Introduction

Metal–organic coordination polymers have attracted considerable interest because of their promising properties and applications in areas such as catalysis, zeolitic behavior, electrical conductivity, luminescence, non-linear optics, and magnetism. The rational design of new compounds with novel topologies and specific chemical and physical properties comprises the basis and purpose of crystal engineering and involves a good understanding of the metal ion, the coordination preferences of the bridging entities, and the supramolecular self-assembly by noncovalent interactions for the development of new strategies for the synthesis of these materials. Carboxylates are interesting ligands for this goal because of their versatile coordination modes and high structural stability, which has allowed the synthesis of compounds ranging from discrete oligonuclear species to one-, two-, and three-dimensional networks. Moreover, organic carboxylate linkers and pillared polypyridines have been demonstrated to be very efficient in the construction of 3D open metal–organic frameworks (MOFs). The wall of channels can be easily functionalized, and their size can be systematically expanded without changing the underlying

We report herein the synthesis and physicochemical characterization of eight new manganese–oxalato compounds with 1,2-bis(4-pyridyl)ethylene (bpe): \( \{\text{Hbpe}\}_2\text{Mn}_2(\mu-\text{ox})_2 \sim 0.8(\text{C}_2\text{H}_4\text{OH}) \sim 0.4(\text{H}_2\text{O}) \} \) \( a \) \( (1) \), \( \{\text{Mn}(\mu-\text{ox})\text{Mn}(\mu-bpe)\text{H}_2\text{O}\}_2 \) \( a \) \( (2) \), \( \{\text{Mn}(\mu-\text{ox})\text{Mn}(\mu-bpe)(\text{bpe})\}_2 \) \( a \) \( (3) \), \( \{\text{Mn}(\mu-\text{ox})(\mu-bpe)\}_4 \) \( a \) \( (4a) \) and \( b \) \( (4b) \), and \( \{\text{Mn}(\mu-\text{ox})_2(\mu-bpe)_4(\text{H}_2\text{O})_4\} \) \( (X_2)_\_\text{MY}_3 \) with \( X = \text{NO}_3 \) \( (5a) \), \( \text{Br}^- \) \( (5b) \), and \( \text{ClO}_4^- \) \( (5c) \) and \( Y \) = salivation molecules. The appropriate selection of the synthetic conditions allowed us to control the crystal structure and to design extended 2D and 3D frameworks. Compound 1 is obtained at acid pH values and its crystal structure consists of stacked \( \{\text{Mn}(\mu-\text{ox})\}_3^{2+} \) layers with cationic Hbpe\(^+\) molecules intercalated among them. Compound 2 was obtained at basic pH values with a manganese/bpe ratio of 1:1, and the resulting 3D structure consists of an interpenetrating framework in which metal–oxalato chains are bridged by bpe ligands, leading to a microporous network that hosts a variable number of water molecules (between 0 and 1) depending on the synthetic conditions. Compound 3, synthesized with a manganese/bpe ratio of 1:3, shows a 2D framework in which linear metal–oxalato chains are joined by bis-monodentate 1,2-bis(4-pyridyl)ethylene ligands. The thermal treatment of compound 3 permits the release of one of the bpe molecules, giving rise to two new 2D crystalline phases of formula \( \{\text{Mn}(\mu-\text{ox})\}_4(\mu-bpe) \) \( 4a \) \( (4a) \) and \( b \) \( (4b) \) depending on the heating rate. The open structures of \( 5a \)–\( 5c \) were synthesized in a medium with a high concentration of nitrate, perchlorate, or bromide salts (potassium or sodium as cations). These anions behave as templating agents directing the crystal growing toward a cationic porous network, in which the anions placed in the voids and channels of the structure present high mobility, as inferred from the ionic exchange experiments. Variable-temperature magnetic susceptibility measurements show an overall antiferromagnetic behavior for all compounds, which are discussed in detail.
topology, showing really interesting storage\(^4\) and catalytic\(^5\) properties.

The rigid bridging oxalato ligand (hereafter abbreviated as ox) has appeared as a very appealing tecton in the construction of a great diversity of homo- and heterometallic compounds with interesting physical properties (magnetic, electric, or optical), due to its ability to mediate electronic effects between paramagnetic centers.\(^6\) The prevalence of its rigid bis-chelating bridging mode provides a degree of predictability with regard to the structural motifs and architectures of the resulting coordination networks. It is well-known that the counterions can exert a template effect on the topology and dimensionality of the oxalato-bridged polymeric networks. Compounds of general formula \(\text{[M(\text{ox})\text{L}]_n}\) or \(\text{[M}^2\text{(\text{ox})\text{L}]_n}\) (\(M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn\); \(M^I = V, Cr, Fe\)) form 2D honeycomb layers with voluminous achiral cations,\(^7\) whereas helical 3D networks are obtained if chiral tris-chelated transition-metal diimi complex

\[\text{[M(L)]_n}^m (L = 2,2'-bipyridine or phenantroline; m = 2, 3)\] are used.\(^8\)

The features of the auxiliary ligands used to complete the metal coordination sphere also play an important role in the dimensional control of these polymeric compounds. Thus, discrete oligonuclear species have been obtained using multidentate N- and/or O-donor flexible ligands that block most of the coordination sites of the metal.\(^9\) In our previous

research, we designed 1D and 2D complexes of the formula \(\text{[M(\text{ox})\text{(L)}_n]}_{\text{m}} (\text{M(II)} = \text{Mn, Fe, Co, Ni, Cu, Zn}; x = 1, 2; L = terminal ligand)\) in which aromatic pyridyl moieties,\(^10\) triazole derivatives,\(^11\) or nucleobases\(^12\) behave as monodentate terminal ligands providing 1D linear or zigzag frameworks and 4,4-dipyridyl derivatives which connect the metal–oxalato chains, forming sheets.\(^13\)

However, the synthetic conditions (reactants, pH, temperature, concentration, stoichiometry) assume special significance in the crystal engineering of new materials.\(^14\) Dan and Rao showed the progress of the conversion from a 0D to a 3D zinc-oxalato-piperazine framework by controlling the time and temperature of the hydrothermal synthesis.\(^15\) The template effect of solvent molecules is also important, as described by Kwon et al. in the benzene-templated hydrothermal synthesis of the solvation compound \(\text{[Co}_{2}(\text{ox}-\text{ndc})(\text{bpe})\text{]-}\text{C}_9\text{H}_8\text{H}_2\text{O}}\) (ndc = 2,6-naphthalenedicarboxylate; bpe = 1, 2-bis(4-pyrydyl)ethylene) or the tripoly interpenetrated \(\text{[Co}_{2}(\text{ox}-\text{ndc})(\text{bpe})\text{]-1.5}\text{H}_2\text{O}}\) structure, depending on whether benzoic acid is present or not.\(^16\) Within this area, we have focused our present work on the synthesis of new manganese–oxalato compounds with bpe in which the solution pH and the relative ratio of the reactants, thermal treatment, and the presence of different counterions play a key role in their final structures. The magnetic properties of the compounds are also investigated, and the magneto-structural correlations are discussed in detail.

