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Experimental and Theoretical Study of Photoluminescence and Magnetic Properties of Metal-Organic Polymers Based on a Squarate and Tetrazolate Moieties Containing Linker

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We report on the synthetic, luminescent and magnetic properties of three new isostructural Zn-, Cd- and Co-based 1D coordination polymers with the novel 3-(1H-tetrazol-5-ylamino)-4-hydroxycyclobut-3-ene-1,2-dione spacer, consisting of a squarate and a tetrazolate moiety linked by a NH group. These compounds exhibit an intense blue-green photoluminescence emissions at room temperature in the solid state (Cd- and Zn- based structures) and antiferromagnetic exchange interactions (Co-based material).

Introduction

Design of coordination polymers is an increasingly attractive field for their potential uses in fields as diverse as luminescence, gas adsorption, catalysis, magnetism and electrical conductivity[1]. Metal–organic frameworks (MOFs) are a rapidly developing class of crystalline multidimensional materials, mostly constructed from clusters of transition-metal ions held in position in a lattice by ligation to organic molecules[2]. Among the most studied ligands, N or O-donor atoms containing multidentate building-blocks are found, which have drawn extensive attention in the construction of these coordination polymers[3] based on carboxylate and/or pyridine-based ligands[4]. The development of Metal Organic Frameworks with unprecedented topologies and market-oriented applications[5] is therefore an area of increasing interest. In addition, the design of new bridging ligands uncovers previously unexplored paths to the preparation of new MOFs with interesting properties. Following our previous works[6], we present here the design and synthesis of three metal-organic polymers with a novel multidentate bridging anionic ligand, 3-(1H-tetrazol-5-ylamino)-4-hydroxycyclobut-3-ene-1,2-dione (H_2TnHsq), which contains one squarate anion

and one tetrazolate ring linked by a NH group (Scheme 1). Thanks to its extended aromaticity and the presence of polyheterosubstituded rings, $TnHsq^{2-}$ is a good candidate for enhanced emissive properties, tuneable by coordination to different metals, which should easily occur as derived from the relative position and orientation of the electron pair-donor heteroatoms present in the four- and five- membered rings of H_2TnHsq or its deprotonated derivative $TnHsq^{2-}$. Here, we report on the synthesis, crystal structure determination and analysis of luminescent and magnetic properties of the first examples of isostructural 1D-coordination polymers [Zn(TnHsq)(H_2O)$_3$]n (1), [Cd(TnHsq)(H_2O)$_3$]n (2) and [Co(TnHsq)(H_2O)$_3$]n (3) with this new multidentate anionic $TnHsq^{2-}$ ligand, obtained for the first time by in situ hydrothermal synthesis from the condensation reaction of squaric acid and 5-aminotetrazole.

Experimental Section

General Procedures: Unless stated otherwise, all reactions were conducted by hydrothermal conditions, with the reagents purchased commercially and used without further purification.

Preparation of complexes.

The general procedure for the in situ formation of $TnHsq^{2-}$ ligand is depicted in Scheme 1. The detailed synthesis of 1, 2 and 3 is explained below.

[Zn(TnHsq)(H_2O)$_3$]n (1): A mixture of ZnCl$_2$ (0.136 g, 1 mmol), 5-aminotetrazole monohydrate (0.103 g, 1 mmol), squaric acid (0.114 g, 1 mmol) and distilled water (10 mL) was sealed in a Teflon-lined acid digestion autoclave and heated at 145 ºC under autogenous pressure. After 24 h of heating, the reaction

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vessel was slowly cooled down to room temperature during a period of about 3 h. Yellow crystals of the compound under study were obtained. Yield: 61%, based on Zn. Anal. calcd $C_5H_7N_5O_6Zn$: C 20.12, H 2.36, N 23.46. Found: C 20.48, H 2.41, N 23.19. IR/cm-1: 3422 (s), 3142 (m), 2831 (w), 1805 (s), 1671 (s), 1537 (s), 1391 (s), 1159 (w), 894 (m), 750 (w), 712 (w), 660 (w).

