

Influence of pseudohalide ligands on the structural versatility and properties of novel ternary metal complexes with 1,2,4-triazolo[1,5-*a*]pyrimidine†

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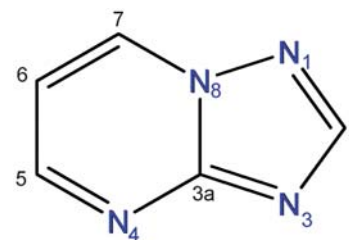
Eight new multidimensional metal(II) complexes $[\text{Zn}(\text{tp})_2(\text{NCS})_2]$ (**1**), $[\text{Ni}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Ni}(\text{NCS})_4]_n$ (**2**), $[\text{Co}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Co}(\text{NCS})_4]_n$ (**3**), $[\text{Cd}(\text{tp})_2(\text{NCS})_2]_n$ (**4**), $[\text{Mn}(\text{tp})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ (**5**), $[\text{Zn}(\text{tp})_2(\text{NCO})_2]$ (**6**), $[\text{Cd}(\text{tp})(\text{NCO})_2]_n$ (**7**) and $[\text{Cd}(\text{tp})(\text{N}_3)_2]_n$ (**8**) have been synthesized by conventional reactions of the 1,2,4-triazolo[1,5-*a*]pyrimidine with metallic(II) salts in the presence of thiocyanate, cyanate and azide as auxiliary ligands. X-Ray diffraction studies on these compounds show that species **1**, **5** and **6** are mononuclear units in which zinc and manganese have tetrahedral and octahedral coordination geometry, respectively. Complexes **2** and **3** are isostructural and consist of neutral chains with triazolopyrimidine bridging ligands through N1, N3 nitrogen atoms. Compound **4** exhibits a 2D rectangular-grid-like structure and complexes **7** and **8** are cyanate-bridged chains formed by defective cubanes. Magnetic and luminescent properties of these materials have also been studied.

Introduction

In recent years, there has been an increasing research interest in the design and synthesis of extended coordination frameworks as potential zeolitic, magnetic, conducting, nonlinear optical materials, *etc.*¹ Among these materials, magnetic coordination compounds have been commonly prepared through a bottom-up approach, connecting paramagnetic transition metal ions with the appropriate bridging ligands. The metal ions are the source of magnetic moments, whereas the bridging ligands allow for the magnetic exchange coupling between the magnetic centers.² It should be pointed out that only a few polyatomic bridging ligands (triazolate, azide, bipyrimidine, imidazole, carboxylate, *etc.*) have been shown to be able to mediate strong magnetic coupling between transition metal ions. Therefore, there is still a great interest in the search for bridging ligands, which can produce new magnetic materials with intriguing structures and magnetic properties. Some substituted-pyrimidine ligands have been shown to be excellent and versatile building blocks, with charge and multi-connectivity ability, to produce under conventional and hydrothermal conditions multidimensional coordination polymers with interesting properties.³ Other pyrimidine based ligands are 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives. These types of ligands are versatile as they have several nitrogen atoms with accessible lone pairs to bind to Lewis acids like metal ions. The presence of auxiliary ligands can also influence their coordination behaviour, either by electronic or steric reasons, giving rise in some cases to compounds with interesting metal–metal interactions through these triazolopyrimidine ligands.⁴ These ligands contain 6–5 condensed rings and therefore resemble the nucleobases, adenine and guanine, of the

natural DNA. A variety of complexes of metal salts with these ligands and other triazoles are already known and reviewed.⁵ Among these types of ligands, 1,2,4-triazolo[1,5-*a*]pyrimidine (tp) (Scheme 1) has been the subject of many studies and its physical and chemical properties as well as ¹H, ¹³C and ¹⁵N NMR spectra have been examined.⁶ Moreover, 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives have been the subject of chemical and biological studies due to their interesting pharmacology including antipyretic, analgesic, antiinflammatory, potential herbicidal, fungicidal, and leishmanicidal properties.⁷

In this paper, we report on the syntheses, structures and physical properties of four novel complexes with several divalent transition metal ions, containing 1,2,4-triazolo[1,5-*a*]pyrimidine (tp), which show wide structural diversity: (a) mononuclear units $[\text{Zn}(\text{tp})_2(\text{NCS})_2]$ (**1**), $[\text{Mn}(\text{tp})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ (**5**) and $[\text{Zn}(\text{tp})_2(\text{NCO})_2]$ (**6**); (b) linear chains $[\text{Ni}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Ni}(\text{NCS})_4]_n$ (**2**) and $[\text{Co}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Co}(\text{NCS})_4]_n$ (**3**); (c) cubane chains of type $[\text{Cd}(\text{tp})(\text{NCO})_2]_n$ (**7**) and $[\text{Cd}(\text{tp})(\text{N}_3)_2]_n$ (**8**); (d) (4,4) rectangular grid $[\text{Cd}(\text{tp})_2(\text{NCS})_2]_n$ (**4**). In these compounds, thiocyanate, cyanate and azide anions are the auxiliary ligands. It should be noted the structural diversity of the mentioned complexes seems to be influenced by the coordination mode of the pseudohalide ligands.



Scheme 1 The unsubstituted ligand tp and its IUPAC ring-numbering system.

