

*Dedicated to Professor Ionel Haiduc  
on the occasion of his 70th anniversary*

## HYBRID ORGANIC/INORGANIC H-BONDED SUPRAMOLECULAR NETWORKS INCLUDING $[\text{Cr}(\text{ox})_2\text{L}]$ (L = 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE) TECTONS

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Self-assembly processes between bisamidinium cations  $[\text{A}-2\text{H}^+]$ , acting as hydrogen bond donors, and  $[\text{Cr}(\text{ox})_2\text{L}]$  metal complexes, as hydrogen bonds acceptors (L = 1-10 phenanthroline and 2,2'-bipyridine), lead to high dimensionality hybrid organic/inorganic supramolecular networks.

### INTRODUCTION

The solid state of molecular compounds, particularly in the crystalline state, is defined by the chemical nature of its molecular components and by their interactions to each other. An interesting way to obtain molecular networks in the solid state is to use the concepts developed in molecular tectonics,<sup>1,2</sup> which deals with the design and formation, under self-assembly conditions,<sup>3</sup> of molecular networks using structurally defined and energetically programmed molecular tectons.<sup>4</sup> This approach affords new coordination networks,<sup>5</sup> hybrid metallo-organic molecular assemblies, that attract much attention over the last decade.<sup>6</sup> The construction strategy, based on iterative processes, may lead to structural complexity even when rather simple tectons are engaged.<sup>7</sup> The precise design of these networks in terms of connectivity (type and number of coordination bonds) and dimensionality (depending on the number of translations of the coordination event leading to chains (1-D), sheets

(2-D) and tridimensional arrangements (3-D)) still remains a challenge.

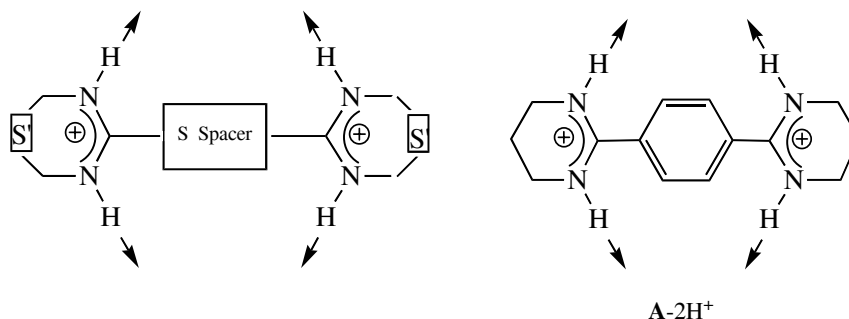
The use of secondary, non covalent interactions, like directional hydrogen bonding, is a powerful tool to build up molecular networks, when combined with electrostatic interactions. We extensively apply this approach to illustrate the rational formation of hybrid (organic/inorganic) hydrogen bonded supramolecular networks when using the complementarity of a family of compounds: bisamidinium cations (scheme 1),<sup>8</sup> able to give four directional hydrogen bonds, and hydrogen bond acceptors like polycyanometallates. The combination of both tectons generates a large variety of compounds,<sup>9</sup> some of them presenting luminescent properties.<sup>10</sup>

Some other candidates for building hybrid molecular networks are the  $[\text{M}(\text{ox})_m\text{L}]^{n-}$  complexes (M = first row transition metals, L = organic polydentate ligand), though the O...O distance between both terminal oxygen atoms from the same oxalato ligand (*ca.* 2.8 Å) doesn't fit the distance between the nitrogen atoms on the same side of the

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chosen bisamidinium cation  $[A-2H^+]$  (*ca.* 7 Å).<sup>11</sup> Along this line, we use polyoxalato derivatives like  $[Cr^{III}(ox)_2L]$  as tectons in designing interesting supramolecular solid-state architectures (L = bipy

and phen). These complex anions were employed as building blocks in constructing a large variety of magnetic heterometallic coordination networks.<sup>12</sup>



Scheme 1

The literature concerning the construction of H-bonded networks with  $[M(ox)_2L]^{n-}$  anions is scarce. Some work has been carried out with  $[Zn_2(C_2O_4)_3]^{2-}$  or  $[Sn_2(C_2O_4)_3]^{2-}$  species and protonated amines, enhancing hydrogen bonding between amines and terminal bridged oxygen atoms, with D-A (N $\cdots$ O) distances (A = acceptor, D = donor) ranging between 2.75 Å and 2.95 Å,<sup>13</sup> but no supramolecular structures have been reported yet.