**Experimental Procedures**

**Syntheses.** All chemicals were of reagent grade and were used as commercially obtained. \([\text{Mn(ox)}\text{(H}_2\text{O})_2]\) has been prepared according to the literature.\(^17\)

\[\{\text{bpe}\}[\text{Mn}(\text{ox})\text{H}_2\text{O}]_{\text{m}}\cdot(0.3\text{H}_2\text{O})\cdot(0.4\text{H}_2\text{O})\] (1). Single crystals of I were grown by layering an ethanolic solution of bpe (0.109 g, 0.6 mmol) and \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) (0.050 g, 0.2 mmol) onto an aqueous solution of \(\text{H}_2\text{O}\cdot2\text{H}_2\text{O}\) (0.038 g, 0.3 mmol). After allowing the solution to stand for two weeks, brown crystals were isolated using filtration. They were washed with cold water and diethyl ether and dried in the air. Yield: 85% (based on metal). Anal. Calcd for \(\text{C}_{15}\text{H}_{38}\text{Mn}_{2}\text{O}_{0.6}\): C, 48.32; H, 3.52; N, 7.14; Mn, 14.00. Found: C, 48.42; H, 3.58; N, 7.13; Mn, 14.15%.

**\([\text{Mn(ox)}\text{(bpe)}]\cdot\text{xH}_2\text{O}]_{\text{m}}\) (2).** Yellow single crystals of 2 were obtained by the slow diffusion of a methanol solution (20 ml) containing \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) (0.075 g, 0.3 mmol) and bpe (0.055 g, 0.3 mmol) into an aqueous solution (10 ml) of \(\text{K}_2\text{ox}\cdot\text{H}_2\text{O}\) (0.184 g, 1.0 mmol). They were washed with cold

water and diethyl ether and dried in the air. The anhydrous phase of compound 2 could be easily obtained as a yellow polycrystalline sample by adding the K₂ox·H₂O aqeous solution to the methanolic one. Yield: 90%. Anal. Calcd for C₁₄H₁₂MnN₂O₆ (X = NO₃ for 5a, Br⁻ for 5b, and ClO₄⁻ for 5c; Y = solution molecules). Complex 5a was prepared by adding a methanolic solution (15 mL) of bpe (0.109 g, 0.6 mmol) drope to an aqueous solution (25 mL) that contained Mn(NO₃)₂·4H₂O (0.100 g, 0.4 mmol) and KNO₃ (0.243 g, 2.4 mmol). After that, 0.074 g of K₂C₂O₄·H₂O (0.4 mmol) dissolved in 10 mL of water was added to the previous solution and was allowed to stir for 2 h. The resulting polycrystalline precipitate of compound 5a was removed (yield 50–60%), and the colorless solution was left to evaporate at room temperature. Pale yellow crystals of the compound appeared in a few days, and they were washed with cold water and diethyl ether and dried in the air.

Complexes 5b and 5c were prepared by the same method, but using MnBr₂·4H₂O (0.115 g, 0.4 mmol), KBr (0.476 g, 4.0 mmol), bpe (0.109 g, 0.6 mmol), and K₂C₂O₄·H₂O (0.074 g, 0.4 mmol). Sodium perchlorate was added to the reaction mixture (5b) and Mn(ClO₄)₂ (0.127 g, 0.5 mmol), NaClO₄ (0.489 g, 4.0 mmol), and K₂C₂O₄·H₂O (0.092 g, 0.5 mmol) for 5c. After filtering off the initial precipitate, the resulting solution was left to evaporate at room temperature, and pale yellow crystals of 5b and 5c appeared in a few days. However, the crystals of compound 5c were not of high enough quality to be analyzed by single crystal X-ray diffraction.

Anal. Calcd for C₁₂₂H₁₉₂Br₂Mn₄N₈O₃₅ (5b, Y = 10H₂O): C, 40.82; H, 4.31; N, 8.82; Mn, 13.83. Found: C, 41.13; H, 4.02; N, 9.01; Mn, 13.52%. Anal. Calcd for C₁₂₂H₁₉₂Br₂Mn₄N₈O₃₅ (5b, Y = 6H₂O·bpe): C, 44.69; H, 3.98; N, 7.90; Mn, 12.39. Found: C, 44.35; H, 3.85; N, 7.43; Mᵃ = 12.35%.

**CAUTION!** Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

**Physical Measurements.** Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 microanalytical analyzer. The metal content was determined by absorption spectrometry. The purity and homogeneity of the polycrystalline samples used for physical measurements were checked using IR spectroscopy, elemental analysis, and X-ray powder diffraction methods. The IR spectra (KBr pellets) were recorded on a FTIR Mattson 1000 spectrometer in the 4000–400 cm⁻¹ spectral region. Magnetic measurements were performed on polycrystalline samples of the complexes taken from the same uniform batches used for the structural determinations with a Quantum Design SQUID susceptometer covering the temperature range 5.0–300 K at a magnetic field of 1000 G. The susceptibility data were corrected for the diamagnetism estimated from Pascal’s tables, the temperature-independent paramagnetism, and the magnetization of the sample holder. Thermal analyses (TG/DTA) were performed on a TA Instruments SDT 2960 thermal analyzer in a synthetic air atmosphere (79% N₂/21% O₂) with a heating rate of 5 °C min⁻¹.

