Heterometallic Anilato-Based Layered Magnets

Samia Benmansour and Carlos J. Gómez-García*
Departamento de Química Inorgánica, ICMOL, Universidad de Valencia, Catedrático José Beltrán 2, 46980 Paterna, Valencia, Spain
Email: carlos.gomez@uv.es (C. J. G. G.)

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 = C₆O₂X₂⁻) 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[MₓM’ₓ(C₆O₂X₂)]·G and A₂[MₓM’ₓ(C₆O₂X₂)]·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 temperature⁴ 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[MₓM’ₓ(C₆O₂X₂)]·G and A₂[MₓM’ₓ(C₆O₂X₂)]·G (A = monocation; X = Cl, Br, CN, ···; G = solvent molecules). 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 NBu₄⁺ as cation.⁷ Since then, more than thirty different heterometallic [MM’ₓ(C₆O₂X₂)]⁻ 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) monomeric layers formulated as [MₓM’ₓ(C₆O₂X₂)]⁻ (i) dianionic layers formulated as [MM’ₓ(C₆O₂X₂)]⁻. 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(II)M(III) series has only been reported for the couples Na[I]Cr(III) and K[I]Fe(III). It is less interesting from the magnetic point of view since it does not show magnetic order. Albeit, it may include conducting cations and one of them constitutes the first example of polymorphism in anilato-based coordination polymers.

Mn(II)Cr(III) Series

As can be seen in Table 1, most of the reported examples...
of the M(II)M(III) series contain Mn(II) and Cr(III) as metal ions. Table 2 lists the structural and magnetic properties of all the reported A[MnII][CrIII(CO4X3)]G compounds. The disposition of the anionic layers can be eclipsed or staggered. In compound 21, the cations are located inside the hexagonal cavities of the honeycomb layers and is only observed in the vertex of the anilato ligands form the sides of the hexagons (Figure 1).

Table 2 Structural and magnetic properties of all the reported A[MnII][CrIII(CO4X3)]G compounds

| CCDC   | A*          | X  | SG± | MII|MIII | Tc/K | Hc/K mT | Ref. |
|--------|-------------|----|-----|------|------|-------|-------|------|
| 22     | MIRFOK      | H2O(ph2)3+ | Br  | P-31m MnFe — — — [17] |
| 23     | QEFPXOJ     | H2O(ph2)3+ | Cl  | P-31m FeFe 2.4 1.0 [31] |
| 24     | QEFPOJ      | H2O(ph2)3+ | Br  | P-31m FeFe 2.1 1.0 [31] |
| 25     | NHJEW       | C(N2H2)3+ | Cl/CN | P3 Fe Fe 4.0 6 [32] |

Table 3 Structural properties of all the reported A2[MII|MIII(CO4X3)]G compounds

| CCDC   | A*          | X  | SG± | MII|MIII Ref. |
|--------|-------------|----|-----|------|----------|
| 26     | PALXUY      | S-TM-ET/PPH4+ | Cl  | P1     KFe [22] |
| 27     | PALTAF      | R-TM-ET/PPH4+ | Cl  | P1     KFe [22] |
| 28     | PALTAEJ     | rac-TM-ET/PPH4+ | Cl  | P1     KFe [22] |
| 29     | QUJUJQ      | PPh2Et+  | Br  | P21   NaCr [21] |
| 30     | QUJUW       | PPh2Et+  | Cl  | P21   KFe [21] |
| 31     | —           | NBu4+   | Br  | NaCr  [21] |
| 32     | QUJUJC      | NBu4+   | Br  | I-43d NaCr [21] |

The disposition of the anionic layers can be eclipsed or staggered (Figure 4). The first disposition generates hexagonal channels perpendicular to the layers and is only observed in the two examples with the [(H2O)(ph2)3+] cation (1 and 2). In five recently reported compounds with NBu4+ cations and benzene.
derivatives solvent molecules (15—19) and in a couple of compounds with H$_2$O as cation (20 and 21) (Figure 4, left). Interestingly, the first reported structure with the NBu$_4^+$ cation showed an alternating disposition of the anionic layers (Figure 4, right). 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$_2$O, CH$_3$COCH$_3$, PhBr, PhCHO, C$_6$H$_5$CN, CH$_3$OH, CH$_2$Cl, ...) 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$_6$O$_7$)$_3$]− (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$_2$O 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 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$_6$O$_7$)$_3$]·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).[21]

Figure 4 (left) Eclipsed packing and (right) alternating packing of the [M]$^+$[Mn($\mu$-carboxylato)$_3$]$^-$ layers.