## EXPERIMENTAL PART

Compounds **1** and **2** were prepared using the same procedure. A suspension of  $Ba[Cr(C_2O_4)_2(L)]_2 \cdot H_2O$  (L = phen (**1**) and bipy (**2**)) (1 mmol) in water (30 mL) was reacted with a stoichiometric amount of  $K_2SO_4 \cdot 4H_2O$  (1 mmol) dissolved in water (10 mL).<sup>12a,b</sup> The resulting mixture was stirred for 4 h to promote the complete precipitation of barium sulfate, which was removed by filtration. An aqueous solution of  $A-2H^+$  (0.5 mmol, 10 mL) was added to the red solutions. Slow evaporation of the resultant solutions led to red single crystals of **1** and **2**. For **1**: Anal.: Calc. N: 10.11%; C: 49.83%; H: 3.27%. Found: N: 10.2%; C: 50.3%; H: 3.6%. For **2**: Anal.: Calc. N: 10.33%; C: 46.5%; H: 4.09%. Found: N: 10.4%; C: 48.23%; H: 4.3%.

X-ray diffraction measurements were performed on a Bruker SMART CCD Diffractometer, using graphite-monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). All non-H atoms were refined anisotropically. Hydrogen atoms were introduced as fixed contributors at calculated positions.

Selected crystal data for **1**:  $C_{46}H_{36}Cr_2N_8O_{19}$  ( $[Cr(C_{12}H_8N_2)(C_2O_4)_2]_2[C_{14}H_{20}N_4] \cdot 3 H_2O$ ),  $M = 1108.83$  g. mol<sup>-1</sup>, Triclinic,  $P-1$ ,  $a = 10.5570(3)$  Å,  $b = 13.1932(3)$  Å,  $c = 17.4787(5)$  Å,  $\alpha = 94.658(2)^\circ$ ,  $\beta = 90.576(3)^\circ$ ,  $\gamma = 98.105(2)^\circ$ ,  $V = 2401.60(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.532$  mm<sup>-1</sup>, 16561 reflections measured, 11729 unique, final  $R$  indices ( $I > 2\sigma(I)$ )  $R = 0.0550$ ,  $R_w = 0.1684$ . CCDC reference number 635157.

Selected crystal data for **2**:  $C_{42}H_{44}Cr_2N_8O_{20}$  ( $[Cr(C_{10}H_8N_2)(C_2O_4)_2]_2[C_{14}H_{20}N_4] \cdot 4H_2O$ ),  $M = 1084.85$  gmol<sup>-1</sup>, monoclinic,  $P2/c$ ,  $a = 9.6540(7)$  Å,  $b = 6.4140(5)$  Å,  $c = 38.105(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 102.423(7)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2304.1(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.562$  mm<sup>-1</sup>, 6702 reflections measured, 5170 unique, final indices  $R$  ( $I > 2\sigma(I)$ )  $R = 0.0463$ ,  $R_w = 0.1244$ . CCDC reference numbers, 635158.

## RESULTS AND DISCUSSION

In this paper, we report on the synthesis and the self assembled structures of two new complexes, **1** and **2**, which are obtained from  $[Cr^{III}(ox)_2L]^-$  (L = phen and bipy respectively) anions and the bisamidinium cation  $[A-2H^+]$  (scheme 1), where S = phenyl and S' = propyl.

Compounds **1** and **2** were synthesised by reacting an aqueous suspension of  $Ba[Cr^{III}(ox)_2L]_2 \cdot nH_2O$  (L = bipy and phen), with the stoichiometric amount of  $K_2SO_4 \cdot 4H_2O$ . After that, the tosylate salt of  $[A-2H^+]$  was added in a 2:1 molar ratio. Slow evaporation of the resulting solutions led to red single crystals, suitable for X ray diffraction.

The crystal structure of **1** consists of neutral dimeric metallic units bridged by bisamidinium cations, as expected according to the stoichiometry of each tecton (Fig. 1). Additional three water molecules are present in the cell, each of them playing a specific role. The bisamidinium cation behaves as a divergent bis-monodentate hydrogen bond donor. The other hydrogen donor sites are occupied by two water molecules (Fig. 1). The additional water molecule connects the dimeric units through hydrogen bonds.

