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The first oxalate-based 2D coordination polymer containing the biomimetic ligand 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7-one

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ABSTRACT

Reaction of 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (HmtpO) with manganese(II) nitrate in presence of oxalic acid yielded the first complex containing this hypoxanthine analog and oxalate, namely $[K_2Mn_2(\mu-mtpO)_4(\mu_6-ox)(\mu-H_2O)_6]_n$, where mtpO is the anionic form of HmtpO derivative. The X-ray structure of this bimetallic polymer is built up of metal-oxalate cationic chains which are further linked by mtpO ligand in an unusual fashion to give a neutral 2D framework.

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Over the past decades, notable research effort has been devoted in the rational design and synthesis of biomimetic systems based on the interaction of biologically relevant molecules with a wide range of organic and inorganic species [1]. The interest in these systems not only stems from the desire to better understand the complex interactions often present in a great diversity of molecular biorecognition processes [2] but also to afford a powerful tool for the improvement of pharmaceutical agents [3] and the development of artificial receptors used as specific nucleotide sensors or even for the determination of low concentrations of biological and therapeutic agents [4]. In this background, nitrogen heterocycles known as 1.2.4-triazolo[1.5-a] pyrimidines may be used as purines analogs to pursue a deeper understanding of interactions between purine nucleobases and metal ions, and to obtain new biomimetic systems with interesting properties. The slightly different atomic arrangement in 1,2,4-triazolo[1,5-*a*] pyrimidines may introduce new structural features and different physical and biological properties compared to purine-based systems [5,6].

Previous studies carried out by our research group, among others, have revealed that 1,2,4-triazolo[1,5-*a*]pyrimidines are versatile ligands as they have several nitrogen atoms to bind metal ions [5,7]. Moreover, their versatility can be increased by the ring-substitution with functional groups containing donor atoms like nitrogen, sulfur or oxygen, leading to a wider range of coordination modes and structural topologies in their metal complexes [5–8]. Therefore, an increasing interest has recently aroused around this type of ligands due to their

great capacity to act as suitable building blocks for the synthesis of novel metal-organic multidimensional systems, [9,10] showing in some cases interesting magnetic, luminescent and biological properties [5].

On the basis of the aforementioned considerations, we have chosen the substituted derivative 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(*4H*)-one (HmtpO) in combination with a bridging and versatile ligand such as the oxalate anion (ox^{2-}) to obtain novel multidimensional metal complexes which may show unusual physical and biological properties. As a result, a novel 2D bimetallic polymer, [K₂Mn₂(μ mtpO)₄(μ ₆-ox)(μ -H₂O)₆]_n, where mtpO is the anionic form of HmtpO, has been obtained under conventional reaction in aqueous media,² and has been characterized by IR spectroscopy, elemental analysis, single-crystal X-ray diffraction and thermal analysis. Magnetic susceptibility measurements have been also carried out. To the best of our knowledge, this is the first oxalate compound which contains such nucleobase analog, and it is part of our preliminary results on a recently

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² Synthesis: Over an aqueous solution of Mn(NO₃)₂·4H₂O (0.3 mmol, 0.075 g, 10 mL), 20 mL of an aqueous solution containing HmtpO (0.6 mmol, 0.0901 g) and KNO₃ (0.3 mmol, 0.030 g) was added. The mixture was heated at 50 °C for 10 min. Then, the resulting clear solution was acidified with diluted HCl at pH 0, and over this solution was added dropwise an aqueous solution of oxalic acid dihydrated (0.3 mmol, 0.038 g, 10 mL) keeping stirring for 30 min. Finally, pH value was raised to 7 by adding diluted KOH very slowly, during one hour approx. (to avoid quick formation and precipitation of manganese oxalate, manganese hydroxide or the binary complex with mtpO). The resulting solution was kept stirring for one hour and then was left evaporating at room temperature. After 4–5 days, crystals of manganese(II) oxalate were formed and filtered off and, a few days later, colorless crystals of the title compound were isolated. (Yield: 20%). Elemental analysis data: % calc. for C₂₆H₃₂K₂Mn₂N₁₆O₁₄ (% found): C, 31.84 (32.02); H, 3.29 (4.26); N, 22.85 (22.04).