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.

Figure 6 (Top) AC susceptibility of the series of compounds NBu$_4$[MnCr(C$_6$O$_7$)$_3$] (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.[22]

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$_2$O 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$_2$O)(phz)$_3$]$^-$ cation (that shows a strong π-π stacking interaction with the anilato ligand and, therefore, modifies its electron density); (ii) to a lack of solvent

---

**Table 1**

| Compound | T$_c$ (K) | $\chi_{m}T$ (emu K/mol) | M$_s$ (emu mol$^{-1}$) |
|----------|-----------|-----------------|---------------------|
| 1        | 5.5       | 50              | -0.5                |
| 16       | 6.3       | 25              | 0.5                 |
| 17       | 8.2       | 10              | 0.7                 |
| 18       | 11.0      | 5               | 0.8                 |
| 19       |           |                 |                    |
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 $\text{NBu}_x[\text{MnCr-(C}_2\text{O}_4\text{C}_6\text{H}_2\text{)}_2]n\text{PhX}$ and $\text{NBu}_y[\text{MnCr(C}_2\text{O}_4\text{B}_2\text{)}_2]n\text{PhX}$ ($n = 1, 2$; $X = \text{Cl}, \text{Br}, \text{I}, \text{CH}_3, \text{CN}$ and $\text{NO}_2$), 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). The only known Mn(II)Fe(III) derivative was also described in $\text{Mn(II)Fe(III)}$ and Fe(II)Fe(III) reported compounds (Table 2). 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 [(H$_3$O)(phz)$_2$]$^+$, 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 $3 \times 10^{-2} - 2 \times 10^{-3}$ 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 [(H$_3$O)(phz)$_2$]$^+$ cations, whereas it is attributed to the presence of some H-bonds between the C(N$_2$H$_5$)$_2$$^+$ cations and the anionic layers in compound 25.[32]

**Figure 7** (Top) Magnetization of compound 20 showing the metamagnetic transition at ca. 0.2 T. (Bottom) Thermal variation of $\chi_m$ 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 $2.3 \times 10^{-8}$ and $2.4 \times 10^{-7}$ 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 [(H$_3$O)(phz)$_2$]$^+$, 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 $3 \times 10^{-2} - 2 \times 10^{-3}$ 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 [(H$_3$O)(phz)$_2$]$^+$ cations, whereas it is attributed to the presence of some H-bonds between the C(N$_2$H$_5$)$_2$$^+$ 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 $A_2[\text{M}^{\text{III}}\text{M}^{\text{II}}\text{(C}_2\text{O}_4\text{X}_2\text{)}_2]\cdot \text{G}$ 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 M’M’$^\text{III}$ compounds is very similar to that observed in the M’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 M’M’$^\text{III}$ series as shown by the different dimensions of the diagonals of the hexagons and the M’—M’—M’ and M’—M—M’ angles (Figure 9, bottom). These differences are attributed to the larger size of the M’ cations compared to the M’$^\text{III}$ ones.

4 www.genchemistry.org
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.

References

1. Wickman, H. H.; Trozzolo, A. M.; Williams, H. J.; Hull, G. W.; Merritt, F. R. Phys. Rev. 1967, 155, 563.
2. Hoskins, B. F.; White, A. H. J. Chem. Soc. A 1970, 1668.
3. Kahn, O. Molecular Magnetism, VCH Publishers, USA, 1993.
4. Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguier, M. Nature 1995, 378, 701.
5. Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. Nature 2000, 408, 447.
6. Zheng, Y.; Zheng, Z.; Chen, X. Coord. Chem. Rev. 2014, 258—259, 1.
7. Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Kokawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. J. Am. Chem. Soc. 1992, 114, 6974.
8. Atovmyan, L. O.; Shilov, G. V.; Lyubovskaya, R. N.; Zhilyaeva, E. I.; Ovanesyan, N. S.; Pirumova, S. I.; Gusakovskaya, I. G.; Morozov, Y. G. J. Chem. Soc. 1993, 58, 766.
9. Coronado, E.; Galán-Mascaro, J. R.; Gómez-Garcia, C. J.; Martínez-Agudo, J. M. Inorg. Chem. 2001, 40, 113.
10. Mathoniere, C.; Nuttall, C. J.; Carling, S. G.; Day, P. Inorg. Chem. 1996, 35, 1201.
11. Clemente-Leon, M.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, C. J. Inorg. Chem. Commun. 1997, 1727.
12. Coronado, E.; Clemente-León, M.; Galán-Mascaro, J. R.; Giménez-Saiz, C.; Gómez-Garcia, C. J.; Martínez-Ferrero, E. J. Chem. Soc., Dalton Trans. 2000, 3955.
Minireview