**X-Ray Diffraction Data Collection and Structure Determination.** Diffraction data of single crystals of 1–3, 5a, and 5b were collected at 293(2) K on an Oxford Diffraction Xcalibur diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data reduction was done with the CrysAlis RED program. All structures were solved with direct methods using the SIR92 program and refined using full-matrix least-squares on F², including all reflections (SHELXL93). All calculations were performed using the WINGX crystallographic software package. After completing the initial structure solution, the difference Fourier map for compounds 5a and 5b showed the presence of substantial electron density at the channels of the structures, and it could not be possible to find a model for the guest molecules. The contribution of these molecules was subtracted from the reflection data by the SQUEEZE method as implemented in PLATON. An estimation of the proportion of guest molecules was obtained from the TG/DTA curves (see the Supporting Information) and elemental analyses. The final geometrical calculations and the graphical manipulations were carried out with the PARST35 and PLATON programs. During the data reduction process, it becomes clear that the crystal specimens of compound 5b were twinned; therefore, the hkl file corresponding to the major domain of the nonmerohedral twin was processed to avoid reflections with significant contributions from the minor domains. Details of the structure determination and refinement of the compounds are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 776261–776265. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44 1223 335033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

The X-ray powder diffraction (XRPD) pattern for compound 5c was collected on a Philips XPERT powder diffractometer with Cu Kα radiation (λ = 1.5418 Å) over the range 5 < 2θ < 40° with a step size of 0.02° and an acquisition time of 4 s per step at 25°C. Indexation of the diffraction profiles was made by means of the FULLPROF program (pattern-matching analysis) on the basis of the space group and the cell parameters found for compound 5a by single crystal X-ray diffraction. The unit cell parameters obtained in the final refinement were a = 13.899(1) Å, b = 11.444(1) Å, c = 24.860(2) Å, and β = 90.32(1)°. The

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(22) Farrugia, L. J. *WINGX*; University of Glasgow: Glasgow, Great Britain, 1998.
calculated and observed diffraction patterns are shown in the Supporting Information. The presence of some small unaccounted for Bragg peaks in the diffraction pattern has been attributed to the presence of a small amount of impurity.

Variable-temperature X-ray powder diffraction measurements of compound 3 were run under an ambient atmosphere in the range 8 < 2θ < 38° with a step size of 0.03° and an acquisition time of 2 s per step. The compound was heated up to 65 °C with a heating rate of 10 °C min⁻¹, and after that, diagrams were collected every 15 °C with a heating rate of 5 °C min⁻¹ up to 470 °C. The indexation of the diffraction patterns of compounds 4a and 4b obtained from the thermal treatment of compound 3 gives rise to the following cell parameters: a = 5.311(5) Å, b = 8.514(2) Å, c = 9.224(2) Å, α = 90.49(3)°, β = 94.13(2)°, and γ = 97.14(4)° for compound 4a and α = 5.832(5) Å, b = 7.872(5) Å, c = 8.854(5) Å, α = 113.68(2)°, β = 90.49(3)°, and γ = 107.20(7)° for compound 4b. The calculated and observed diffraction patterns are shown in the Supporting Information.

Results and Discussion

Synthesis of the Mn(II)/Oxalate/bpe System. As we will describe in the article, we were able to obtain a wide variety of crystal structures based on the same system, Mn(II)/oxalate/bpe, by controlling the synthetic conditions (Scheme 1). In acid media, the bpe ligand is monoprotonated, and it acts as a template during the crystallization process and allows the formation of the anionic 2D honeycomb [Mn₂(μ-ox)]3⁻ sheets. At neutral or basic pH, two neutral compounds build up in the reaction solution depending on the relative Mn/bpe ratio. The three-dimensional compound 2 with formula [Mn ox)(bpe)] is grown in an equimolecular mixture of the reactants [Mn(NO₃)₂/bpe/K₂C₂O₄]. The increase of the Mn/bpe ratio of the reaction leads to complex 3, composed of [Mn₄(ox)₂(bpe)]₃ sheets. The two different crystal structures also imply a change in the metal–oxalate skeleton, which varies from zigzag chains with cis-coordinated bpe ligands in compound 2 to a linear one in which the bpe molecules are trans-coordinated.

It is worth highlighting that the slow diffusion of the reagents in the synthesis of compound 2 produces the hydrated form, while the direct reaction leads to the anhydrous phase. This fact seems to indicate that the slow crystal growth process permits water molecules to move into the 3D network up to where they were occluded, while if the structure is built up very fast, the compact framework prevents the hydration. It is possible to obtain different hydration rates according to the crystal growth speed, which would explain the different occupancy factors of the water molecules found in compound 2.

Finally, we also observed that the presence of an excess of counterions in the reaction media acted as a template in the crystallization of the open framework structure 5. This compound can be synthesized with bromide, nitrate, or perchlorate, and a partial substitution of the anions for chloride was realized, although it could not be directly synthesized. The use of more voluminous ions such as BF₄⁻ or PF₆⁻ did not direct the growth toward any crystalline phase containing these ions, which implies that the size of the counterion acting as a template is a crucial factor in the crystallization process of compound 5.

Crystal Structure of {Hbpe)}₂[Mn₃(μ-ox)]₃₁⁻.0.8-(C₂H₅OH)·0.4(H₂O) n (1). The crystal structure of compound 1 consists of stacked [Mn₃(μ-ox)]₃⁻ layers with cationic Hbpe⁺ molecules intercalated between them. Manganese(II) metal centers are coordinated to three independent centrosymmetric bis-bidentate oxalato ligands, yielding a slightly distorted octahedral O₆ donor set. A view of the coordination sphere of the metal center and cationic bpe molecules is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The Mn–O bond distances and the separation of the manganese atoms along the oxalato bridge (5.583, 5.617, and 5.655 Å) are in the range observed for other manganese–oxalato compounds. The oxalato ligands link the Mn(II) atoms to form anionic honeycomb layers of alternative Δ- and Λ-[Mn₃(μ-ox)]₃⁻ units with a distance between layers of 10.22 Å. These sheets are piled up, creating hexagonal channels along the c axis.
Crystal Structure of \([\text{[Mn(μ-ox)(μ-bpe)]:}x\text{H}_2\text{O}]_n\) (2).

