Heterometallic Anilato-Based Layered Magnets

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Abstract In this review, we present the recent use of anilato-based ligands (derivatives of the 3,6-disubstituted-2,5-dihydroxy-1,4-benzoquinone dianion = $C_6O_4X_2^{2-}$) to build heterometallic 2D magnets. Among the different metal couples, the Mn(II)Cr(III)-containing layers are, by far, the most studied and characterized ones. We will show the structures and properties of the extended families of layered magnets formulated as $A[M^{II}M^{III}(C_6O_4X_2)_3] \cdot G$ and $A_2[M^IM^{III}(C_6O_4X_2)_3] \cdot G$ (A = monocation; X = Cl, Br, CN, ...; G = solvent molecules). We also focus on how it is possible to modulate the magnetic properties of these magnets (ordering temperatures and coercive fields) by simply changing the cation, the X groups, the solvent molecules and the oxidation state of the anilato ligand. Moreover, the tune of the magnetic properties of these layered magnets in a post-synthetic way is also shown.

Keywords layered magnets, anilato ligands, heterometallic compounds, magnetic properties, molecule-based magnets

Introduction

The design, synthesis and characterization of molecule-based magnets has been one of the most active areas in materials chemistry since the discovery of the very first molecule-based magnet: a diethyl-dithio-carbamato Fe(III) complex more than fifty years ago.^[1,2] The efforts devoted to this area lead to the preparation of hundreds of molecular magnets.^[3] Some of them have critical temperatures above room temperature^[4] or combine the magnetic order with a second interesting property as metallic conductivity.^[5]

Most of these molecule-based magnets have been prepared with simple ligands as cyanide, oxalate or carboxylates.^[6] One of the most versatile family of molecule-based magnets is the oxalate-based family formulated as $A[M^{II}M^{III}(C_2O_4)_3]$ (A = monocation; M^{II} = Mn, Fe, Co, Ni, Cu, ...; M^{III} = Cr, Fe, ...) initially reported by Okawa *et al.*^[7] in 1992 and latter enlarged by other groups. This family of heterometallic magnets may present two different topologies: a 2D honey comb (6,3) lattice^[8] and a 3D chiral (10,3) lattice.^[9] In both lattices, the change of M^{II} and M^{III} leads to a large family of ferro- and ferrimagnets with ordering temperatures of up to 48 K^[10–13] and coercive fields at 2 K above 1 T.^[14] Albeit, this family presents an important drawback: the oxalate ligand cannot be modified in order to tune the magnetic properties (Scheme 1). This drawback has recently been overcome with the family of anilato-type ligands that present a similar coordination mode (Scheme 1) and give rise to the same topologies than oxalato but can be easily modified.^[15,16] Thus, we and others have recently reported the preparation of the first heterometallic anilato-based magnets, formulated as $A[MnCr(C_6O_4X_2)_3] \cdot G$ (A = NBu_4^+ and $[(H_3O)(phz)_3]^+$; X = H, Cl, Br and I; G = H_2O and CH_3COCH_3).^[17] This initial work took advantage of the observation, initially made by Lu *et al.*^[18] and later by Shilov *et al.*^[19] that the phenazine molecule perfectly fits the size of the hexagonal cavities formed in the $[M_2(C_6O_4X_2)_3]^{n-}$ layers (Scheme 1), facilitating the crystallization of these, otherwise, difficult to crystallize, layered compounds. Before the work of Lu *et al.*,^[18]

Scheme 1 Bis-bidentate coordination mode of the oxalato (left) and anilato (center) ligands. The phenazine molecule (right)

only the sodium salt of the homometallic $[Mn_2(C_6O_4H_2)_3]^{2-}$ layer had been crystallized.^[20]