[Cd(TnHsq)(H$_2$O)$_3$]n (**2**): The same reaction was carried out as in the above compound but using CdCl$_2$ (0.183 g, 1 mmol). White powders of the compound under study were obtained. Yield: 35%, based on Cd. Anal. calcd $C_5H_7N_5O_6Cd$: C 17.38, H 2.04, N 20.27. Found: C 17.69, H 2.12, N 20.01. IR/cm-1: 3221 (m), 2842 (m), 1803 (m), 1612 (s), 1554 (s), 1381 (s), 1082 (m), 813 (m), 665 (m).

[Co(TnHsq)(H$_2$O)$_3$]n (**3**): It was carried out the same reaction as in the above compounds but using CoCl$_2$·6H$_2$O (0.238 g, 1 mmol). Pink crystals of the compound under study were obtained. Yield: 57%, based on Co. Anal. calcd $C_5H_7N_5O_6Co$: C 20.56, H 2.42, N 23.98. Found: C 20.69, H 2.53, N 23.71. IR/cm-1: 3416 (s), 3030 (m), 1803 (w), 1699 (s), 1527 (s), 1442 (s), 1098 (w), 750 (w), 660 (w).
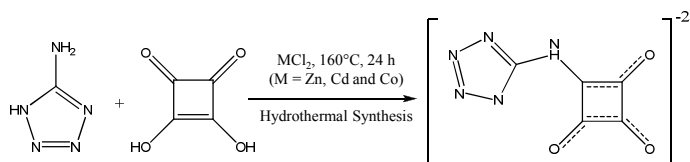
Scheme 1. *In situ* formation of TnHsq^{2-} ligand.

Physical measurements.

Elemental analyses were carried out at the "Centro de InstrumentaciónCientífica" (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108.

Single-Crystal Structure Determination.

The crystal structures of **1** and **3** were determined by single crystal X-ray crystallography[7]. Suitable crystals of **1**-**3** were mounted on a glass fibre and used for data collection on a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71073Å). Lorentz-polarization and empirical absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares calculations on F2 using the program SHELX-2014-7[8]. Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Details on the data collection and analysis can be found in Table 1. Compounds **1-3** are isostructural and CCDC reference numbers for **1** and **3** are 1402544 and 1402545, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ ccdc.cam.ac.uk).

Luminescence measurement.

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter was used to obtain the fluorescence 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.

Table 1. Crystallographic Data and Structural Refinement Details for **1** and **3**.

compound	1	3
chemical formula	$C_5H_7N_5O_6Zn$	$C_5H_7N_5O_6Co$
M/gmol-1	298.53	292.09
T(K)	100(2)	100(2)
λ/Å	0.71073	0.71073
Cryst syst	Monoclinic	monoclinic
Space group	P21/c	P21/c
a/Å	8.1736(8)	8.193(2)
b/Å	10.0387(10)	10.046(3)
c/Å	11.0871(11)	10.966(3)
β/deg	106.5680 (10)	106.514(4)
V/Å3	871.95(15)	865.3(4)
Z	4	4
ρcalcd (g cm-3)	2.274	2.242
μ(mm-1)	2.851	2.018
R(int)	0.0358	0.0434
GOF on F2	1.031	1.045
R_1 [I>2σ(I)]	0.0378	0.0419
wR^2 [I>2σ(I)]	0.0869	0.0944

$R_I = \Sigma||F_0|-|F_c|| \: / \: \Sigma|F_0|; \: wR^2 = [\Sigma w(F_0^2 - F_c^2)^2 \: / \: \Sigma wF_0^2]^{1/2};$

Computational calculations.

