIR spectra were obtained on a Bruker IFS 113v infrared spectrophotometer as polyethylene mulls (600–100 cm^{-1} , Mylar 6 μ , res. 2 cm^{-1}). X-band powder EPR spectra were obtained on a Bruker EMXplus electron spin resonance spectrometer (field calibrated with DPPH ($g = 2.0036$)).

2.5. X-ray diffraction studies

For each coordination compound a suitable crystal was selected from the mother liquid and mounted to a glass fiber using the oil-drop method. Diffraction data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation).



Scheme 2. Synthesis scheme of substituted triazolopyrimidines; for tntp: R = Me.

The structures were solved by direct methods. The programs COLLECT [23], SHELXS-97 [24], SHELXL-97 [25] 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. The water Hydrogen atoms of compounds **6**, **9** and **10** were picked from difference maps and refined isotropically. All other H-atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Details of compound **5**: one of the two methanol molecules and the water molecule were found to be severely disordered. The methanol C7 and the water O9 were each refined with an occupancy factor of 0.5, while the methanol O8 atom was refined in three positions with site occupancy factors of 1/3. The H-atoms of these water and disordered methanol molecules could neither be determined, nor fixed.

Crystallographic data of the compounds are summarized in Table 1. Compound **11**, was found to be isomorphous with compounds **9** and **10**, as deduced from infrared and X-ray powder diffraction.

3. Results and discussion

3.1. General observations and spectral analyses

A variety of metal salts has been reacted in alcoholic or aqueous solution with the ligand, and a (micro)crystalline, reproducible product was formed, irrespective of the used metal to ligand ratio. The so-obtained products are listed in Table 2 with their composition and with some spectral characteristics. All compounds have been characterized by common physical methods, i.e. infrared, ligand field, and C, H, N analysis. The Cu compounds were also characterized by EPR, and the Zn compound also by NMR. In 10 cases an X-ray structure determination was carried out to obtain molecular structure details (*vide infra*). These compounds are numbered **1–10**.

3.2. Description of the X-ray structures

The compound $[\text{CuCl}_2(\text{tntp})_2]$ (**1**) crystallizes in the monoclinic space group $P2_1/c$. An ortep perspective view of **1** is shown in Fig. 1. Selected bond lengths and angles are given in Table 3. The Cu(II) ion is in a distorted tetrahedral environment formed by two tntp ligands and two chlorides. Such tetrahedrally distorted geometries are not uncommon for Cu(II) with N donor ligands [26]; a packing diagram is given in Fig. S1. The degree of distortion of the Cu(II) ion can be expressed by the parameter τ_4 ($\tau_4 = 0.46$ for Cu; $\tau_4 = 0$ for a square planar geometry and $\tau_4 = 1$ for a tetrahedral geometry) [27]. The Cu–N and Cu–Cl bond distances are in typical ranges for this type of $[\text{CuN}_2\text{Cl}_2]$ tetrahedron, see Table 3 [28,29].

The corresponding bromide $[\text{CuBr}_2(\text{tntp})_2]$ (**2**), crystallizes in the orthorhombic space group $Pca2_1$. The unit cells contains two slightly different chromophores, but both very similar to the chloride in Fig. 1. An ortep perspective view of **2** is shown in Fig. S2 and a packing figure in Fig. S3. Both Cu ions are in quite distorted tetrahedral environment ($\tau_4 = 0.54$ for Cu; $\tau_4 = 0$ for a square planar geometry and $\tau_4 = 1$ for a tetrahedral geometry) [27], formed by two bromido ligands and to monodentate tntp ligands. The Cu–N and Cu–Br bond distances are in typical ranges for this type of $[\text{CuN}_2\text{Br}_2]$ tetrahedron [28,29].

The compound $[\text{ZnBr}_2(\text{tntp})_2]$ (**3**) crystallizes in the monoclinic space group $P2_1/c$. An ortep perspective view of compound **3** is depicted in Fig. S4 and a packing diagram is given in Fig. S5. In this case the distortion from tetrahedral is much smaller, as commonly seen for Zn(II) d^{10} ions. The Zn(II) ions are in an almost perfect tetrahedral environment ($\tau_4 = 0.89$ for Zn; $\tau_4 = 0$ for a square planar

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