The crystal structure of compound 2 consists of zigzag Mn(II)--oxalato chains joined between them by cis-coordinated bpe ligands forming a three-dimensional network. The asymmetric unit is comprised by one metal center, two centrosymmetric oxalate dianions, two centrosymmetric bpe ligands, and a water solvation molecule (Figure 3). Selected bond distances and angles are reported in Table 3. The metal centers are joined by bis-bidentate oxalate dianions (M···M = 5.681 and 5.684 Å) forming a zigzag chain, with a dihedral angle of 85.5° between them. The pyridine molecules coordinated to the Mn(II) atoms are twisted 53.1° between them, establishing within the sheet C-H···π interactions (H···Cent, 3.15 Å; C-H···Cent, 133.6°; C-···Cent, 3.85 Å, where Cent is the centroid of the pyridine ring) between C26 and the aromatic ring of the other molecule.30 Each chain is joined to the other four by bis-monodentate bpe ligands, building up an open three-dimensional network with channels of approximate dimensions of 24 × 16 Å running along the b axis (Figure 4).

However, three networks are interpenetrated, giving rise to a compact 3D framework that reduces drastically the size of the channels. The topological analysis carried out by means of the TOPOS program package31 indicates a three-interpenetrating diamond-like 3D network (4-c net), the Schläfli symbol being \((6^3)^6\).

Each interpenetrated 3D network is involved in an extended system of C-H···O ox hydrogen bonds established between bpe molecules and the oxalato oxygen atoms belonging to adjacent 3D frameworks (see the Supporting Information). The crystallization water molecule was occluded in the structure, and its occupancy factor was refined up to 25%. The position of the hydrogen atoms of the water molecule was calculated using Nardelli’s method.32 The occluded water molecule establishes two hydrogen bonds, with an oxalate oxygen atom and with the aromatic pyridine ring of a bpe molecule from a neighboring 3D network.

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The thermogravimetric measurements of compound 2 performed over samples obtained from the diffusion test tube show a first exothermic process that starts at 175 °C, and it is completed around 220 °C and corresponds to the release of one water molecule (DTA peak, 190 °C; weight loss, exp., 5.80%, calcd, 5.25%). The anhydrous phase is stable up to 300 °C. In both cases, the molecule is near planar twisted by 2.5° for the oxalate bridges of 5.539 Å. In both cases, the molecule is near planar twisted by 2.5°.

The metal atom is coordinated by two different bpe molecules which serve as either a terminal or a bridging ligand with an angle of 46° between them, giving rise to a broken ladder-like 2D polymer. The centrosymmetric bridging bpe ligand generates the layers by joining the metal oxalato bridges of 5.539 Å. In both cases, the molecule is near planar twisted by 2.5°. In both cases, the molecule is near planar with a dihedral angle between the pyridine rings of 7.3°.

**Figure 1.** View of the Mn(II) coordination sphere and the two crystallographically independent cationic bpe molecules in compound 1. Only the major component of bpe with a population of 78% is shown (bpe1). Symmetry codes: (a) 1 − x, − y, − z; (b) 1 − x, 1 − y, 1 − z; (c) − x, − y, 1 − z; (d) 2 − x, 1 − y, 1 − z; (e) − x, − y, 1 − z.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) of \{(Hbpe)_{2}[Mn_{2}(μ-ox)]_{n}\}·0.8(C_{17}H_{10}O)·0.4(H_{2}O)_{n} (1)

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The metal atom is coordinated by two different bpe molecules which serve as either a terminal or a bridging ligand with an angle of 46° between them, giving rise to a broken ladder-like 2D polymer. The centrosymmetric bridging bpe ligand generates the layers by joining the metal oxalato chains with a Mn−Mn angle of 168.7° and a distance through the oxalato bridges of 5.539 Å. In both cases, the molecule is near planar with a dihedral angle between the pyridine rings of 7.3°.
1,2-Bis(4-pyridyl)ethylene ligand exhibits an almost coplanar conformation in the great majority of its complexes, although rare examples have been reported with dihedral angles up to 74°. As is shown in Figure 6, there are two terminal bpe molecules between the bridging ones, and they are near planar between them, which allows the presence of face-to-face intralayer π–π contacts (see the Supporting Information). The polymeric metal–organic sheets are stacked by weak C–H···O hydrogen bonds involving the aromatic pyridine rings, the ethylene hydrogen atoms, and the oxalato bridging ligand, which leads to the overall three-dimensional supramolecular architecture with an interlayer distance of 5.37 Å (see the Supporting Information).

It is worth pointing out that the orientation of the terminal bpe molecules with respect to the adjacent metal–oxalato framework locates the noncoordinated nitrogen atom just above the carbon–carbon bond of the oxalato ligand. The N···C distances range from 2.85 Å to 2.91 Å, and the dihedral angle between the pyridine ring and the mean plane of the oxalato anion is of about 85°. The same perpendicular arrangement of the oxalato ligand and N-containing aromatic rings has been previously observed by our group in a family of metal–oxalato one-dimensional compounds with purine (pur). The crystal structure of these compounds of general formula [M(μ-ox)(H₂O)(pur)] (M(II) = Mn, Co, Cu and Zn) consists of one-dimensional zigzag chains in which the purine molecule coordinated to the metal center is parallel to the propagation direction of the chain. The nonprotonated pyrimidinic N3 atom is located over the carbon–carbon bond of the oxalato ligand with a mean distance of 3.0 Å and a dihedral angle between the two ligands of about 90°. This fact precludes the involvement of the potential hydrogen-bonding N3 atom in any other interaction. Although not cited, this arrangement could

Table 3. Selected Bond Lengths (Å) and Angles (deg) of [Mn(μ-ox)(μ-bpe)]₂

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<th>Length (Å)</th>
<th>Bond/Angle</th>
<th>Length (Å)</th>
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<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (a) −x, −y, −z; (b) −x, 1 − y, −z.

also be observed in the closely related bidimensional compounds \([\text{M}_3(\mu\text{-ox})_3(4\text{bpy})_4]\) (M(II) = Mn, Fe, Cu, Zn; 4bpy = 4,4\(^\prime\)-bipyridine\(^34\)) and \([\text{Cu}_2(\mu\text{-ox})_2(\text{pyz})_3]\) (pyz = pyrazine\(^35\)) which are built up by metal–oxalato chains joined by 4bpy or pyz ligands.