TD-DFT theoretical calculations were performed using the Gaussian 09 package[9] at the B3LYP/6-311++G** level, on the free (TnHsq)$^{2-}$ ligand (see ESI, Table S3 and Figure S5) as well as on a suitable molecular model of 1, which includes all ligands on the first coordination sphere of a central [Zn(TnHsq)(H$_2$O)$_3$] unit, with a modified bridging (TnHsq)$^{2-}$ ligand, reduced to a N1-protonated C2-methyl-capped tetrazolate derivative. Only singlet states transitions were observed.

Magnetic measurements.

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 different magnetic fields. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Results and Discussion

Description of the structures

Compounds **1**-**3** are isostructural materials and crystallize in *P21/c* group. The structures consist of hydrogen bonded networks formed by chains containing [M(TnHsq)(H$_2$O)$_3$] units joined together by bridging TnHsq^{2-} ligands (Figure 1).
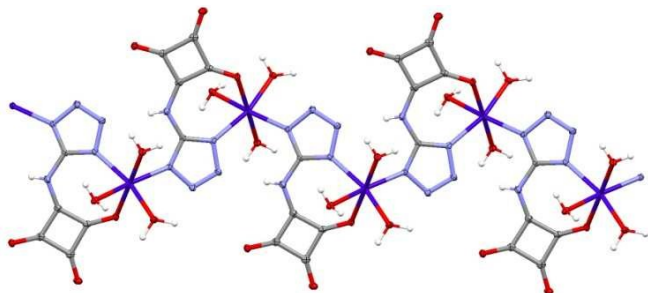

Figure 1. Perspective of the chains along the *b* axis containing [M(TnHsq)(H$_2$O)$_3$] units joined together by bridging TnHsq^{2-} ligands. (M = Zn^{2+} in **1**, Cd^{2+} in **2** and Co^{2+} in **3**). Carbon atoms, grey; nitrogen, light blue; oxygen, red; hydrogen, white; metal, blue. Thermal ellipsoids are drawn at the 50 % probability level.

The metal displays a distorted octahedral MN$_2$O$_4$ environment (N4⋯M⋯O3W angle of 167,19(10)° or 167,45(10)° in **1** and **3**, respectively), where a seven membered chelating ring is formed when N1 and O1 atoms of the tridentate *μ*-TnHsq-*κ*2N,O:*κ*N' ligand occupy two positions of the coordination sphere of the metal center (Figure 2); in addition, three water molecules are in a *fac* disposition and the coordination sphere is completed by the N4 atom of a second (*μ*-TnHsq)$^{-2}$ ligand (see ESI Tables S1 and S2 for additional distances and bond angles). An intramolecular hydrogen bond established between the N2 and H5 atoms of (TnHsq)$^{-2}$ imposes a quasi-planar conformation to the ligand with a torsion angle of 19.6° (**1**) or 17.86 (**3**) between the planes containing the squarate and tetrazole moieties. The (*μ*-TnHsq)$^{-2}$ bridges join the metal centers with a M-M-M angle of 105.39 and 105.29 ° along the chain for **1** and **3**, respectively (See Figure S1 in ESI for compound **2**).
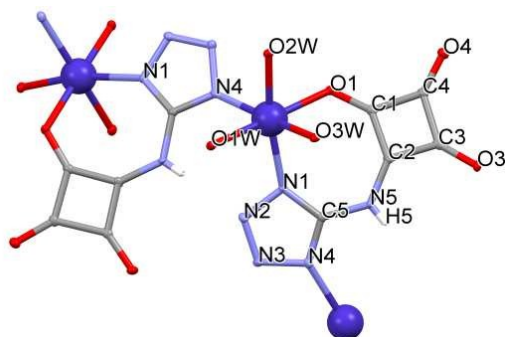

Figure 2. A view of the coordination mode of (TnHsq)$^{2-}$ in compounds **1**-**3.** Carbon atoms, grey; nitrogen, light blue; oxygen, red; hydrogen, white; metal, blue.