The 2013 publication with the first heterometallic anilato-based layers with phenazine as a template agent, also reported the first layered anilato-based structure with NBu_4^+ as cation.^[17] Since then, more than thirty different heterometallic $[MM'(C_6O_4X_2)_3]^{n-}$ layers have been reported with different metal ions, anilato ligands and counter cations (Tables 1–3). Herein, we will revise the structures of these heterometallic layered compounds and their magnetic and electrical properties. These heterometallic layers can be classified into two different families depending on the oxidation state of the metal ions: (i) mono-anionic layers formulated as $[M^{II}M^{III}(C_6O_4X_2)_3]^-$ and (ii) dianionic layers formulated as $[M^IM^{III}(C_6O_4X_2)_3]^{2-}$. The M(II)M(III) series is by far the largest one and has been reported for three different couples of metals: Mn(II)Cr(III), Mn(II)Fe(III) and Fe(II)Fe(III). The M(I)M(III) series has only been reported for the couples Na(I)Cr(III) and K(I)Fe(III).^[21,22] It is less interesting from the magnetic point of view since it does not show magnetic order. Albeit, it may include conducting cations^[22] and one of them constitutes the first example of polymorphism in anilato-based coordination polymers.^[21]

Mn(II)Cr(III) Series

As can be seen in Table 1, most of the reported examples

Table 1 Structural and magnetic properties of all the reported $A[Mn^{II}Cr^{III}(C_6O_4X_2)_3] \cdot G$ compounds

#	CCDC	A ⁺	X	SG ^a	P ^b	T _c /K	H _c ^c /mT	Ref.
1	MIRFEA	H ₃ O(phz) ₃ ⁺	Cl	P3	E	5.5	19.4	[17]
2	MIRFIE	H ₃ O(phz) ₃ ⁺	Br	P-31m	E	6.3	34.0	[17]
3	MIRFUQ	NBu ₄ ⁺	Cl	C2/c	A	5.5	11.8	[17]
4	HOWHAE	Fe(sal ₂ -trien) ⁺	Cl	C222 ₁	A	10.0	35	[29]
5	HOWHEI	Fe(4-OH-sal ₂ -trien) ⁺	Cl	P6 ₃ 22	A	10.4	87	[29]
6	HOWHIM	Fe(sal ₂ -epe) ⁺	Br	P21/c	A	10.2	10	[29]
7	HOWHOS	Fe(5-Cl-sal ₂ -trien) ⁺	Br	P21/c	A	9.8	66	[29]
8	MUMKUC	[Fe(acac ₂ -trien)] ⁺	Cl	C2/c	A	10.8	65	[28]
9	MUMLAJ	[Fe(acac ₂ -trien)] ⁺	Br	C2/c	A	11.1	77	[28]
10	MUMLEN	[Ga(acac ₂ -trien)] ⁺	Br	C2/c	A	11.6	72	[28]
11	SEPLAD	Me ₂ NH ₂ ⁺	Br	P-31c	A	7.9	90	[27]
12	SEPLEH	Et ₂ NH ₂ ⁺	Br	P-31c	A	8.9	100	[27]
13	SEQCID	Et ₃ NH ⁺	Cl	P-31c	A	8.0	150	[27]
14	SEPROX	Et(<i>i</i> -Pr) ₂ NH ⁺	Br	P-31c	A	9.0	4 ^d	[27]
15	HORMAF	NBu ₄ ⁺	Br	P2 ₁	E	9.5	33	[23]
16	FOJYAH	NBu ₄ ⁺	Cl	P2 ₁	E	7.0	7.6	[24]
17	FOJYEL	NBu ₄ ⁺	Br	P2 ₁	E	6.7	10	[24]
18	FOJYUB	NBu ₄ ⁺	Cl	P2 ₁	E	6.8	5.0	[24]
19	FOJZAI	NBu ₄ ⁺	Br	P2 ₁	E	6.7	20	[24]
20	—	H ₃ O ⁺	Cl	P21/n	E	10.5	90	[30]
21	—	H ₃ O ⁺	Br	P21/n	E	3.6 ^e	210 ^e	[30]

^a Space group. ^b Packing: A = alternating, E = eclipsed. ^c Coercive field at 2 K. ^d A solvated phase of this compound is metamagnetic with a critical field of 490 mT at 2 K. ^e This compound is metamagnetic with a T_N of 3.6 K at low fields and a critical field of 210 mT at 2 K.