[13] Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, C. J.; Martínez-Agudo, J. M.; Martínez-Ferrero, E.; Waerenborgh, J. C.; Almeida, M. J. Solid State Chem. 2001, 159, 391.
[14] Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, C. J.; Martínez-Agudo, J. M. Adv. Mater. 1999, 11, 588.
[15] Mercuri, M. L.; Congiu, F.; Concas, G.; Sahadevan, S. A. Magnetochemistry 2017, 3, 17.
[16] Kitagawa, S.; Kawata, S. Coord. Chem. Rev. 2002, 224, 11.
[17] Atzori, M.; Benmansour, S.; Mínguez Espallargas, G.; Clement-León, M.; Abhervé, A.; Gómez-Claramunt, P.; Coronado, E.; Artizzu, F.; Sessini, E.; Deplano, P.; Serpe, A.; Mercuri, M. L.; Gómez García, C. J. Inorg. Chem. 2013, 52, 10031.
[18] Luo, T.; Liu, Y.; Tsai, H.; Su, C.; Ueng, C.; Lu. K. Eur. J. Inorg. Chem. 2004, 4253.
[19] Shilov, G. V.; Nikitina, Z. K.; Ovanesyan, N. S.; Aldoshin, S. M.; Makahev, V. D. Russ. Chem. Bull. 2011, 60, 1209.
[20] Weiss, A.; Riegler, E.; Robl, C. Z. Naturforsch. B: Chem. Sci. 1986, 41, 1501.
[21] Benmansour, S.; Vallés-García, C.; Gómez-Claramunt, P.; Mínguez Espallargas, G.; Gómez-Garcia, C. J. Inorg. Chem. 2015, 54, 5410.
[22] Atzori, M.; Pop, F.; Auban-Senzier, P.; Clérac, R.; Canadell, E.; Mercuri, M. L.; Avarvari, N. Inorg. Chem. 2015, 54, 3643.
[23] Martínez-Hernández, C.; Gómez-Claramunt, P.; Benmansour, S.; Gómez-García, C. J. Dalton Trans. 2019, 48, 13212.
[24] Martínez-Hernández, C.; Benmansour, S.; Gómez García, C. J. Polyhedron 2019, 170, 122.
[25] Taniguchi, K.; Chen, J.; Sekine, Y.; Miyasaka, H. Chem. Mater. 2017, 29, 10053.
[26] Martínez-Hernández, C.; Benmansour, S.; Gómez-Garcia, C. J. Magnetochemistry 2019, 5, 34.
[27] Palacios-Corella, M.; Fernández-Espejo, A.; Bazaga-Garcia, M.; Losilla, E. R.; Cabeza, A.; Clemente-León, M.; Coronado, E. Inorg. Chem. 2017, 56, 13865.
[28] Abhervé, A.; Manías-Valero, S.; Clemente-León, M.; Coronado, E. Chem. Sci. 2015, 6, 4665.
[29] Abhervé, A.; Clemente-León, M.; Coronado, E.; Gómez-García, C. J.; Verneret, M. Inorg. Chem. 2014, 53, 12014.
[30] Gómez-Claramunt, P. Anilato-Based Multifunctional Molecular Materials, Ph. D. Dissertation, University of Valencia, Valencia, Spain, 2018.
[31] Benmansour, S.; Abhervé, A.; Gómez-Claramunt, P.; Vallés-García, C.; Gómez-García, C. J. ACS Appl. Mater. Interfaces 2017, 9, 26210.
[32] Sahadevan, S. A.; Abhervé, A.; Monni, N.; Sáenz, d. P.; Galán-Mascarós, J. R.; Waerenborgh, J. C.; Vieira, B. J. C.; Auban-Senzier, P.; Pillet, S.; Bendic, E.; Alemany, P.; Canadell, E.; Mercuri, M. L.; Avarvari, N. J. Am. Chem. Soc. 2018, 140, 12611.

Received December 1, 2019
Accepted December 27, 2019