A complex hydrogen-bond network (see ESI Figure S2) links a central octahedral metal to three contiguous chains (see ESI, Figure S1) with H-bond distances in the 2.811(3)-3.024(3) Å range, particularly short in the case of the N2⋯H5-N5 distance, with a value of 2.818(3) and 2.811(4) Å in **1** and **3**, respectively.

Luminescent studies

The emission spectra of **1** and **2** in the solid state at room temperature are shown in Figure 3. Broad intense emission bands are observed, centred about λ = 515 and 526 nm, respectively, upon excitation at λ = 350 nm. Two shoulders can also be sensed at both sides of each band (see ESI, Figure S3). The luminescence decay curves of the compounds were obtained at room temperature (see ESI Figure S4). Data were fitted to a mono-exponential function: $I = I_0 + A \exp(-t/\tau)$, where I and I_0 are the luminescence intensities at time t and 0, and τ is defined as the luminescence lifetime. For this function, the best fit of the experimental luminescence intensities to the above equation led to the lifetimes of 0.121 ± 0.03 ms and 0.098 ± 0.04 ms for **1** and **2** complexes respectively, thus indicating phosphorescence.
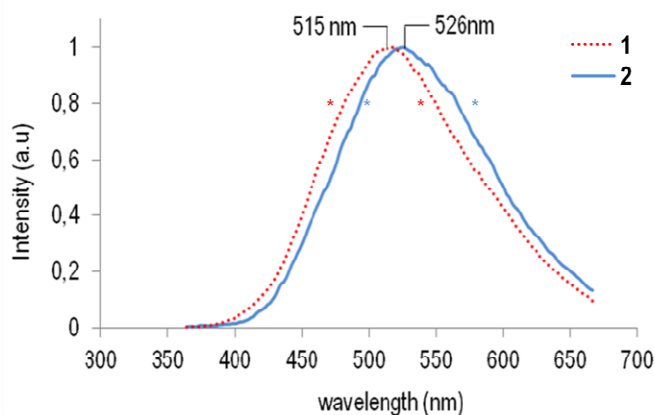

Figure 3. Experimental emission spectra of **1** (red dashed line) and **2** (blue solid line). Horizontal axis: wavelength (nm); vertical axis: intensity (arbitrary units, a.u.). Asterisks localize shoulders existing in each emission bands (see ESI, Figure S3).

Theoretical studies revealed that absorption and emission spectra of compound **1** (and **2**) are mainly related to interligand charge transfer mechanisms between the two (TnHsq)$^{2-}$ ligands coordinated to the same metal centre. Model 1 (see ESI Figure S5) shows two absorption bands at 337 and 371 nm, respectively (see ESI, Figure S7 and Table S3), and two emission bands, at 484 and 559 nm (Table 2 and Figure 4), respectively. Theoretical data were smoothed applying a Gaussian Kernel Smoothing with a bandwidth of 25 using GNU Octave (version 3.8.1) imsmooth function. The smoothed theoretical band shows a single maximum (488nm) in close agreement with the experimental results for compound **1** (515 nm). In any case, emission spectra of **1** originated from interligand electron relaxations[10] taking place between molecular orbitals delocalized mainly over the squarate moiety

of the $(TnHsq)^{-2}$ ligand model to energetically low lying molecular orbitals delocalized, mainly, over the tetrazolate moiety of the second $TnHsq^{-2}$ ligand (Table 2 and Figure 4).

Table 2. Calculated emission bands and involved electronic transitions in model 1.

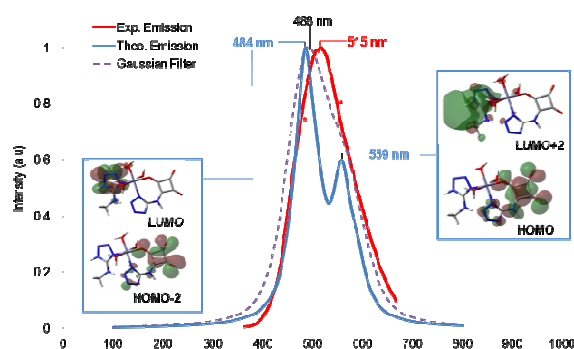| Max. λ (nm)	Calc. Transitions	Osc. Strength
Emission		
484	H-2→L (99%);	0.0010
559	H→L+2 (99%)	0.0010

Figure 4. Normalized calculated emission (solid blue line) and experimental emission (solid red line) spectra of model 1. Normalized calculated emission upon application of a Gaussian filter to theoretical data (dashed blue line). Shoulders sensed in the experimental emission spectra are indicated as *.