Table 2 Structural and magnetic properties of all the reported $A[Mn^{II}Fe^{III}(C_6O_4X_2)_3] \cdot G$ and $A[Fe^{II}Fe^{III}(C_6O_4X_2)_3] \cdot G$ compounds

#	CCDC	A ⁺	X	SG ^a	M ^{II} M ^{III}	T _c /K	H _c ^b /mT	Ref.
22	MIRFOK	H ₃ O(phz) ₃ ⁺	Br	P-31m	MnFe	—	—	[17]
23	QEFPOJ	H ₃ O(phz) ₃ ⁺	Cl	P-31m	FeFe	2.4	1.0	[31]
24	QEFPID	H ₃ O(phz) ₃ ⁺	Br	P-31m	FeFe	2.1	1.0	[31]
25	NIHJEW	C(N ₂ H ₃) ₃ ⁺	Cl/CN	P3	FeFe	4.0	6	[32]

^a Space group. ^b Coercive field at 2 K.

Table 3 Structural properties of all the reported $A_2[M^{II}M^{III}(C_6O_4X_2)_3] \cdot G$ compounds

#	CCDC	A ⁺	X	SG ^a	M ^{II} M ^{III}	Ref.
26	PALXUY	S-TM-ET/PPh ⁴⁺	Cl	P1	KFe	[22]
27	PALYAF	R-TM-ET/PPh ⁴⁺	Cl	P1	KFe	[22]
28	PALYEJ	rac-TM-ET/PPh ⁴⁺	Cl	P-1	KFe	[22]
29	QUJJIQ	PBu ₃ Me ⁺	Br	P2 ₁	NaCr	[21]
30	QUJJOW	PPh ₃ Et ⁺	Cl	P2 ₁	KFe	[21]
31	—	NBu ₃ Me ⁺	Br	—	NaCr	[21]
32	QUJJUC	NBu ₃ Me ⁺	Br	I-43d	NaCr	[21]

^a Space group.

of the M(II)M(III) series contain Mn(II) and Cr(III) as metal ions.

The few Mn(II)Fe(III) and Fe(II)Fe(III) examples are shown in Table 2. NOTE: Although the Fe(II)Fe(III) derivatives are not

heterometallic, we include them here because they present similar magnetic properties to the heterometallic ones, given the different oxidation state and, therefore, the different spin ground state of both metal ions.

All the reported M(II)M(III) derivatives show the typical 2D honeycomb structure, where the M(II) and M(III) ions alternate in the vertex and the anilato ligands form the sides of the hexagons (Figure 1).

Figure 1 Honey comb structure of the $[M^{II}M^{III}(C_6O_4X_2)_3]^-$ layers.

Both metal ions show an octahedral coordination environment (except in a few cases, see below) and appear coordinated to three chelating anilato ligands (Figure 2, left).

Figure 2 (Left) Tris-quelated coordination environment of the metal ions in the $[M^{II}M^{III}(C_6O_4X_2)_3]^-$ layers. (Right) Hepta-coordination of the Mn(II) centers in compounds 16–19.

The tris(anilato)metallate(III) complexes show alternating Δ and Λ configurations, giving rise to the hexagonal layers. The $[M^{II}M^{III}(C_6O_4X_2)_3]^-$ layers alternate with layers containing the cations (A⁺) (Figure 3). However, there are some exceptions in compounds 8–13, where the cations are located inside the hexagonal cavities of the honey comb layers and in compound 14, that shows double anionic layers alternating with simple cationic ones.

Figure 3 Alternating cationic and anionic layers in the series of compounds $A[M^{II}M^{III}(C_6O_4X_2)_3]$.