The thermal analysis of compound 3 shows a first weight loss between 165 and 215 °C (exptl, 20.1%; calcd, 21.9%) that provides crystalline compound 4, which remains stable up to 300 °C. Then, it undergoes one very exothermic process to lead Mn\(_2\)O\(_3\) above 380 °C. The variable-temperature X-ray powder diffraction measurements (Figure 7) agree with the thermal analysis. The XRPD profile at 65 °C matches the simulated pattern generated from the crystal structure of 3, and no change is observed up to 155 °C, when the diffraction diagram changes to provide a new crystalline phase 4\(_a\) (the elemental analysis of compound 4\(_a\) agrees with the molecular formula \([\text{Mn}(\text{ox})(\text{bpe})]\); Anal. Calcd for C\(_{14}\)H\(_{10}\)MnN\(_2\)O\(_4\): C, 51.71; H, 3.10; N, 8.61; Mn, 16.89. Found: C, 51.15; H, 2.95; N, 8.35; Mn, 16.93%). The XRPD patterns remain unaltered up to 290 °C, after which a decrease in the crystallinity was observed, leading to an amorphous phase. Finally, when a temperature of 365 °C is reached, peaks of Mn\(_2\)O\(_3\) appear.

To provide a deeper insight into the thermally obtained compound 4\(_a\), the starting compound 3 was heated from...
room temperature up to 215 °C at a constant rate of 5 °C/min. Although the elemental analysis and IR spectroscopy agree with the formula [Mn(ox)(bpe)], the X-ray powder diffraction pattern was completely different, indicating the isolation of a new phase, 4b. Compound 4b is only obtained when a heating program similar to that which takes place during the TDX is applied. On the other hand, the diffraction patterns of compounds 4a and 4b differ also from those previously reported for analogous [M(ox)(bpe)], M being Fe, Co, Ni, Cu, and Zn (Figure 8a).13

Taking into account the broken ladder-like structure of starting compound 3 and the rectangular 2D network present in other [M(ox)(bpe)] systems, it is reasonable to expect a 2D crystal structure for compounds 4a and 4b (Figure 9). The main difference between them is the disposition of the sheets on the crystal structure. Depending on the heating rate, the system can acquire
enough energy to surpass the energy barriers present during the rearrangement of the sheets. In fact, intermediate heating rates give rise to mixtures of compounds 4a and 4b.

The cell parameters obtained for compounds 4a and 4b could be easily related to the M⋯M distances through the oxalato and bpe bridging ligands. It allows us to draw a schematic description of the structures in which we can observe that the hydrogen bonding interaction among the bpe entities and the oxalato ligand takes place with just one of the coordinated oxygen atoms, so the bpe ligand is placed at one side of the oxalato ligand. The same disposition between the oxalato and bpe ligands is found in the starting compound 3. In the related \([M(\mu-\text{ox})(\mu-\text{bpe})]\) (M\(^{II}\) = Fe, Co, Ni, Cu, and Zn) compounds, the interaction takes place simultaneously with two oxygen atoms of the same oxalato ligand through a bifurcated hydrogen bond, and as a consequence, the bpe molecule is placed just above the middle of the oxalato ligand. It indicates that during the thermal treatment, the supramolecular interactions present on the starting material direct the crystal structure of the resulting compound toward a thermodynamically unstable crystal structure which is more closely related to the starting crystal structure.

It is worth noting that the angle between the oxalato and bpe bridging ligands in compound 3 is similar to that found when the sample is rapidly heated: compound 4b (ca. 100°). In the case of compound 4a, which is obtained when a prolonged heating process takes place, a value of ca. 92° is presented, closer to that observed on the previously reported \([M(\mu-\text{ox})(\mu-\text{bpe})]\) compounds (90°).

**Crystal Structure of** \(\{[\text{Mn}_4(\mu-\text{ox})_3(\mu-\text{bpe})_4(H_2O)_4]^+\cdot(X)_2\cdot mY\}_n\) (X = NO\(_3^−\) for 5a, Br\(^−\) for 5b, and ClO\(_4^−\) for 5c; Y = Solvation Molecules). Each metal center in compounds 5a and 5b has a pentagonal bipyramid O\(_5\)N\(_2\) donor set in which the basal plane is formed by five O atoms from one water molecule and two oxalato anions, whereas the bpe ligands are located in the axial positions (Figure 10). Selected bond lengths and angles are gathered in Table 5. The tris-bidentate ox1 anion sequentially bridges Mn1 atoms to form corrugated chains that run parallel to the b axis and Mn2 metal centers with one carboxylic group through O11 and O12 atoms, forming a \(\mu\)-oxo bridge. Bis-bidentate ox2 ligands connect Mn2 atoms between them, building \([\text{Mn}_4(\mu-\text{ox})_3(H_2O)_4]^+\) sheets in the plane bc (Figure 11a).

It is noteworthy that Mn—O\(_{\text{ox}}\) distances that imply \(\mu\)-oxo bridge oxygen atoms are substantially longer (>2.38 Å) than those that are not involved (<2.27 Å).
The trans-coordinated bpe ligands bridge metal centers of consecutive sheets constructing the three-dimensional cationic net $[\text{Mn}_4(\text{ox})_3(\text{H}_2\text{O})_4(\text{bpe})_4]^{2+}$, as shown in Figure 11c. These molecules are perpendicular to the 2D Mn–ox framework (with angles higher than 80° between the pyridinic rings and the bc plane), generating cylindrical channels along the a axis ($d \sim 6$ Å) and rectangular ones parallel to the b axis ($4 \times 13$ Å), which lends a high porosity to the structure. An empty volume per unit cell of 1275.3 Å³ (32.6%) and 1092.8 Å³ (28.5%) has been calculated for compounds 5a and 5b, respectively. The guest molecules placed on the channels of both compounds could not be crystallographically located and were determined by elemental analyses and TG/DTA measurements.

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The crystal structure is completed with the presence of nitrate, bromide, or perchlorate anions that counterbalance the charge of the metal–organic framework. The anions are placed on specific voids of the net (Supporting Information) in which three bpe ligands are orientated to the anions holding them by hydrogen bonds.