Magnetic Properties

The magnetic properties of compound **3** were measured in the temperature range of 2–300 K. The temperature dependence of χ_M and the $\chi_M T$ product (χ_M is the molar susceptibility per Co atom) under an applied magnetic field of 1000 Oe is given in Figure 5.
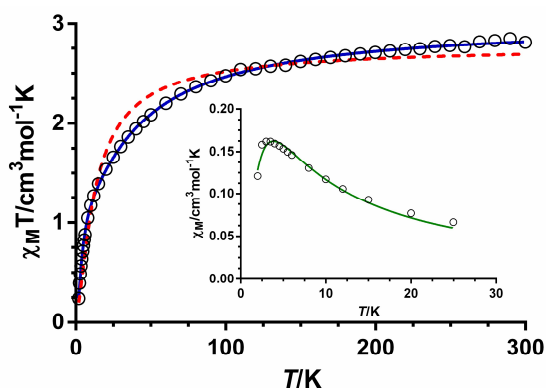

Figure 5. Temperature dependence $\chi_M T$ (circles) for compound **3**. The lines correspond to the best fits to classical spin (red dotted), Rueff (solid blue) and Ising (inset, solid green) models.

The temperature dependence of the magnetic susceptibility shows a broad maximum at 3.5 K with a value of

0.161 $cm^3 mol^{-1}$. This maximum is due to a weak intrachain antiferromagnetic coupling between the Co(II) ions through the tetrazolate bridging fragment of the ligand. The room-temperature $\chi_M T$, value of 2.61 $cm^3 mol^{-1} K$, substantially exceeds the spin-only value of 1.875 $cm^3 mol^{-1} K$ expected for an uncoupled high-spin Co^{II} (S = 3/2) ion with g = 2, thus indicating that an important orbital contribution due to the distorted octahedral Co(II) ion exists. On cooling, the $\chi_M T$ product continuously decreases with the temperature first slowly until approximately 75 K and then more sharply to reach a value 0.24 $cm^3 mol^{-1} K$ at 2 K.

This value is much lower than that expected for a magnetically isolated Co^{II} ion with an effective spin doublet and $g_0 \approx 4.3$ ($\chi_M T = 1.73$ $cm^3 mol^{-1} K$), thus supporting the existence of an antiferromagnetic exchange interaction. Therefore, the decrease of the $\chi_M T$ product in the 300–2 K temperature range is due to both the spin–orbit coupling effects of the distorted octahedral Co^{II} ion and the antiferromagnetic interaction between the Co^{II} ions along the chain through the tetrazolate bridging moiety.

In first approach, the magnetic data were fitted to the Fischer equation[11] for the magnetic susceptibility of an infinite chain of classical spins S = 3/2. The best fit led to the following magnetic parameters: J = -2.7 cm^{-1} and g = 2.43. However, the fit is not very satisfactory (see Figure 5), as expected for crudeness of the model. We have also fitted the magnetic data for T< 30 K, where only the ground Kramers doublet is thermally populated, to the equation for a chain of S_{eff} =1/2 local Ising spins derived by Fischer. [12] The best fit (shown in the inset of Figure 5) afforded the parameters: j = -8.54 cm^{-1}, $g_{x,y}$ = 2.64 and g_z = 6.874. The extracted j value for S =1/2 can be converted to the J value for S =3/2 by multiplying by the factor 9/25, so that J = -3.1 cm^{-1}. Finally, the magnetic data have been also modelled using the phenomenological approach proposed by Rueff et al:[13]