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Experimental

General

All analytical reagents were purchased from commercial sources and used without further purification.

Preparation of $[\text{Zn}(\text{tp})_2(\text{NCS})_2]$ (1)

The reaction in aqueous solution of the tp ligand (0.1226 g, 1 mmol, 10 mL) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1307 g, 0.5 mmol, 5 mL) in a 2 : 1 molar ratio led to a colourless solution. After 10 minutes of stirring a KSCN solution (0.0972 g, 1 mmol, 10 mL) was added. The resulting solution was allowed to stand at room temperature for several days, whereupon colourless crystals of **1** formed, which were filtered off and air-dried. Yield: 61%, based on Zn. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_{10}\text{S}_2\text{Zn}$: C, 34.17; H, 1.91; N, 33.21; S, 15.21. Found: C, 34.21; H, 1.95; N, 33.29; S, 15.23%. Main IR bands: 1624s, 1541s, 1526s, 2092vs.

Preparation of $[\text{Ni}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Ni}(\text{NCS})_4]_n$ (2), $[\text{Co}(\text{tp})_2(\text{H}_2\text{O})_2(\mu\text{-tp})_2\text{Co}(\text{NCS})_4]_n$ (3) and $[\text{Cd}(\text{tp})_2(\text{NCS})_2]_n$ (4)

The used synthetic methods in these compounds were the same as that for the above compound but using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, for **2**, **3** and **4**, respectively.

Compound 2. Yield: 53%, based on Ni. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{NiN}_{10}\text{OS}_2$: C, 33.28; H, 2.33; N, 32.34; S, 14.81. Found: C, 32.93; H, 2.42; N, 31.93; S, 14.53%. Main IR bands: 1624s, 1547s, 1526s, 2101vs.

Compound 3. Yield: 78%, based on Co. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{CoN}_{10}\text{OS}_2$: C, 33.28; H, 2.33; N, 32.34; S, 14.81. Found: C, 33.15; H, 2.48; N, 32.62; S, 14.37%. Main IR bands: 1623s, 1546m, 1524m, 2090vs.

Compound 4. Yield: 75%, based on Cd. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{CdN}_{10}\text{S}_2$: C, 30.74; H, 1.72; N, 29.88; S, 13.68. Found: C, 30.46; H, 1.77; N, 29.48; S, 13.24%. Main IR bands: 1622s, 1542s, 1520s, 2053vs.

Preparation of $[\text{Mn}(\text{tp})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ (5)

To an aqueous mixture of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.4 mmol, 0.1004 g) and tp ligand (0.8 mmol, 0.0981 g), an aqueous solution of KSCN (0.8 mmol, 0.0777 g) was added slowly. From the resulting clear yellow solution, yellow microcrystalline powder corresponding to the formula $[\text{Mn}(\text{tp})_2(\text{NCS})_2]^{14}$ was obtained after several days at room temperature. Two days later, yellow prismatic crystals of the title compound, suitable for XRD analysis were isolated. Yield: 34%, based on Mn. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{MnN}_{10}\text{OS}_2$: C, 32.22; H, 2.70; N, 31.31; S, 14.34. Found: C, 32.29; H, 2.30; N, 31.07; S, 14.82%. Main IR bands: 1619s, 1539s, 1523s, 2073vs.

Preparation of $[\text{Zn}(\text{tp})_2(\text{NCO})_2]$ (6)

To an aqueous mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.1307 g) and tp ligand (1 mmol, 0.1251 g), an aqueous solution of NaNCO (1 mmol, 0.0677 g) was added slowly. From the

resulting solution, a brown powder appeared gradually and filtered off later. After several days, yellow prismatic crystals of the title compound were isolated from the mother solution. Yield: 67%, based on Zn. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_{10}\text{O}_2\text{Zn}$: C, 36.99; H, 2.07; N, 35.95. Found: C, 36.89; H, 2.11; N, 35.59%. Main IR bands: 1623s, 1542s, 1528s, 2235vs.

Preparation of $[\text{Cd}(\text{tp})(\text{NCO})_2]_n$ (7)

To an aqueous mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.3085 g) and tp ligand (2 mmol, 0.2451 g), an aqueous solution of NaNCO (2 mmol, 0.1354 g) was added slowly. From the resulting solution, an orange powder appeared gradually and filtered off later. After several days, yellow needled crystals of the title compound were isolated from the solution. Yield: 23%, based on Cd. Anal. Calcd for $\text{C}_7\text{H}_4\text{CdN}_6\text{O}_2$: C, 26.56; H, 1.27; N, 26.55. Found: C, 26.39; H, 1.30; N, 26.42%. Main IR bands: 1621s, 1526s, 2208vs, 2172vs.

Preparation of $[\text{Cd}(\text{tp})(\text{N}_3)_2]_n$ (8)

To an aqueous mixture of $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ (0.25 mmol, 0.0566 g) and tp ligand (0.5 mmol, 0.0613 g) an aqueous solution of NaN_3 (0.5 mmol, 0.0325 g) was added slowly. From the resulting solution, a yellow powder appeared gradually and filtered off later. After several days, yellow needled crystals of the title compound were isolated from the solution. Yield: 47%, based on Cd. Anal. Calcd for $\text{C}_5\text{H}_4\text{CdN}_{10}$: C, 18.87; H, 1.27; N, 44.04. Found: C, 19.18; H, 1.31; N, 44.78%. Main IR bands: 1621s, 1535s, 1525s, 2110vs.