The loss of guest molecules takes place from room temperature to 160 and 175 °C for compounds 5a and 5b, respectively. The weight loss has been attributed to 10 water molecules for compound 5a (exptl, 11.65%; calcd, 11.34%) and to five water and four methanol molecules for 5b (exptl, 13.20%; calcd, 13.14%). The remaining molecular framework is stable up to 240 °C (5a) and 220 °C (5b), when the coordinated water molecules are released with the breakdown of the overall structure leading to the formation of Mn$_2$O$_3$ as a final residue. The decomposition process takes place through successive processes in which the anion influences the thermal stability of the complex, as is proved by the difference in the temperature range of the process, 105 °C for 5a and 175 for 5b.

**Ion Exchange.** The capability to exchange the host anions in the open structure of compounds 5a, 5b, and 5c was analyzed by FTIR and powder X-ray diffraction (Supporting Information). Powder samples of the compounds (0.1 g) were added to 0.1 M solutions of KBr, NaClO$_4$, or KNO$_3$ at room temperature and stirred for different time periods. The ion exchange could be easily determined by FTIR because the signals of the anions used in the experiments appear at different values: an intense peak at $1385$ cm$^{-1}$ for the nitrate anion; three signals at $1120, 1090, \text{and} 625$ cm$^{-1}$ for the perchlorate anion; and no signal for the bromide ion. Powder X-ray diffraction showed that during the ion exchange the crystal structure of the compounds is retained.
In conclusion, we can confirm that the exchange between the three anions along the channels is possible without a loss of the initial 3D structure. The mobility of the anions decreases in the following order: \( \text{NO}_3^- > \text{Br}^- > \text{ClO}_4^- \). The nitrate anion could be easily replaced by bromide or perchlorate anions, and after 24 h the exchange is completed. The substitution of the bromide anions by nitrate ones was also fast, but only a partial replacement of bromide by perchlorate anions could be obtained after 6 days. Finally, the perchlorate ions were only partially exchanged by nitrate or bromide anions. These facts seem to indicate a selectivity of the holes for
the shape and size of the anions. We tried the replacement of the anions by smaller ones such as Cl\textsuperscript{-} or bigger ones such as BF\textsubscript{4}\textsuperscript{-} and PF\textsubscript{6}\textsuperscript{-}, but no results were obtained. It is worth highlighting that although the bromide ion is smaller than the nitrate ion, its mobility was lower, showing a shape dependence in the exchange process.

**Magnetic Properties.** The temperature dependence of the molar magnetic susceptibility (\(\chi_M\)) for compounds 1–3 and 5 increases upon cooling up to a maximum around 15 K for complexes 1–3 and 5 K for 5a–5c (Table 6). The room temperature value of \(\chi_M T\) for compounds 1–3 is similar to the spin-only value expected for a high-spin d\textsuperscript{5} Mn(II) ion (4.38 cm\textsuperscript{3} mol\textsuperscript{-1} K\textsuperscript{-1}), and two Mn(II) ions for complexes 5a–5c. The thermal variation of the \(\chi_M^{-1}\) for all compounds could be described by the Curie–Weiss law, obtaining in all cases a negative value for \(\theta\). All of these facts are indicative of the presence of predominant antiferromagnetic interactions between the metal centers.

Additionally, the \(\chi_M\) curve for compounds 5a–5c shows a local minimum below 4 K (Figure 12), which can be due to a ferromagnetic ordering of the network at low temperatures (spin canting). Attending to the crystal structure, these compounds can be described as magnetic metal–oxalato sheets joined by bpe ligands. As can be observed in Figure 13, these 2D magnetic structures are built up by triangular Mn(II) fragments forming chains along the \(b\) axis and connected by a bis-bidentate oxalato. The manganese atoms are bridged by a \(\mu_2\)-oxalato anion with two magnetic paths: its usual bis-bidentate coordination mode, which shows values for the magnetic coupling (\(J_D\)) ranging from \(-0.81\) to \(-3.0\) cm\textsuperscript{-1} (Table 7), and the \(\mu_3\)-O bridge (\(J_D\)) with \(J\) values of \(-1.8\) cm\textsuperscript{-1} for a M–O–M angle of 150°–155°, similar to that observed for compounds 5a–5c (154°–155°). The presence of these triangular fragments with similar antiferromagnetic \(J\) values implies that the magnetic moments cannot be completely coupled obtaining non-null magnetic values at low temperatures.

Figure 14 shows the thermal evolution of the \(\chi_M\) and the \(\chi_M T\) products of compounds 2 and 3. These compounds can be considered, from a magnetic point of view, as 1D due to the long M⋯M distances (>13 Å) along the bpe molecules that allow for an assumption of a negligible magnetic exchange through the organic ligands\textsuperscript{37} and for analysis of their magnetic properties on the basis of a chain model. The experimental data have been successfully fitted by means of an \(S = 5/2\) Fisher antiferromagnetic chain model derived through the Hamiltonian \(H = -J \sum_i S_i S_{i+1}\).\textsuperscript{38} The best fit parameters are \(J = -2.43\) cm\textsuperscript{-1}, \(g = 2.00\), and \(R = 7.4 \times 10^{-7}\) for 2 and \(J = -2.16\) cm\textsuperscript{-1}, \(g = 2.00\), and \(R = 6.4 \times 10^{-7}\) for 3 (solid line in Figure 14), where \(R\) is the agreement factor defined as \(R = \left(\frac{\sum(\chi_M)_{\text{obs}} - \sum(\chi_M)_{\text{calc}}}{\sum(\chi_M)_{\text{obs}}}\right)^{1/2}\).