$$= A exp\left(-\frac{E}{kT}\right) + B exp\left(-\frac{E1}{kT}\right)$$

in which A+B is equal to the Curie constant and E and E1 represent the activation energies corresponding to the spin-orbit coupling and the antiferromagnetic interaction, respectively. The fit is rather good and leads to the following parameters: A+B = 3.033, E=32.88 cm^{-1} and E1 = 2.69 cm^{-1} (J = 5.4 cm^{-1}). The J values extracted for the three model are of the same magnitude and comparable to those observed for other tetrazolate-bridged Co^{II} complexes. [14]

Conclusions

In summary, we have succeeded in the design, synthesis and characterization of the first coordination polymers containing the novel 3-(1H-tetrazol-5-ylamino)-4-

hydroxycyclobut-3-ene-1,2-dione ligand. *In situ* formation of this linker by hydrothermal routes has provided a tool to generate novel materials with interesting physical properties such as intense photoluminescence luminescent properties at room temperature in the solid state as well as magnetic properties.

Acknowledgements

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7 Crystal Data. **1** (CCDC 1402544): [C$_5$H$_7$N$_5$O$_6$Zn)], *M* = 298.53, monoclinic, space group *P21/c*, *a* = 8.1736(8), *b* = 10.0387(10), *c* = 11.0871(11) Å, *β* = 106.5680 (10) °, *V* = 871.95(15) Å^3, *Z* = 4, *ρc*$_{alcd}$ = 2.274 g cm^{-3}, *μ*(Mo-K*α*) = 2.851 mm-1, *R*$_{int}$ = 0.0358, *T* = 100 K, *R$_1$(F$_o$)* = 0.0378, (w*R$_2$(F$_o$*^{2}) = 0.0869) with a goodness-of-fit on *F*^{2} 1.031. **2** (CCDC 1402545): [C$_5$H$_7$N$_5$O$_6$Co)], *M* = 292.09, monoclinic, space group *P21/c*, *a* = 8.193(2), *b* = 10.046(3), *c* = 10.966(3) Å, *β* = 106.514(4) °, *V* = 865.3(4) Å^3, *Z* = 4, *ρc*$_{alcd}$ = 2.242 g cm^{-3}, *μ*(Mo-K*α*) = 2.018 mm-1, *R*$_{int}$ = 0.0434, *T* = 100 K, *R$_1$(F$_o$)* = 0.0419, (w*R$_2$(F$_o$*^{2}) = 0.0944) with a goodness-of-fit on *F*^{2} 1.045. Data were collected by *ω* and *ψ* scans (on a Bruker APEXII diffractometer with graphite-monochromated MoK*α* radiation (▢ = 0.71073 Å). The structures were solved by direct methods and refined on *F*^{2} by the SHELX-2013 program.[13] CCDC reference numbers are 1402544 and 1402545.

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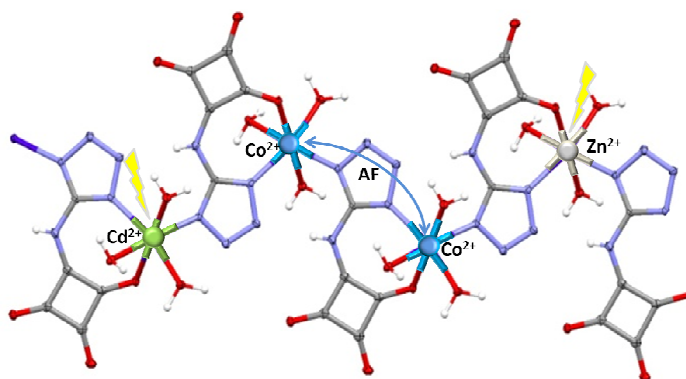
Cd²⁺, Zn²⁺ or Co²⁺ based luminescent and magnetic properties of isostructural Metal Organic chains.