The disposition of the anionic layers can be eclipsed or alternated (Figure 4). The first disposition generates hexagonal channels perpendicular to the layers and is only observed in the two examples with the $[(H_3O)(phz)_3]^+$ cation (1 and 2),^[17] in five recently reported compounds with NBu₄⁺ cations and benzene

Figure 4 (left) Eclipsed packing and (right) alternating packing of the $[M^{II}M^{III}(C_6O_4X_2)_3]^-$ layers.

derivatives solvent molecules (**15–19**) and in a couple of compounds with H_3O^+ as cation (**20** and **21**) (Figure 4, left).^[23,24] Interestingly, the first reported structure with the NBu_4^+ cation showed an alternating disposition of the anionic layers (Figure 4, right).^[17] It seems that the benzene-derivative solvent molecules may play a template role favouring the formation of the eclipsed packing. The crystallization solvent molecules (H_2O , CH_3COCH_3 , $PhBr$, $PhCHO$, C_6H_6 , CH_3CN , CH_3OH , CH_2Cl_2 , ...) are located in these hexagonal channels (Figure 4, left) or in the hexagonal cavities when the layers are alternated.

Finally, it is worth to mention that, although the anionic layers are formulated as $[MnCr(C_6O_4X_2)_3]^-$ ($X = Cl$ or Br), in compounds **1** and **16–19** the $Mn(II)$ ion is additionally coordinated to a seventh oxygen atom (from a H_2O molecule in **1** and from a $PhCHO$ molecule in **16–19**, Figure 2, right). This hepta-coordination has only been observed for $Mn(II)$ and may be attributed to the large size of this ion.

From the magnetic point of view, all the $Mn(II)Cr(III)$ compounds are ferrimagnets since the $S = 5/2$ $Mn(II)$ ions are antiferromagnetically coupled to the $S = 3/2$ $Cr(III)$ ions, resulting in a long range ferrimagnetic ordering. The ferrimagnetic couplings are clearly shown by the decrease of the $\chi_m T$ product when the samples are cooled and by the presence of a minimum at low temperatures with a sharp increase at lower temperatures (Figure 5, top). The critical temperatures, determined

Figure 5 (Top) Thermal variation of the $\chi_m T$ product for compounds **16–19**. (Bottom) Hysteresis cycles at 2 K of compounds **16–19**.

with AC susceptibility measurements, range from 5.5 to 11.6 K and the coercive fields at 2 K range from 4 to 150 mT (Table 1, Figure 5, bottom).

An interesting possibility offered by these materials is the fine tuning of the ordering temperatures by simply changing the X group in the anilato ligand. This capacity was evidenced in the series of compounds $NBu_4[MnCr(C_6O_4X_2)_3] \cdot G$, where the ordering temperature can be modulated as a function of the electronegativity of X ($T_c = 5.5, 6.3, 8.2$, and 11.0 K for $X = Cl$, Br , I , and H , respectively, Figure 6).^[2]

Figure 6 (Top) AC susceptibility of the series of compounds $NBu_4[MnCr(C_6O_4X_2)_3]$ ($X = H, Cl, Br$ and I). (Bottom) Variation of T_c with the electronegativity of the X group in the same series.

A second way to tune the ordering temperatures is provided by the possibility to reduce (chemically or electrochemically) the anilato ligands to form the corresponding semiquinone radical form. This strategy has already given a very interesting example of increase of the ordering temperature from 10 to 36 K by electrochemical reduction.^[25]

Although in this family of layered ferrimagnets the ordering temperature mainly depends on the $Mn-Cr$ magnetic coupling through the anilato bridge (that can be controlled with X and with the reduction of the ligand), there are other ways to fine tune the magnetic properties of this family of layered magnets. As can be seen in Table 1, the presence of solvent molecules in the hexagonal cavities (either coordinated or not to the $Mn(II)$ ion) and in the hexagonal channels formed when the packing is eclipsed, may also play an important role in T_c . A close look at the T_c values for $X = Cl$ shows that, when there is an additional ligand (H_2O or $PhCHO$) coordinated to the $Mn(II)$ centre (as in compounds **1**, **16** and **18**), T_c is lower (5.5, 7.0 and 6.8 K, respectively) than in the other compounds (Table 1). For $X = Br$, we observe the same trend in compounds **17** and **19** that also present a $PhCHO$ molecule coordinated to the $Mn(II)$ center. The lower T_c value observed in compound **2** (where no additional ligand is coordinated to the $Mn(II)$ center) may be attributed to: (i) the presence of the $[(H_3O)(phz)_3]^+$ cation (that shows a strong $\pi-\pi$ stacking interaction with the anilato ligand and, therefore, modifies its electron density); (ii) to a lack of solvent