Physical measurements

Elemental analyses were carried out at the “Centro de Instrumentación Científica” (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108. The IR spectra on powdered samples were recorded with a Thermo Nicolet IR200FTIR by using KBr pellets. Magnetization and variable temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at 1000 Oe. Magnetization *versus* applied field measurements were carried out at 2.0 K in the field of 0.1 T. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal’s tables.

Single-crystal structure determination

The data were processed with APEX2⁸ and corrected for absorption using SADABS.⁹ The structures were solved by direct methods using SIR97,¹⁰ revealing positions of all non-hydrogen atoms. These atoms were refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters.¹¹ A summary of the crystallographic data and structure refinements is given in Table 1.

Luminescence measurements

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter liquid sample holder accessory was used to obtain the fluorescence

Table 1 Crystallographic data and structural refinement details for compound 1–8

Compound	1	2	3	4	5	6	7	8
Chemical formula	C ₁₂ H ₈ N ₁₀ S ₂ Zn	C ₂₄ H ₂₀ N ₂₀ Ni ₂ O ₂ S ₄	C ₂₄ H ₂₀ N ₂₀ Co ₂ O ₂ S ₄	C ₁₂ H ₈ CdN ₁₀ S ₂	C ₁₂ H ₁₂ N ₁₀ MnO ₂ S ₂	C ₁₂ H ₈ N ₁₀ O ₂ Zn	C ₇ H ₄ CdN ₆ O ₂	C ₇ H ₄ CdN ₁₀
CCDC	744699	744700	744701	744702	765777	765778	765779	765780
M/g mol ⁻¹	421.77	866.26	866.70	468.80	447.38	389.65	316.56	316.58
T/K	293	293	293	293	293	293	293	293
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Ab</i> a2	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> /Å	8.356(1)	12.318(1)	12.510(3)	8.380(2)	8.688(1)	11.918(5)	3.562(1)	3.615(2)
<i>b</i> /Å	9.861(1)	12.891(1)	12.902(3)	19.526(4)	12.648(1)	11.340(5)	11.410(1)	11.450(7)
<i>c</i> /Å	11.207(1)	12.102(1)	12.175(3)	10.357(2)	9.064(1)	12.434(5)	12.052(1)	12.165(8)
<i>α</i> /deg	86.606(1)	90	90	90	90	90	71.286(2)	70.789(1)
<i>β</i> /deg	71.833(1)	115.818(1)	116.431(3)	90	111.736(1)	115.472(5)	83.404(2)	82.385(1)
<i>γ</i> /deg	71.391(1)	90	90	90	90	90	87.609(2)	86.674(1)
<i>V</i> /Å ³	830.7(1)	1729.7(2)	1759.8(7)	1694.7(7)	925.18(13)	1517.1(11)	460.84(9)	471.22(5)
<i>Z</i>	2	2	2	4	2	4	2	2
<i>ρ</i> /g cm ⁻³	1.686	1.663	1.636	1.837	1.606	1.706	2.281	2.231
<i>μ</i> /mm ⁻¹	1.749	1.389	1.238	1.554	0.971	1.652	2.363	2.307
Unique reflections	2914	4078	3038	1415	4790	7937	5332	5464
<i>R</i> (int)	0.019	0.056	0.052	0.029	0.016	0.039	0.024	0.017
GOF on <i>F</i> ²	1.058	1.028	1.061	1.008	1.076	1.009	1.148	1.062
<i>R</i> ¹ [<i>I</i> > 2σ(<i>I</i>)]	0.030	0.046	0.039	0.024	0.029	0.039	0.021	0.018
<i>wR</i> ² [<i>I</i> > 2σ(<i>I</i>)]	0.083	0.095	0.085	0.055	0.078	0.094	0.054	0.046

$$^a R(F) = \sum \|F_o\| - |F_c| / \sum \|F_o\|, wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

spectra. The spectrofluorimeter was equipped with a xenon discharge lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary Eclipse software for Windows 95/98/NT system. The photomultiplier detector voltage was 700 V and the instrument excitation and emission slits were set at 5 and 5 nm, respectively.

Results and discussion

Compounds containing thiocyanate anion show different structural topologies depending on the metal ion used, varying their dimensionality from mononuclear 0D to 2D species. When starting with a salt of Zn(II), the mononuclear compound **1** was isolated. Compound **1** crystallizes in the triclinic *P*1 space group. A POV-Ray perspective view of **1** is shown in Fig. 1. Selected bond lengths are given in Table 2. The structure consists of one mononuclear [Zn(tp)₂(NCS)₂] complex. Each Zn(II) ion shows an almost perfect tetrahedral ZnN₄ stereochemistry ($\tau_4 = 0.928$; $\tau_4 = 0$ for a square planar geometry and $\tau_4 = 1$ for a tetrahedral geometry),¹² formed by two thiocyanate anions and two monodentate tp ligands. The Cu–N_{tp} and Cu–N_{thiocyanate} bond distances are in typical ranges for Zn–N distances in compounds with nitrogen ligands and this type of tetrahedral geometry.¹³ The N–Zn–N angles vary from 100.84(9)° to 118.10(10)°. The crystal packing of **1** shows the presence of π – π interactions between the heteroaromatic rings of the tp ligands of two adjacent Zn units (3.67 Å) adopting an *anti* conformation.