Fig. 1. View of the coordination environment of the metal atoms, along with the atom numbering scheme. It is also clearly shown the bridging fashion of oxalate ligand (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

started approach to design new biomimetic systems which may show either physical or biological properties for their use as chemotherapeutic agents.

The infrared spectrum of the title compound shows two intense bands at 1637 and 1528 cm⁻¹, which are displaced to lower frequencies than those for the neutral form of HmtpO, due to the ligand deprotonation. These bands may be assigned to a combination of stretching vibrations of C=O bond and pyrimidinic and triazolic rings C=C and C=N bonds: ν (C=O) + ν (pym) + ν (trz) [11]. The stretching vibration of the oxalate C=O bonds is not observed as may be overlapped with those of the triazolopyrimidine ligand. The IR spectrum also shows a broad band around 3400 cm⁻¹ due to the ν (O–H) stretching vibrations of the water molecules.

According to single crystal X-ray diffraction studies,³ the structure of $[K_2Mn_2(\mu\text{-mtpO})_4(\mu_6\text{-}ox)(\mu\text{-H}_2O)_6]_n$ exhibits a 2D heterometallic coordination framework in which K⁺ and Mn²⁺ ions and three different bridging ligands are coexisting, namely mtpO, oxalate and water molecules. The asymmetric unit consists of two manganese (II) ions, two potassium ions, one oxalate ligand, four mtpO ligands and six water molecules. Both potassium and manganese ions display distorted octahedral coordination geometry (Fig. 1). Each potassium ion is coordinated to six oxygen atoms, two belonging to two different oxalate anions, another two pertaining to two mtpO ligands and two water molecules. The coordination environment of Mn(II) atoms is of MnN₂O₄ type and formed by two nitrogen atoms (N3) of two



Fig. 2. Two-dimensional framework along *a* axis direction.

mtpO ligands, two oxygen atoms of an oxalate ligand and two water molecules. Cis angle values are ranging from $80.5(2)^{\circ}$ to $109.7(2)^{\circ}$. while for manganese center, they vary from $74.5(2)^{\circ}$ to $96.4(2)^{\circ}$. Fig. 1 also shows the simultaneous coordination of the oxalate anion to two Mn²⁺ ions and four K⁺ ions while two water molecules are connecting two neighboring potassium ions; it should be noted that the chelating effects of both oxalate and water ligands are the main responsible for the distortion in the coordination geometry of both metal atoms. In this way, both oxalate and water bridges sequentially connect metal centers to form a linear 1D polymeric ribbon. These metal-oxalate cationic ribbons or double chains are further linked by mtpO ligands acting as spacers (through their N3 and O7 atoms) to result in a neutral 2D framework as shown in Fig. 2 (see also Fig. S1). This coordination mode for the triazolopyrimidine derivative is rather unusual since it has only been observed previously in the coordination polymer { $[Cu(\mu-HmtpO)_2(H_2O)_2](ClO_4)_2 \cdot 2HmtpO$ }_n, which has been recently reported by us [8]. These ligands are not paralelly arranged but their molecular planes form a dihedral angle of ca. 65°, so there are any π -stacking forces between aromatic systems. It should be highlighted the rare coordination behavior of the oxalate ligand, which is also quite unusual in metal-organic systems [12]. Selected bond distances and intermetallic distances are listed in Table S1.

The resulting sheets are packed, just by weak van der Waals forces, in an ABAB sequence. However, strong intra-sheet hydrogen bonds establish between oxygen atoms of water and mtpO ligands and nitrogen atoms N1 and N4.