molecules in the structure. In fact, the presence/absence of solvent molecules represents an additional way to tune the magnetic properties. This role of the solvent molecules has been very recently demonstrated in a couple of series of isostructural compounds formulated as $\text{NBu}_4[\text{MnCr}(\text{C}_6\text{O}_4\text{Cl}_2)_3] \cdot n\text{PhX}$ and $\text{NBu}_4[\text{MnCr}(\text{C}_6\text{O}_4\text{Br}_2)_3] \cdot n\text{PhX}$ ($n = 1, 2$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CH}_3, \text{CN}$ and NO_2), where the insertion, removal and exchange of the solvent molecules leads to changes in T_c .^[23,26] This solvent exchange and/or removal results in a change of the ordering temperatures and constitutes an additional post-synthetic and easy way to modulate the ordering temperatures.

Furthermore, in a few cases, the ferrimagnetic layers present a weak antiferromagnetic inter-layer coupling leading to a metamagnetic behaviour, as in compounds **14** and **21**, where the antiferromagnetic inter-layer coupling can be overcome by the application of a moderate field (Figure 7).

Figure 7 (Top) Magnetization of compound **20** showing the metamagnetic transition at ca. 0.2 T. (Bottom) Thermal variation of χ_m for compound **20** with different magnetic fields.

Additionally, in some cases, the A^+ cations also provide interesting magnetic properties. Thus, the A^+ cations in compounds **4–9** are typical spin crossover (SCO) cations, although their confinement in between the layers or inside the hexagonal cavities precluded the SCO, at least in these examples. Proton conductivity is another interesting additional property that can be supplied by the cations, as in compounds **11–14**, that show proton conductivities in the range 2.3×10^{-6} and 2.4×10^{-5} S/cm at 70 °C and 95 % relative humidity, with activation energies of ca. 0.2 eV.^[27]

Furthermore, compounds **4** and **8–10** have been exfoliated in thin layers with heights down to 2 nm, introducing novel possibilities of those magnetic materials.^[28]

Other M(II)M(III) Derivatives

As mentioned above, there are also a few examples of Mn(II)Fe(III) and Fe(II)Fe(III) reported compounds (Table 2). The only known Mn(II)Fe(III) derivative was also described in

the original report with the first heterometallic examples.^[17] The magnetic properties of the MnFe derivative show, as expected, an antiferromagnetic Mn-Fe coupling but now both ions present the same $S = 5/2$ spin ground state and this compound does not show any long range order. As observed in all the reported examples with the cation $[(\text{H}_3\text{O})(\text{phz})_3]^+$, the packing of the anionic layers is also eclipsed.

The three reported Fe(II)Fe(III) examples are more interesting since they show ferrimagnetic order with ordering temperatures in the range 2.1–4.0 K and simultaneously they present a semiconducting behaviour with room temperature conductivities in the range 3×10^{-2} to 2×10^{-3} S/cm (Figure 8, top).^[31,32] This electrical conductivity is attributed to the mixed valence state of the Fe(II)/Fe(III) layer. Besides the simultaneous presence of magnetic ordering and conducting properties, two of the Fe(II)Fe(III) derivatives have been delaminated in thin films of only a few monolayers (Figure 8, bottom). The packing of the layers is also eclipsed in all cases. In compounds **23** and **24**, this eclipsed packing is due to the presence of the $[(\text{H}_3\text{O})(\text{phz})_3]^+$ cations, whereas it is attributed to the presence of some H-bonds between the $\text{C}(\text{N}_2\text{H}_3)^{3+}$ cations and the anionic layers in compound **25**.^[32]

Figure 8 (Up) DC electrical conductivity of compounds **23** and **24**. (Bottom) Nanoflakes of compounds **23** (left) AFM image (thickness = 7 nm) and **24** (right) HR-TEM image.