However, chain structures were formed by using Ni(II) and Co(II) metal ions in the same conditions as before. The structure of **2** consists of an alternating arrangement of [Ni(tp)₂(H₂O)₂] and [(μ-tp)₂Ni(NCS)₄] units bridged by the N1 and N3 pertaining to the 1,2,4-triazolo[1,5-*a*]pyrimidine ligands to give a neutral 1D chain running along the *a* axis (see Fig. 2). The tp bridging ligands are coordinated in *trans* position resulting in a linear chain [Ni(tp)₂(H₂O)₂(μ-tp)₂Ni(NCS)₄]_n with the aromatic ring of the tp-bridge displaying a zigzag distribution along the *a* axis. Metal(II) ions exhibit a slightly distorted octahedral coordination geometry with bond distances and angles similar to those observed for others complexes with nickel(II) atoms containing tp ligands.⁴ Selected bond lengths are given in Table 2. Ni1 and Ni2

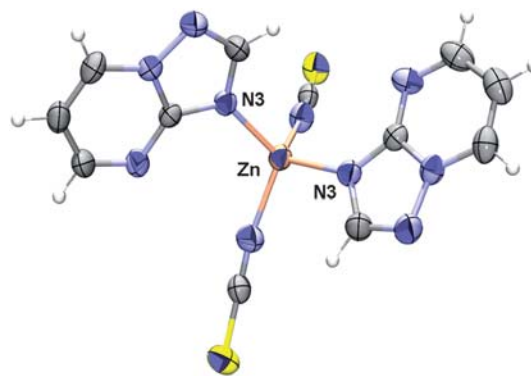
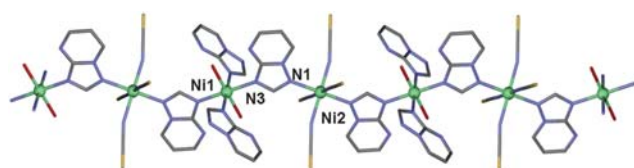


Fig. 1 Asymmetric unit of [Zn(tp)₂(NCS)₂] **1**. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented as spheres of arbitrary radii.

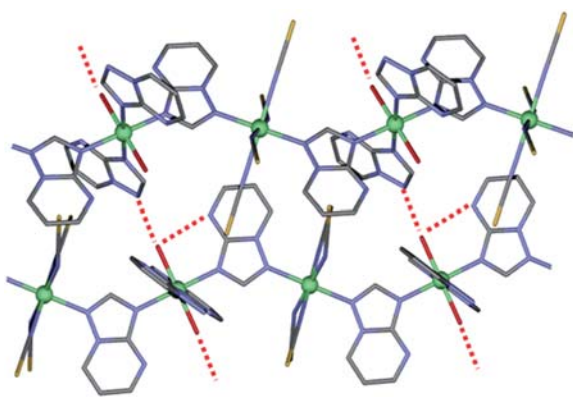
Table 2 Selected distances (Å)

Compound	1	2	3	4	5	6	7	8
M–N _{tp}	2.015(2)	2.080(2)	2.083(2)	2.355(6)	2.274(2)	2.027(3)	2.308(2)	2.306(2)
	2.019(2)	2.105(2)	2.129(2)	2.447(6)	—	2.046(3)	—	—
	—	2.135(2)	2.166(3)	—	—	—	—	—
M–N _{ligand}	1.925(2)	2.048(3)	2.048(3)	2.247(3)	2.179(2)	1.909(3)	2.321(2)	2.326(2)
	1.934(2)	2.062(3)	2.063(3)	—	—	1.915(3)	2.348(2)	2.342(2)
	—	—	—	—	—	—	2.351(2)	2.358(2)
M···M*	—	—	—	—	—	—	2.403(2)	2.391(2)
	—	—	—	—	—	—	2.428(3)	2.438(2)
	—	6.159(3)	6.255(3)	6.661(3)	—	—	3.562(3)	3.615(3)
	—	—	—	—	—	—	3.602(3)	3.638(3)
	—	—	—	—	—	—	3.674(3)	3.671(3)

**Fig. 2** Perspective view of the chain structure of **2**.

ions exhibit a distorted octahedral coordination environment. In the case of Ni1, four nitrogen atoms from four different tp ligands and two oxygen water atoms coordinate to the metal centre. However, in the case of Ni2, two nitrogen atoms from two different tp ligands and four nitrogen thiocyanate atoms are coordinated. The *cis* angles are in the 87.48(9)–92.52(9)° and 88.70(11)–91.30(11)° ranges for Ni1 and Ni2, respectively, whereas the *trans* angles are 180° imposed by symmetry.