Regarding thermal behavior of the polymer $[K_2Mn_2(\mu-mtpO)_4(\mu_6-ox)(\mu-H_2O)_6]_n$, its dehydration takes place in the 90–170 °C temperature range in a well-defined weight loss effect in TG diagram, which corresponds to the loss of all water molecules; the associated enthalpy is -60.5 kJ per water mol (average value). The anhydrous compound is stable until 300 °C; at this temperature decarboxylation begins followed by the pyrolysis of the organic moiety, which finishes at 770 °C. The inorganic residue is a mixture of MnO₂ and KO₂.

The magnetic characterization of the title compound was carried out through measurements of the variation of the molar magnetic susceptibility, χ_m , with temperature (Fig. S2).⁴ The χ_m T value continuously decreases on cooling, more quickly below 100 K. The value of χ_m T at room temperature is 8.48 cm³ mol⁻¹ K (μ_{eff} =8.24 BM), which is in good agreement with that expected for two isolated Mn(II) ions of

³ Crystal data: crystal diffraction intensities were collected, at room temperature, in a Xcalibur diffractometer equipped with an area detector and graphite monochromated MoK α (λ = 0.71073 Å). The data reduction was done with the CrysAlis RED software of the diffractometer. The structure was solved by direct methods using SIR92 program and refined by full-matrix least-squares on F² including all reflections (SHELXL97). All calculations were performed using the WINGX crystallographic software package. During the data reduction process it became clear that the crystal specimen was a non-merohedral twin, in which both parts of the twin are related by means of a binary rotation axis along the [100] direction (twin law: 1 0 0/0.5–1 0/0–1 1). Structure refinements were carried out through SHELX97 using HKLF5 and BASF entries, which revealed a fractional value of 0.35 for the minor domain.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the heterocycles were placed in ideal positions with U_{iso} 20% larger than U_{eq} for the atoms to which they are attached. H atoms belonging to the methyl group and to the water molecules were located in the difference Fourier maps and kept fixed at these positions with U_{iso} 50% larger. Crystal dimensions $0.42 \times 0.18 \times 0.15$ mm, formula $C_{26}H_{32}K_2Mn_2$. $N_{16}O_{14}$, fw 1422.84, triclinic, space group P-1, a = 8.0349(4) Å , b = 15.1016(8) Å, c = 16.6821(8) Å, α = 106.118(4)°, β = 90.056(4)°, γ = 97.687(4)°, V = 1925.62(17) Å³, Z = 2, T = 293(2), ρ calcd = 1.691 g cm⁻³, μ = 0.958 mm⁻¹, F(000) = 1000, 6612 reflections collected, 6612 unique (Rint = 0.0000). Goodness of fit on F² = 1.079, R = 0.0706 (I>2 σ (I)), wR² = 0.1903 (all data).

⁴ Magnetization and variable temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline sample were carried out on a Quantum Design SQUID MPMS-7 device operating at 0.1 T. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

high spin (S=5/2, g=2.008). Above 10 K, the magnetic susceptibility follows a Curie–Weiss law with $C_{\rm m}$ =8.881 cm³ K mol⁻¹ and θ = -12.4 K. Both, the negative temperature intercept and the decrease of the magnetic effective moment at low temperatures are in agreement with weak antiferromagnetic interactions in the compound. Taking into account the crystal structure the experimental data were fitted to a model of S=5/2 dimers, from which a satisfactory fit was obtained with a coupling constant (*J*) value of -1.76 cm^{-1} for the interaction between manganese ions through oxalate bridging ligand. The obtained *J* value lies in the lower range found for others trans-MnO₄N₂ chromophores bridged by bisbidentated oxalato ligands (-2.16 < J < -1.74 cm^{-1}), probably because the relatively long Mn···Mn distance present in this compound (5.76 Å for compound **1** vs 5.54–5.71 Å for other examples of oxalate bridged Mn(II) compounds) weakens the antiferromagnetic exchange coupling [13].

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Appendix A. Supplementary data

Figures S1 and S2; and Table S1. CCDC 842758 contains the supplementary crystallographic data for the manganese complex. 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. Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2012.01.031.

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