The \(J\) values of compounds 2 and 3 are in the range found for other reported oxalato-bridging manganese(II) complexes, which show a weak antiferromagnetic coupling ranging from \(-0.81\) to \(-3.00\) cm\textsuperscript{-1}. Table 7 includes the magnetostuctural data of previously reported Mn(II) compounds in which the magnetic interaction is transmitted by bis-bidentate oxalato ligands. The exchange pathway for this significant antiferromagnetic interaction is well-known\textsuperscript{39} and takes place between the \(d_{x^2-y^2}\) type

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
compound & \(\chi_M T\) & \(Z M^2 T^0\) & \(T_1\) & \(\chi_M^0\) & \(T_2\) & \(\Delta T\) & \(C\) & \(\theta\) \\
\hline
1 & 4.12 & 7.4 & 19 & 50–300 & 4.54 & 29.4 & 2 & 0.81 \\
2 & 4.14 & 10.2 & 13 & 30–300 & 4.60 & 23.1 & 2 & 0.81 \\
3 & 4.48 & 9.2 & 15 & 40–300 & 4.92 & 29.2 & 2 & 0.81 \\
5a & 8.11 & 17.5 & 6.0 & 17.2 & 3.2 & 9.05 & 34.8 & 2 & 0.81 \\
5b & 8.21 & 19.5 & 4.7 & 19.4 & 4.2 & 9.16 & 35.2 & 2 & 0.81 \\
5c & 8.22 & 18.9 & 5.5 & 18.3 & 3.0 & 9.14 & 31.4 & 2 & 0.81 \\
\hline
\end{tabular}
\caption{Relevant Magnetic Data for Compounds 1–3 and 5 Including the Curie–Weiss Law Fitting.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12}
\caption{(b) Magnetic interactions in compounds 5a–5c through the oxalato bridges. (b) Schematic representation of the 2D magnetic framework.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13}
\caption{(a) Magnetic interactions in compounds 5a–5c through the oxalato bridges. (b) Schematic representation of the 2D magnetic framework.}
\end{figure}

\begin{thebibliography}{99}
The table includes only those examples in which only a crystallographically independent metal center and oxalato bridging ligand are present. Abbreviations used, $D_{man}$: metal–metal distance. $h$: displacement of the manganese atom out of the basal plane. $\gamma$: dihedral angle between the equatorial and oxalato mean planes. $S_{oc}$: octahedral distortion. $S_{tp}$: trigonal prism distortion. $dpyo$ = 4,4′-bipyridine-N,N′-dioxide; $adp$ = adenine; $tpm$ = pyrimidine; $bpm$ = 2,2′-bipyrimidine; $bpy$ = 2,2′-bipyridine; $phen$ = 1,10-phenanthroline; $bpe$ = bis(4-pyridyl)ethylene; $titm$ = 1,3,5-tris(imidazol-1-ylmethyl)-1,2,4,6-tetramethylbenzene; $4atr$ = 4-amino-1,2,4-triazole; $bpa$ = bis(4-pyridyl)ethane; $bppa$ = N-benzyl-N-(6-pivaloylamido-2-pyridyl)ethylene; $dpy$ = 2,2′-bipyrimidine-N,N′-dioxide; $cis$ and $trans$ conformations correspond to the relative orientation of the oxalato ligands in the polymeric compounds. *Structure not reported. Mn–Mn distance of the first compound was determined by the corresponding crystallography axis of the powder X-ray diffraction. This article. More than one crystallographically independent Mn(II) atom reported in the structure. Although a 1D structure, oxalato bridges join heterometal cyanide squares, and they can be considered, for our study, dimeric units. The table includes only those examples in which only a crystallographically independent metal center and oxalate bridging ligand are present.

**Table 7.** Magnetostuctural Data (Å, cm$^{-1}$) for Oxalato-Bridged Mn(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>$D_{man}$</th>
<th>$h$</th>
<th>$\gamma$</th>
<th>$S_{oc}$</th>
<th>$S_{tp}$</th>
<th>$g$</th>
<th>$J$ ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mn(ox)(H}_2\text{O)}<em>2]</em>{\text{2}}^+$</td>
<td>1D</td>
<td>5.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Mn(ox)(Dpyo)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.65</td>
<td>0.00</td>
<td>0.1</td>
<td>0.86</td>
<td>15.82</td>
<td>2.00</td>
<td>$-0.81$ 43</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(dpyo)}]_{\text{2}}^+$</td>
<td>2D</td>
<td>5.66</td>
<td>0.00</td>
<td>0.0</td>
<td>0.97</td>
<td>15.94</td>
<td>2.00</td>
<td>$-1.89$ 37a</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(pur)(H}_2\text{O)}<em>2]</em>{\text{2}}^+$</td>
<td>1D</td>
<td>5.60</td>
<td>0.21</td>
<td>0.29</td>
<td>6.1</td>
<td>13.2</td>
<td>1.07</td>
<td>12.53</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(4atr)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.60</td>
<td>0.26</td>
<td>8.6</td>
<td>0.89</td>
<td>15.74</td>
<td>2.00</td>
<td>$-1.94$ 11b</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(bpa)}]_{\text{2}}^+$</td>
<td>2D</td>
<td>5.59</td>
<td>0.34</td>
<td>15.8</td>
<td>0.98</td>
<td>14.82</td>
<td>2.00</td>
<td>$-1.41$ 13</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(2-μ-bpe)(bpe)}]_{\text{2}}^+$</td>
<td>2D</td>
<td>5.54</td>
<td>0.21</td>
<td>0.57</td>
<td>3.7</td>
<td>22.5</td>
<td>2.27</td>
<td>10.82</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(μ-bpm)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.61</td>
<td>0.07</td>
<td>12.3</td>
<td>13.2</td>
<td>3.16</td>
<td>7.51</td>
<td>1.99</td>
</tr>
<tr>
<td>$[\text{Mn(μ-ox)(μ-bpy)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.62</td>
<td>0.07</td>
<td>11.0</td>
<td>13.6</td>
<td>2.39</td>
<td>9.93</td>
<td>1.97</td>
</tr>
<tr>
<td>$[\text{Cr}_2\text{Mn}_2\text{(ox)(phen)}_3(bpy)_4\text{H}_2\text{O}<em>3(Dpyo}</em>{0.5}\text{ClO}_4]_2$ tetramer</td>
<td>2D</td>
<td>5.70</td>
<td>0.09</td>
<td>9.5</td>
<td>1.89</td>
<td>11.41</td>
<td>1.99</td>
<td>$-2.20$ 48</td>
</tr>
<tr>
<td>$[\text{Mn(ox)(bpe)}]_{\text{2}}^+$</td>
<td>3D</td>
<td>5.68</td>
<td>0.09</td>
<td>10.9</td>
<td>1.62</td>
<td>11.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Mn(μ-bpe)(bpe)}]_{\text{2}}^+$</td>
<td>2D</td>
<td>5.67</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Mn(μ-ox)(4atr)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.61</td>
<td>0.07</td>
<td>12.3</td>
<td>13.2</td>
<td>3.16</td>
<td>7.51</td>
<td>1.99</td>
</tr>
<tr>
<td>$[\text{Mn(μ-ox)(μ-bpy)}]_{\text{2}}^+$</td>
<td>1D</td>
<td>5.62</td>
<td>0.07</td>
<td>11.0</td>
<td>13.6</td>
<td>2.39</td>
<td>9.93</td>
<td>1.97</td>
</tr>
<tr>
<td>$[\text{Cr}_2\text{Mn}_2\text{(ox)(phen)}_3(bpy)_4\text{H}_2\text{O}<em>3(Dpyo}</em>{0.5}\text{ClO}_4]_2$ tetramer</td>
<td>2D</td>
<td>5.70</td>
<td>0.09</td>
<td>9.5</td>
<td>1.89</td>
<td>11.41</td>
<td>1.99</td>
<td>$-2.20$ 48</td>
</tr>
</tbody>
</table>