Chains running along the *a* axis are not isolated but connected by hydrogen bonds involving one of the oxygen water atoms of a chain and the non-coordinated N3 atoms of the non-bridging tp ligands of the neighboring chain, with a distance of 2.91 Å. In this description, only the [Ni(tp)₂(H₂O)₂] units are involved in the hydrogen bonds. As a consequence of these hydrogen bond interactions, neighboring chains are turned by 39.6° with respect to each other and shifted by half of a unit, being the shortest interchain metal–metal distance of 8.841 Å (Fig. 3). It should also be remarked that the mentioned hydrogen bond interactions generate a supramolecular 3D network. Besides, within a chain it

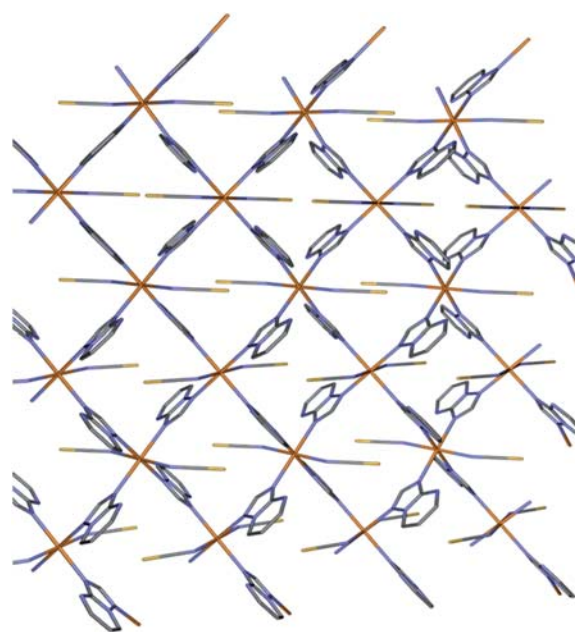
**Fig. 3** A view of the chains arrangement and hydrogen bond interactions in the *ac* plane of **2**.

is stuck out a strong hydrogen bond (2.789 Å) involving the water molecule O1w and the N4 of the tp bridged ligand.

The structure of [Co(tp)₂(H₂O)₂(μ-tp)₂Co(NCS)₄]_n (**3**) is isostructural with **2** but with cobalt instead of nickel ions. Selected bond lengths are given in Table 2.

By replacing previous metal ions by Cd(II), structural dimensionality is increased, giving rise to bidimensional layers. This is the case of compound [Cd(tp)₂(NCS)₂]_n (**4**), which consists of a bidimensional coordination polymer (Fig. 4 and 5) in which the metal atom, lying on a crystallographic two-fold axis, is planarly surrounded by four symmetry-related tp molecules, each of which is coordinated to two metal atoms through both non-bridgehead triazole nitrogen atoms. The nitrogen atoms from two monodentate NCS groups in *trans* position complete the octahedral environment around the cadmium atom. The relevant bond distances and angles are given in Table 2.

Whereas the Cd–N_{thiocyanide} bond distance is 2.247(3) Å, the Cd–N_{tp} bond lengths involving nitrogen atoms from tp-bridged

**Fig. 4** Perspective view down [0 1 0] of the two-dimensional [Cd(tp)₂(NCS)₂]_n layer present in compound **4**. Hydrogen atoms have been omitted for clarity. Significant bond distances: intralayer Cd···Cd 6.661(5) Å; shortest interlayer Cd···Cd 10.624(6) Å.

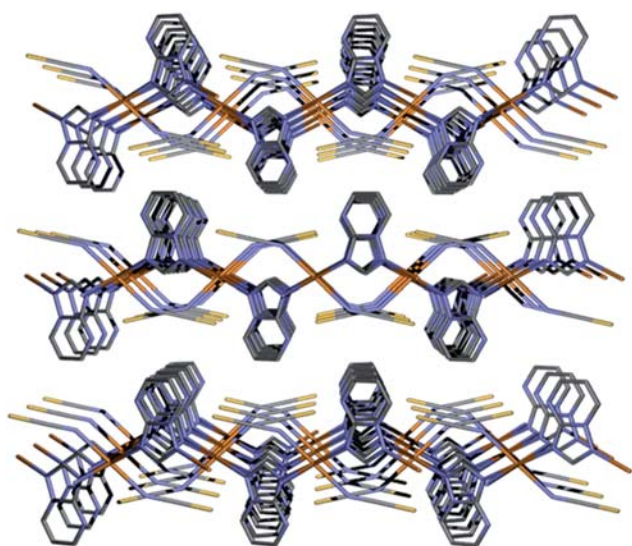


Fig. 5 Perspective view down $[0\ 0\ 1]$ of the two-dimensional $[\text{Cd}(\text{tp})_2(\text{NCS})_2]_n$ layer present in compound **4**. Hydrogen atoms have been omitted for clarity.

molecules are 2.355(6) and 2.447(6) Å. The NCS group is linear. Isostructural compounds of type $[\text{M}(\text{tp})_2(\text{NCS})_2]$, ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$ and Ni)¹⁴ have already been reported.

Also, a bidimensional species was obtained when using $\text{Mn}(\text{II})$, which was previously reported. After removing this compound, a mononuclear complex was isolated from the remaining solution, $[\text{Mn}(\text{tp})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ (**5**). It crystallizes in the $P2_1/n$ monoclinic space group. A MERCURY perspective view of **5** is shown in Fig. 6. Selected bond lengths are given in Table 2. The manganese(II) centre has an octahedral coordination environment formed by two tp ligands, two nitrogen atoms pertaining to the thiocyanate anions and two water molecules, all of these in *trans* position respectively.