M(I)M(III) Derivatives

The second series of heterometallic anilato-based layered compounds can be formulated as $\text{A}_2[\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{X}_2)_3] \cdot \text{G}$ and has only been reported for two couples: Na(I)Cr(III) and K(I)Fe(III) (Table 3).^[21,22]

The structure of these heterometallic $\text{M}^{\text{I}}\text{M}^{\text{III}}$ compounds is very similar to that observed in the $\text{M}^{\text{II}}\text{M}^{\text{III}}$ series. They also present alternating cationic and honey comb anionic layers (Figure 9, top). The main difference is the shape of the hexagonal cavities since they are slightly irregular in the $\text{M}^{\text{I}}\text{M}^{\text{III}}$ series as shown by the different dimensions of the diagonals of the hexagons and the $\text{M}^{\text{I}}\text{M}^{\text{III}}\text{M}^{\text{I}}$ and $\text{M}^{\text{III}}\text{M}^{\text{I}}\text{M}^{\text{III}}$ angles (Figure 9, bottom). These differences are attributed to the larger size of the M^{I} cations compared to the M^{III} ones.

Figure 9 (Top) A $[\text{NaCr}(\text{C}_6\text{O}_4\text{Br}_2)_3]^{2-}$ layer in compound **29**. (Bottom) Detail of one hexagonal cavity in compound **30**. Colour code: C = grey, O = red, Cl = light green, Br = brown, Cr = dark green, Fe = orange, K = purple.

As expected, these compounds are paramagnetic and their magnetic properties correspond to those of the M(III) cations, since the M(I) cations are diamagnetic and isolate the M(III) ions from the magnetic point of view. In some of these compounds, the cationic layers show conducting properties as in compounds **26–28**, which are semiconductors with room temperature conductivities of ca. $3 \times 10^{-4} \text{ S/cm}$.^[22]

Another interesting finding in the M^{III} series is the existence of polymorphism between compounds **31** and **32**. Thus, compound **31** is the 2D polymorph of compound **32**, which presents a 3D structure formed by two interpenetrated chiral 10,3-*gon* lattices (Figure 10).

Figure 10 3D structure of compound **32** showing the two interpenetrated $[\text{NaCr}(\text{C}_6\text{O}_4\text{Br}_2)_3]^{2-}$ lattices (only the positions of the metal ions are shown). The lines linking the metal ions represent the anilato bridges.

Conclusions and Perspectives

The design and synthesis of heterometallic anilato-based compounds have proven to be a successful strategy to prepare new molecule-based magnets and multifunctional molecular materials. The large stability of these heterometallic lattices and their anionic character have allowed the synthesis of many

molecular magnets presenting, in some cases, additional properties as electrical conductivity, proton conductivity, solvent exchange, etc.

The possibilities opened by these series of magnets are enormous. Many other cations with other interesting properties as single molecule magnets (SMM), luminescence, non linear optic properties, SCO, and so on, can be intercalated in between the heterometallic layers to construct multifunctional magnets.

The possibility to reduce (chemically or electrochemically) the anilato ligands to form the corresponding semiquinone radical form constitutes a very promising research line in these materials and is expected to yield layered magnets with very high ordering temperatures, as already observed in other homometallic anilato based magnets.

Acknowledgement

We thank the Spanish MINECO (project CTQ2017-87201-P AEI/FEDER, UE) and the Generalidad Valenciana (project Prometeo/2019/076) for financial support.

Author Contributions

Both authors have contributed to the writing and revision of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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Received December 1, 2019

Accepted December 27, 2019