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several dimeric entities with a MnO$_2$N$_4$ environment show $J$ values ranging from $-1.2$ to $+2.5$ cm$^{-1}$, lower than those expected for this chromophore, which implies that other factors such as structural parameters and distortions must also be taken into account.

Figure 15 shows the decrease of the magnetic coupling with the Mn – Mn distance along the oxalato bridge, but in a deep analysis it has been observed that trans-coordinated oxalato ligands provide lower $|J|$ values than the cis-coordinated ones with similar metal–metal distances, while dimeric entities present values between the previous ones. This trend is expected for polymeric compounds with a MnO$_3$N$_2$ chromophore, because trans complexes present two nitrogen atoms in axial positions, while for cis-coordinated complexes, one N atom is axial and the other one equatorial, which implies higher values according to the previously discussed ones. But the fact that the O$_6$ donor set also follows this trend seems to indicate that the relative orientation of the bridged ligands between them is more relevant for the magnetic coupling than the electronegativity of the peripheral ligands.

Indeed, the MnO$_2$N$_4$ dimeric entities have lower values than the polymeric cis-coordinated compounds although they have more N atoms in the coordination sphere of the metal.

To study in depth the different structural parameters that influence the magnetic properties of the oxalato-bridged Mn(II) compounds, we have analyzed the distortion of the metal polyhedron on the basis of the continuous shape measures (CSHM). Avnir and co-workers$^{40}$ defined “symmetry measures” to quantify the degree of distortion of the metal environment from an ideal polyhedron, it means a quantitative measure of the minimal distance to the desired perfect symmetry ($S_i$). A useful tool for analysis of families of compounds is the scatter-plots of their shape measures over the interconversion path between the two ideal polyhedra with the same number of vertices, which are called “shape maps”.$^{51}$ Obviously, these measures take into account all possible structural factors that influence the distortion of the polyhedra, giving an overall single parameter, but the CSHM has found many novel correlations between symmetry or chirality and molecular properties.$^{52}$ In our case, all compounds present a hexacoordinated metal environment, the octahedron (O$_6$) and trigonal prism (D$_3$h) being the most common polyhedra. The characteristic distortion that interconverts these two ideal polyhedra is the Bailar twist,$^{53}$ which allows calculation of their shape map.$^{54}$ Figure 16 shows the pathway between the two ideal polyhedra and the calculated symmetry measures for the octahedral [S(O$_6$)] and trigonal prism [S(tp)] coordination sphere of the experimental structures using the program SHAPE,$^{55}$ which can be obtained from the authors upon request.

The first conclusion that we obtain is that most of the experimental compounds are octahedral with a slight distortion, and the lowest $S(Oh)$ values correspond to the trans-coordinated compounds. It has been determined that the intermediate geometry, isosymmetric with respect to the ideal octahedron and the trigonal prism, has $S(Oh) = S(tp) = 4.42$, a higher value than most of the experimental M(II)-oxalato shape measures. Second, it has been shown that the compounds appear along the Bailar path, despite the fact that the bite angle of the oxalato ligand and the presence of polydentate ligands could turn the experimental values away from the path.

Previously reported studies have shown different electronic and magnetic correlations with the CShM of different Cu(II) complexes. The representation of the experimental data with the shape measure (Figure 17, structures with different $S(Oh)$ values but only one magnetic coupling reported have been omitted) surprisingly shows a linear correlation in which the $|J|$ increases with the octahedral distortion. Further work is in progress to relate this magnetostructural correlation with the variations that take place on the electronic structure of the complexes.

Conclusions

In this paper, a family of extended metal(II)-oxalato compounds has been characterized from magnetic and structural points of view. This work emphasizes that, although using the same building blocks, several different crystal structures could be obtained just modifying the synthetic conditions: pH, stoichiometry, thermal treatment, and counterions. In this way, it has been demonstrated that the presence of counterions in the reaction media is crucial for the building process of charged multidimensional frameworks. The qualitative ion exchange experiments indicate that the shape and size of the anions placed on the channels play a major role in determining their relative mobility within these channels. The paper also pays special attention to the heating rate in the solid state transformation taking place in the broken ladder-like structure of compound 3 to provide two polymorphs with a 2D rectangular grid structure.

On the other hand, the continuous shape measurements realized in the metal polyhedra allow us to establish a magnetostructural relationship that depends on the degree of distortion of the metal environment with regard to ideal polyhedra. This magnetostructural correlation has the same relevance as that previously found for the $\text{Mn} \cdots \text{Mn}$ distance and, altogether with the chromophore type, could allow the prediction of the magnetic exchange for oxalato-bridged manganese(II) complexes.

Acknowledgment.

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Supporting Information Available: IR spectra, thermoanalytic curves, and noncovalent interactions for compounds 1–5. XRPD analysis of compounds 4a, 4b, and 5c. IR and XRPD monitoring of the ion exchange experiments in compounds 5a, 5b, and 5c. Magnetic data of compounds 1, 5a, and 5b. This material is available free of charge via the Internet at http://pubs.acs.org.