The basal plane of the $[\text{MnN}_4\text{O}_2]$ octahedron includes two *trans* NCS thiocyanate anions and two water molecules exhibiting normal $\text{Mn}-\text{N}_{\text{NCS}}$ and $\text{Mn}-\text{O}_{\text{w}}$ bond lengths for Mn^{II} species.¹⁵ The apical positions are occupied by the nitrogen N3 of

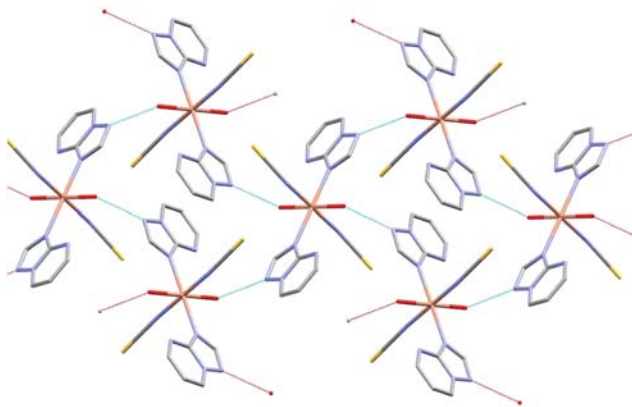


Fig. 6 Representation, down $[0\ 1\ 0]$, of the two-dimensional $[\text{Mn}(\text{tp})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ layer present in compound **5**. Hydrogen atoms have been omitted for clarity.

a tp ligand at typical distances for this type of coordination geometry.^{4,16} The *cis* angles vary between 87.19(6)° and 92.81(6)°, reflecting an almost perfect octahedral geometry. The coordinated water molecule (O1) is hydrogen bonded to the nitrogen atom N1A of tp ligand (H bond: $\text{N1A}\cdots\text{O1} = 2.860(2)$ Å). These H bonds are generating a bidimensional network (Fig. 6). The face-to-face π - π stacks are separated by a distance of about 3.48 Å.

Similar synthesis methods were carried out in order to obtain new metal complexes containing cyanate instead of thiocyanate anions. As a result, we obtained two new compounds with $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$. From the corresponding $\text{Zn}(\text{II})$ salt, compound **6** was isolated. It crystallizes in the triclinic $P2_1/n$ space group, and is similar to compound **1** but is not isostructural. A figure of **6** is essentially the same as Fig. 1 for compound **1**. Selected bond lengths are given in Table 2. The structure consists of one mononuclear $[\text{Zn}(\text{tp})_2(\text{NCS})_2]$ complex. Each $\text{Zn}(\text{II})$ ion shows an almost perfect tetrahedral ZnN_4 stereochemistry formed by two thiocyanate anions and two monodentate tp ligands.

Also in this case, increase of the structural dimensionality is raised when using $\text{Cd}(\text{II})$, which leads to the isolation of a monodimensional polymer, $[\text{Cd}(\text{tp})(\text{NCO})_2]_n$ (**7**), made of cyanate-bridged Cd^{2+} defective cubanes (Fig. 7). Selected bond distances are given in Table 2. Each metal exhibits a distorted octahedral MN_6 coordination environment, which is formed by one nitrogen atom N3 pertaining to the tp ligand, two cyanate anions that bridge two manganese atoms and three cyanate anions in *fac* disposition bridging three metallic centres (Fig. 7). *Cis* and *trans* angle values are in the ranges 80.37(8)–99.64(8)° and 172.21(7)–172.77(7)°.

This polymer can be described as defective cubane type chains, in which these cubanes have a missing vertex and each one shares two adjacent faces. The defective cubanes are formed by three cadmium cations and four nitrogen atoms of four different cyanate ligands. The $\text{Cd}\cdots\text{Cd}$ distances along the chain are 3.562, 3.602 and 3.674 Å, whereas the shortest $\text{Cd}\cdots\text{Cd}$ interchain distance is 8.807 Å. There are intrachain stacking interactions among the tp ligands (3.360 Å).

As well as thiocyanate and cyanate anions, azide anion is considered another pseudohalide anion and, therefore, it is

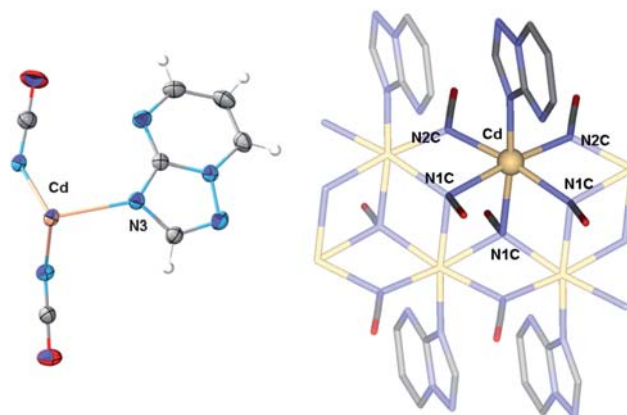


Fig. 7 Left: asymmetric unit of $[\text{Cd}(\text{tp})(\text{NCO})_2]_n$ **7**. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented as spheres of arbitrary radii. Right: coordination environment of the metallic centre of **7**.

expected that it shows similar properties to the former anions. Following the same synthetic scheme as used for the compounds described above, we obtained a new Cd(II) complex, $[\text{Cd}(\text{tp})(\text{N}_3)_2]_n$ (**8**). The structure of compound **8** is isostructural with **7** but in this case, the pseudohalide ligand is the azide anion. Selected bond distances are given in Table 2. In this compound, *cis* and *trans* angle values are in the range 78.35(6)–101.71(6)° and 170.14(6)–172.97(5)°. The Cd⋯Cd distances along the chain are 3.615, 3.638 and 3.671 Å, whereas the shortest Cd⋯Cd interchain distance is 8.883 Å. There are intrachain stacking interactions among the tp ligand (3.394 Å).