From both oxalato ligands on the  $[\text{Cr}^{\text{III}}(\text{ox})_2\text{phen}]^-$  unit, only one is involved in a hydrogen bond with  $[\text{A}-2\text{H}^+]$ , and only one of the oxygen atoms of this bridging bisamidinium cation has a short  $\text{N}\cdots\text{O}$  distance ( $\text{O4-N50} = 2.74$  and  $\text{O14-N40} = 2.75$  Å), which is a normal hydrogen bond between N and O.<sup>14</sup> The other  $\text{N}\cdots\text{O}$  distances involving the water molecules are equal to 2.79 Å ( $\text{O53-N46}$ ) and 2.80 Å ( $\text{O54-N44}$ ). The geometry around the chromium atoms is a distorted octahedron, as already observed.<sup>12</sup> In the dimeric unit the chromium atoms have opposite chirality, leading thus to an achiral compound. The distances and angles observed with  $[\text{A}-2\text{H}^+]$  are consistent with what was already observed in other organic/inorganic compounds, with a  $\text{N}\cdots\text{N}$  distance equal to 7.12 Å.<sup>9</sup> The NCCC dihedral angle between the phenyl group and the 6 members amidine ring is rather small: 28.2°. The dimeric units interact through offset  $\pi$ - $\pi$  stacking between the phenanthroline ligands, the associated distances with aromatic interactions being in the range of 3.32-3.68 Å, as represented in Fig. 2, leading to a supramolecular system. Thus, the chromium-chromium nearest distances between two dimers, mediated through  $\pi$ - $\pi$  stacking is 8.96 Å.

The remaining water molecule (O51 or O52 with occupancy factor equal to 0.5) connects through hydrogen bonding between these 1D systems, with  $\text{O}\cdots\text{O}$  distances of 2.93 Å ( $\text{O51-O10}$ ), 3.124 Å ( $\text{O52-O6}$ ) and 2.94 Å ( $\text{O52-O51}$ ), resulting in a 2D supramolecular architecture.

The crystal structure of **2** also consists of neutral dimeric metallic units bridged by bisamidinium cations (Fig. 3), which presents an inversion center. The bisamidinium cations present the same coordinating behaviour and the same geometry as in compound **1**, with a  $\text{N}\cdots\text{N}$  distance equal to 6.98 Å. As in the above case, hydrogen bonding are established between the organic tecton and only one oxygen atom of the oxalato ligand, with short  $\text{N}\cdots\text{O}$  distance ( $\text{N4-O8} = 3.01$  Å). (Fig. 3). Compared to **1**, compound **2** has 4 water molecules for one dimeric unit, which drastically influence the feature of the final network.

A water molecule (O9) is involved in hydrogen bonds with the other hydrogen atoms of the bisamidinium cation, with the  $\text{N3-O9}$  distance of 2.81 Å. These water molecules bridge also the dimeric units, resulting in a ladder like topology, as presented in Fig. 4a. Hydrogen bonds ( $\text{O9-O7} = 2.94$  Å and  $\text{O9-O1} = 2.83$  Å) occur between a water molecule and a non-terminal oxygen atom of a free oxalato ligand. (Fig. 4a).

The geometry around the chromium is a distorted octahedron, and again, in the dimeric unit both chromium complex anions have opposite chirality, leading thus to an achiral compound. In this arrangement, the nearest  $\text{Cr}\cdots\text{Cr}$  distance is equal to 6.41 Å. This supramolecular architecture is also sustained by graphitic-like  $\pi$ - $\pi$  stacking of the pyridyl rings belonging to the bipy ligands with distances in the range of 3.31-3.51 Å, as represented in Fig 4b. These ladders are connected to each other with other water molecules (O10), with short  $\text{O}\cdots\text{O}$  distances ( $\text{O6-O10} = 2.74$  Å,  $\text{O10-O10} = 2.88$  Å) (between the non bridging terminal oxygen atom of oxalato ligand and between two molecules of water) leading thus to an overall 2D supramolecular system, as shown in figure 4b.

## CONCLUSION

In conclusion, we presented here two new hybrid inorganic/organic systems, built essentially through strong hydrogen bonding between anionic bisoxalatometallates and bisamidinium cations. The construction of both networks is also sustained by  $\pi$ - $\pi$  stacking interactions, as well by the intervention of water molecules, leading to high dimensional systems. This is a rare example of supramolecular hybrid inorganic/organic supramolecular network obtained by hydrogen bonding involving polyoxalato metallates anions.

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