Magnetic properties

The magnetic properties of **2**, in the form of $\chi_{\text{M}}T$ vs. T are represented in Fig. 8. The magnetic data between 40 and 300 K were fitted with the Curie–Weiss law ($\chi_{\text{M}} = C/(T - \theta)$) yielding a Curie constant $C = 1.193 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $g = 2.183$ and a negative Weiss constant $\theta = -8.98 \text{ K}$, indicating net antiferromagnetic interactions between the Ni^{II} centres. This is also obvious by the decrease of the $\chi_{\text{M}}T$ values upon cooling. This compound exhibits strong antiferromagnetic exchange, as evidenced by a maximum in the susceptibility at $T = 10 \text{ K}$. The magnetic susceptibility data for **2** were modelled based on the linear chain structures proposed for these materials. This was accomplished using the isotropic Heisenberg model for exchange-coupled linear chains of $S = 1$ metal centres developed by Weng¹⁷ and Hiller *et al.*,¹⁸ obtaining a value of $J = -5.9 \text{ K}$.

The magnetic properties of **3**, in the form of $\chi_{\text{M}}T$ vs. T are represented in Fig. 9. The room-temperature $\chi_{\text{M}}T$ value of $5.81 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is larger than the spin-only value of $1.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for an uncoupled high-spin octahedral Co^{II} ion ($S = 3/2$, $g = 2$), according to the well-documented orbital contribution of the distorted octahedral Co^{II} ions. Upon lowering the temperature, $\chi_{\text{M}}T$ decreases, attains a minimum at 2 K ($\chi_{\text{M}}T = 2.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). The magnetic susceptibility in the 40–300 K range obeys the Curie–Weiss law with a Curie constant $C = 3.309 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $g = 2.66$ and $\theta = -23.9 \text{ K}$. The continuous decrease in $\chi_{\text{M}}T$ from room temperature to 20 K can be attributed to both the spin–orbit coupling of the octahedral Co^{II} ions with a $^4\text{T}_{1\text{g}}$ ground term and the moderate antiferromagnetic coupling

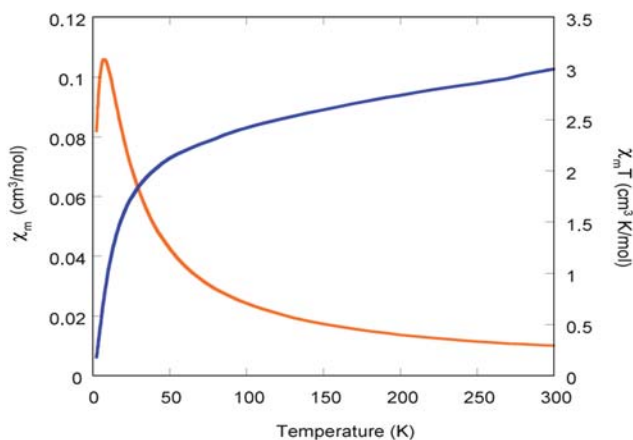


Fig. 8 Temperature dependence of χ_{M} (left) and $\chi_{\text{M}}T$ (right) for **2**.

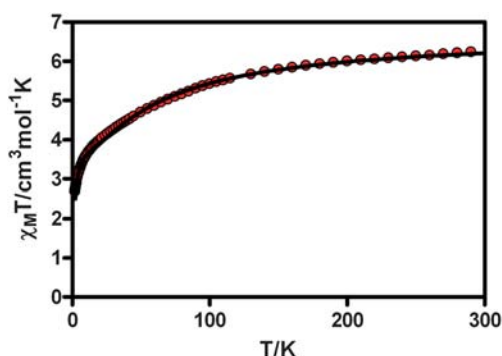


Fig. 9 Temperature dependence of $\chi_{\text{M}}T$ for **3**.

between the Co^{II} centres through the triazolopyrimidine bridging ligand.

No analytical expression is available in the literature describing the temperature dependence of χT for chains of Co^{II} ions with spin–orbit coupling. In order to get an estimate of the strength of the antiferromagnetic exchange interaction, it has been shown in previous works¹⁹ that one may use the simple phenomenological equation,²⁰ where $A + B$ equals the Curie constant, and E_1 , E_2 hold for “activation energies” corresponding to the spin–orbit coupling and to the antiferromagnetic exchange interaction, respectively.

$$\chi T = A^{-E_1/kT} + B^{-E_2/kT}$$

This equation describes the spin–orbit coupling well; this coupling results in a splitting between discrete levels, and exponential low-temperature divergence of the susceptibility. The experimental data have been fitted and are very well described by this model (Fig. 9). The values found for $C = A + B$ ($A = 2.749$ and $B = 3.968$) are larger than those obtained from the Curie–Weiss law in the high temperature range, however, the values for E_1/k (41.80 K) are consistent with those given in the literature for both the effects of spin–orbit coupling and site distortion.²¹ As for the value found for the antiferromagnetic exchange interaction, it is very weak indeed, $-E_2/k = -0.703 \text{ K}$ corresponding to interactions $J = -1.406 \text{ K}$.²²

Spectroscopic and luminescent properties

A comparison of the infrared spectra of the tp ligand and its metal complexes described above reveals in all cases a small displacement of tp bands due to combined stretching vibrations of the ligand C=C and C=N aromatic bonds to higher wavenumbers.²³ These minor displacements suggest a coordination of tp ligand to the metal center. In addition, one or two bands corresponding to thiocyanate (2052–2101 cm^{-1}), cyanate (2215–2207 cm^{-1}) and azide (2110 cm^{-1}) anions respectively are also observed.^{14,24,25}

Among the most studied properties of materials containing aromatic molecules, such as molecular crystals, organic polymers, coordination compounds or even donor–acceptor pairs, luminescence occupies a special ranking, due to the potential applications of visible light emitters²⁶ in a number of

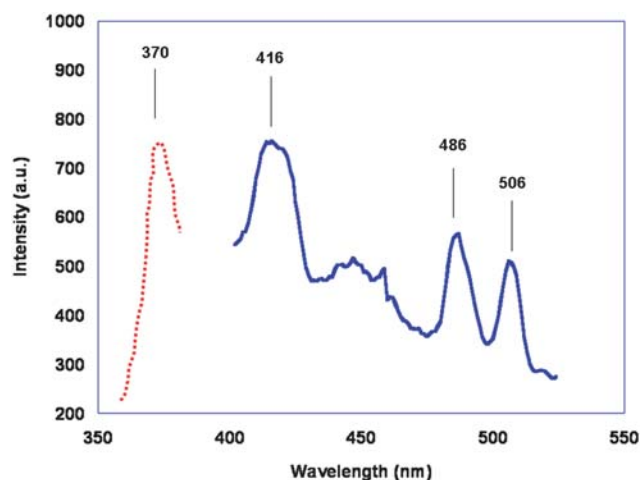


Fig. 10 Excitation (red) and emission (blue) spectra of 1,2,4-triazolo[1,5-*a*]pyrimidine at room temperature in solid state. Horizontal axis: wavelength (nm); vertical axis: intensity (a.u.).

technologically advanced fields. Thanks to its extended aromaticity and to the presence of hexa-atomic rings, triazolopyrimidine derivative ligands are good candidates for enhanced emissive properties. To the best of our knowledge, there is no previously reported tp ligand showing luminescent properties. Taking it into account, we decided to carry out a study of luminescent properties of tp ligand and their coordination compounds. The excitation and emission spectra of the ligand 1,2,4-triazolo[1,5-*a*]pyrimidine at room temperature in solid state are shown in Fig. 10.

Using a 370 nm incident radiation, intense emission bands at 416, 486 and 506 nm were observed. However, when we registered the spectra of **1**, **4**, **6**, **7** and **8**, we found that there is not a significant change in the position of the maximum emission. When we excited at 372, 367, 371, 370 and 373 nm, we obtained three emission bands nearly at the same position as that of the tp ligand. Previous reports, about analogous cadmium complexes with azolate ligands, show similar intense bands, which were attributed to ligand-to-ligand electronic transitions.²⁷ These bands were assigned to an intraligand transition, which was affected by the coordination of the ligand to the Cd(II) and Zn(II) atoms. In this case, the luminescent properties of these compounds do not vary with the coordination of the ligand to the metal centres.

Conclusions

In this work, we have shown that new polymers with interesting properties can be synthesized by using classic ligands such as tp (1,2,4-triazolo[1,5-*a*]pyrimidine). The results reported in this paper clearly show that tp is a versatile ligand, which is able to afford a rich variety of multidimensional complexes with interesting properties. We present eight new coordination compounds with great structural diversity in which tp ligand can act as a monodentate (N3) and a bidentate bridging ligand (through N1 and N3) generating monomeric and polymeric compounds, respectively. It should be noted that structural dimensionality is strongly influenced by the metal ion used. Therefore, when Zn(II)

is used, mononuclear species are obtained for both compounds containing thiocyanate and cyanate. However, dimensionality is raised up to 1D or 2D when transition metal ions like Co(II), Ni(II) or Cd(II) are employed. By using Mn(II), 2D and mononuclear compounds are isolated in the same reaction media, being the 2D structure reported previously. These results open the door toward the preparation of new polymers synthesized with this ligand showing novel physical properties, such as magnetism, combined with a biological interest. Work is in progress in our laboratory in order to obtain new homo- and heterometallic complexes with several ligands derivated of 1,2,4-triazolo[1,5-*a*]pyrimidine because of the great interest in the study of the influence of the anionic auxiliary ligands on the final structure²⁸ and the important magnetic and leishmanicidal properties displayed by these compounds. Moreover, antiparasital studies *in vivo* are currently being developed over Zn(II) compounds, due to their promising activities showed *in vitro*, specially against some *Trypanosoma cruzi* species.

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